ODC 425.1 : 111.18 : 425 : 1976.3 - (004)

PROCEEDINGS of THE FIRST INTERNATIONAL SYMPOSIUM ON ACID PRECIPITATION AND THE FOREST ECOSYSTEM

USDA FOREST SERVICE GENERAL TECHNICAL REPORT NE-23
1976

FOREST SERVICE, U.S. DEPARTMENT OF AGRICULTURE
NORTHEASTERN FOREST EXPERIMENT STATION
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PUBLISHER'S NOTE

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U. S. D. A. FOREST SERVICE
NORTHEASTERN FOREST EXPERIMENT STATION

THE OHIO STATE UNIVERSITY
ATMOSPHERIC SCIENCES PROGRAM

PROCEEDINGS OF

THE FIRST INTERNATIONAL SYMPOSIUM ON ACID PRECIPITATION AND THE FOREST ECOSYSTEM

May 12-15, 1975 Columbus, Ohio

L. S. Dochinger T. A. Seliga

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ACID PRECIPITATION AND THE FOREST ECOSYSTEM

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ACKNOWLEDGEMENTS

The conduct of a Symposium of this breadth and magnitude is a product of the labor of many individuals and the support of their institutions. The success of the Symposium ultimately lies in the contributions of those who presented papers and participated in discussions, in newly found acquaintances, and in its ability to stimulate further scientific inquiry. We believe the First International Symposium on Acid Precipitation and the Forest Ecosystem achieved all of these things thanks to the collective efforts of many people from many nations.

Primary support of the Symposium was provided by the U. S. D. A. Forest Service and The Ohio State University. We are especially thankful for the continuing encouragement of many Forest Service and University officials in this effort.

The review and selection of papers were the responsibility of the Technical Program Committee. Although the entire Committee participated in this process, the contributions of Dr. Thomas A. Seliga on atmospheric transport, chemistry and precipitation, Dr. Gene E. Likens on acid precipitation and aquatic ecosystems, Dr. Garth K. Voigt on acid precipitation and forest soils and Dr. Ellis B. Cowling on acid precipitation and forest vegetation provided the major directions for the Symposium.

We especially commend and thank Ms. Joan Arnfield for handling most of the arrangements and coordinating many of the details associated with both the Symposium and the preparation of these Proceedings. The success of this venture was due in great part to her personal dedication and tireless efforts.

Finally, we are grateful to the National Science Foundation and the Office of Water Research and Technology of the United States Department of the Interior for their support.

Leon S. Dochinger

Thomas A. Seliga

PREFACE

These Proceedings report on the results of The First International Symposium on Acid Precipitation and the Forest Ecosystem which was held at The Ohio State University, Columbus, Ohio, U. S. A., on May 12-15, 1975. The Symposium was organized and held to assess what is known about acidity in precipitation and to focus attention on its ecological effects throughout the world. Furthermore, the Symposium was to serve as a forum for academic, industrial, governmental and public interest groups to meet and debate the magnitude, extent, nature and consequences of acid precipitation.

Approximately 300 persons from 12 countries attended the Symposium which focused on four related topics: (1) atmospheric chemistry, transport and precipitation; and effects of acidic precipitation on (2) aquatic ecosystems, (3) forest soils, and (4) forest vegetation. The Proceedings are organized accordingly.

Major findings presented at the Symposium indicated that: (1) precipitation is becoming increasingly acidic in northwestern Europe, northeastern United States and eastern Canada; (2) this increase is related to greater emissions of sulfur and other acid-forming compounds into the atmosphere from various industrial and urban sources; (3) the acidity may be associated with both indigenous and remote sources; (4) the acidifying pollutants are deposited on the land in both wet and dry forms; and (5) serious effects of acid precipitation have been observed in Scandinavia and North America. In addition to major impacts already identified, such as loss of fisheries and changes in some forest ecosystems, scientists at the Symposium expressed concern for other more subtle, long-term effects on the biosphere which might result from acid precipitation.

Unfortunately, our knowledge of the problem as witnessed by the content of these Proceedings is inadequate for any overall asessment of the atmospheric acidity problem. Many questions on all the related topics considered by the Symposium remain unanswered. Statements and discussions at the Symposium strongly suggest the need for further research, including potential beneficial aspects, on the ecological effects of acid precipitation and other atmospheric contaminants. Commitments to long-term atmospheric monitoring of precipitation and related atmospheric pollutants are also necessary.

We hope the Symposium and these Proceedings will provide the basis for future discussion and research guidelines and that these, in turn, will answer whether acid precipitation is one of the most significant international environmental problems of our time.

Leon S. Dochinger

Thomas A. Seliga

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KEYNOTE PAPERS

THE ACIDITY PROBLEM -- AN OUTLINE OF CONCEPTS

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INTRODUCTION

The changing acidity of air and precipitation over most of Europe and part of U. S. is only part of a larger problem--changes of the chemical climate caused by a variety of emissions into the atmosphere (13, 36). These emissions may create a local, a regional or a global situation depending only on the life-time of the pollutants in the atmosphere. The atmospheric sciences give some answers in this respect, but not all. Soils, vegetation and surface waters act not only as a passive sink for elements in the atmosphere. Several feed-back mechanisms take place including continuous exchange, increased or reduced storage in the soil, changes in the flux of chemical compounds from soils and surface waters, and so on. The problem of air pollution or the impact of a specific pollutant can only be understood when reactions and interactions between all reservoirs are taken into account.

The increasing acidity of the atmosphere is in fact the most interdisciplinary environmental problem we have at present. *Soils and surface waters are affected, plant growth is retarded; ecosystems are changed; the biota in lakes and rivers are changed; some organisms die, microorganisms, pathogens and the soil fauna change their activity and living patterns, deterioration of buildings takes place as well as corrosion in a wide sense, and human health is affected.* With very few exceptions, increasing acidity has proved to be detrimental in all these respects. Attitudes, however, are highly polarized at all levels from almost a total denial of any problem on one end to my original presentation of the impact of acid rain enlarged in this keynote address, on the other (1). Environmental effects in other fields have created the same phenomena of attudinal behavior. This arises from the fact that short-term economic gains achieved by pollution of air or water stands against the cost of long-term deterioration of the environment. Satisfactory resolution of this conflict is a question of proper political decisions based on facts. The many papers at this Symposium will certainly provide facts on vital points with respect to the increasing acidity in Nature. I will start with an outline of the acidity problem and discuss more specifically some crucial points. The

early work by Gorham (2, 3, 4, 5) give substantial support to this presentation.

CHANGES OF THE CHEMICAL CLIMATE

The increasing acidity of air and precipitation in Europe and its effects on soils, vegetation and surface waters was first presented in 1967 in a Swedish Governmental Report (6). The basic facts in this report originated from long-term network data regarding the chemistry of air and precipitation in Europe and to some extent of surface waters in Scandinavia. The frame-work of the acidity problem was published by Odén (1) in 1968. At that time the records extended for almost a 10 year period for certain areas in Europe. When plotting these data for the different elements at individual stations it became evident, that certain elements showed either a positive or a negative trend with respect to time. The chemical climate was obviously changing in Europe.

Figure 1 illustrates the European atmospheric chemical network. Each dot represents a sampling station, where precipitation and to some extent air have been sampled on a monthly basis. The major cations and anions have been determined and also pH, alkalinity and electrical conductivity. The network started in Sweden in 1948, extended to the rest of Scandinavia in 1952-54 and to other parts of Europe during the years thereafter. The International Geophysical Year (IGY) comprised a 1-year study in some countries in 1957. USSR started a network all over Asia to the Pacific in 1958, and to my knowledge this network is still operating. The Polish network started in 1964. Data from the last two countries are available for some years. All together these data make it possible to evaluate changes of the chemical climate of Europe at individual stations, and also to map the geographical distribution of certain elements for a number of years. The network of about 130 stations (at maximum level) is not dense enough, however, to evaluate the details. The discontinuity between sea and land and between industrialized and non-industrialized areas necessitates a much more dense network to give a correct picture of the geographical distribution pattern. The US continent is more homogeneous in this respect and the wide-spread network, that have existed now and then, seems appropriate for mapping atmospheric chemical constituents. The present drawback is the lack of consistency with time.

Figure 2 shows the time records of the fallout of nitrate (NO_3) and ammonia (NH_4) from some stations of the European network. A more or less continuous increase with time takes place and the rate of this increase is more pronounced at stations closer to the center of Europe. This is therefore likely to be the source center for NO_3 and NH_4 in the atmosphere. Data from the individual stations vary to some extent

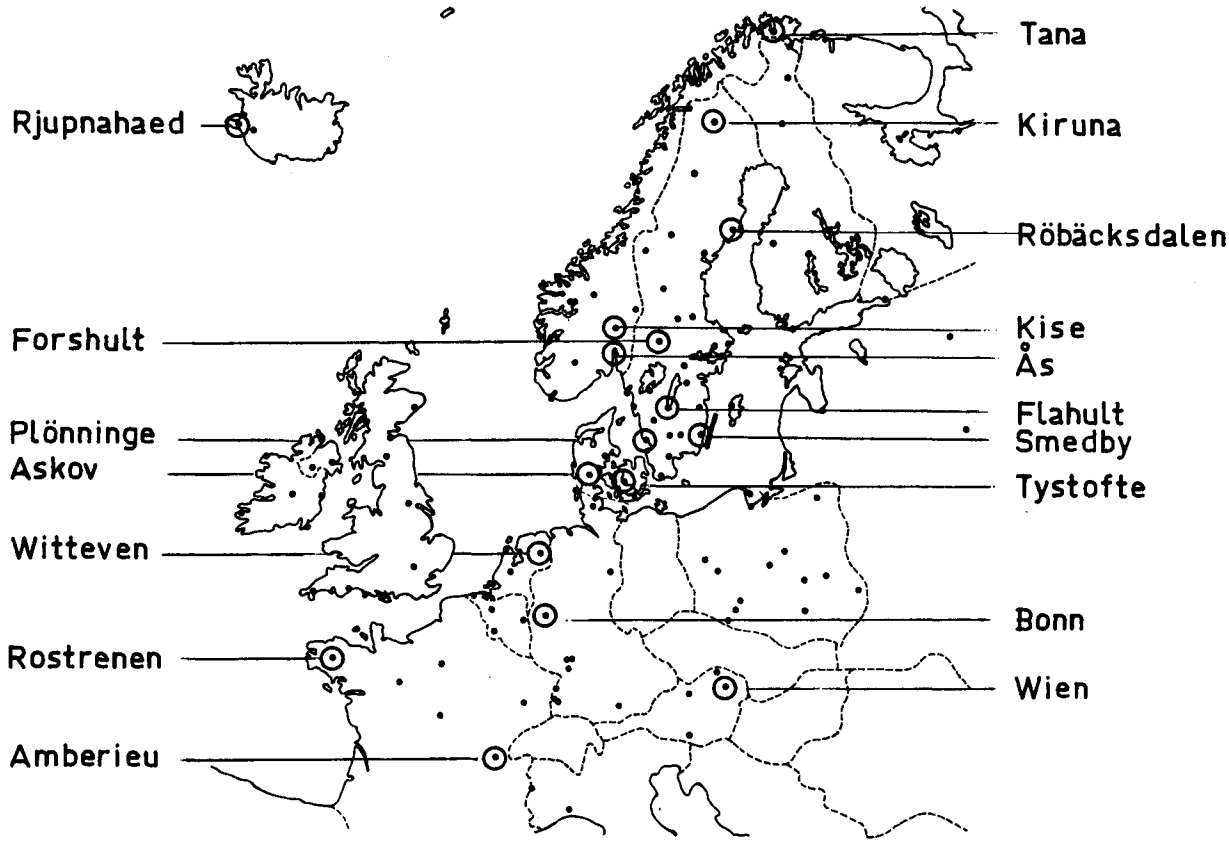


Figure 1. Each dot on the map represents a sampling station for precipitation and air. Long-term data are available for the circled stations. Part of the network is coordinated by the International Meteorological Institute in Stockholm.

from year to year; this reflects variations in both source and sink conditions and large-scale meteorological influences. Occasionally very high figures may appear (cf. NH_4-N at Ås in 1967 and 1972). Other stations show some kind of periodic pattern with simultaneous increasing or decreasing values. The large scatter between different years occurs for almost every element and points out the necessity of long-term records in order to determine any trends in the data for a given period of time.

An example of an abrupt change in the fallout is shown in Figure 2. The gradual increase of the fallout of NO_3-N shown at the Witteven station from 1957 to 1968 shows a trend equivalent to that at the stations Askov, Ås and Forshult. However, in 1971 and 1972 the fallout drops drastically and this effect takes place at almost all the other stations in France and the Benelux countries. The high degree of correlation between these stations shows that both the increasing

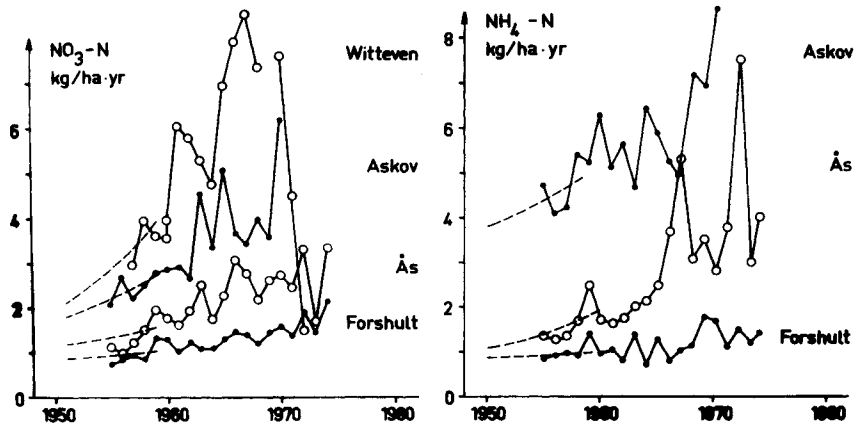


Figure 2. Time records of the wet fallout of nitrate and ammonia at some stations of the European network. The stations vary latitudinally from 60° N (Ås and Forshult) to 53° N (Witteven). See Figure 1 for location of each station.

and decreasing values depend on a regional phenomenon. The records also illustrate the extreme uncertainty in forecasting the fallout in the future based on trends in the past. Other examples of the same kind will be given.

Nitrate in precipitation is basicly man-made. The increase in Central Europe is very pronounced. In the middle of the 1950's the fallout was less than 2 kg/ha/year but 10 years later this figure increased to 6-8 kg/ha/year. Prior to 1950 the fallout of NO_3-N did not vary too much between different stations in Europe as shown by the dashed trend lines in Figure 2. The base-line figure for most parts of Europe appears to be about 1 kg/ha/year or less. The very pronounced increase of NO_3-N is due to the large emissions of NO_x from various industries, high temperature engines and oil-based power plants. In the atmosphere NO_x is oxidized to nitric acid at high altitudes. This compound forms a part of the atmospheric acidity. An explanation to the low fallout figures in W. Europe in 1971-72 cannot be given at present.

The station records for NH_4-N are somewhat different. The increase with time is not so pronounced and the background values for the different stations seem to be fairly well separated, at least around 1950. Going further back in time the differences between these values may narrow but it is very unlikely that they, like NO_3-N, will coincide at a single value applicable to all parts of Europe. The reason for this is that NH_3 is liberated from soils and eutrophicated surface waters giving rise to diffuse and local source areas. Such areas

include the intensely farmed parts of Europe (especially those with large livestock populations) and the shelf areas of the North Sea. The increase of NH_4-N during the last decades also reflects (but differently from NO_3-N) the influence of man. Farming intensity has increased during this time (the use of fertilizers, among others) and it is well known that the eutrophic level of the North Sea as well as lakes and rivers in Europe has become higher. Consequently the diffuse emissions of NH_3 has increased. By contrast, Likens and Borman (7) report that the concentrations of NH_4-N in precipitation in the Eastern part of US show decreasing values.

The wet fallout of total nitrogen forms a distinct pattern over Europe. In 1958-59 (Figure 3) three areas with more than 8 kg/ha/year

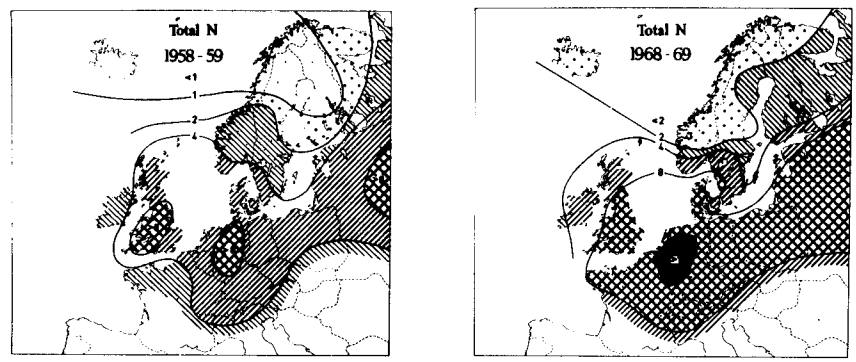


Figure 3. The maps show the geographical distribution of the wet fallout of total nitrogen (NO_3-N and NH_4-N) averaged for the period 1958-59 in comparison with 1968-69. Figures are given in kg/ha/year.

appear and the fallout is reduced extending outwards from the center of Europe. In northern Scandinavia the value was less than 1 kg/ha/year. Ten years later there was an overall, two-fold increase of the fallout. The concentric pattern, however, still exists. The data from Poland have been extrapolated for the years 1968-69.

NH_4-N takes part in the processes of atmospheric acidity in several ways. NH_3 neutralizes sulfurous and sulfuric acids, which are formed when SO_2 is oxidized. This leads to a continuation of the oxidation of SO_2 which otherwise would have been stopped or retarded. As a consequence, the formation of acids take place within a small geographical area. On the other hand, the acids formed will be more or less neutralized but only from a pure chemical point of view. Furthermore, particles of $(NH_4)_2\ SO_4$ or $NH_4H\ SO_4$ formed in the atmosphere (8, 9) are very small and consequently widely dispersed. The

net effect of the different counteracting reactions of NH_3 have not yet been evaluated. The rapid increase of the acidity of lakes and rivers in Scandinavia indicates, however, that both the increased production of acids and the spreading of these acids or pseudo-acids has enhanced the acidification of remote areas in Europe.

The acidifying effect of neutral or acidic ammoniumsulphate on biologically active soils and surface waters, however, will be just as strong as that of the pure acid since the ammonia part of the salts will be resorbed by the plants. This forms part of the processes I have called "biological acidification".

Other elements in precipitation also show time trends. Both S and H increase with time, as will be discussed later. Cations like Ca, Mg and K appear very irregular in the data. At some stations they increase with time; at others they decrease. This state of contrast seems to be related to local industrial activities giving rise to increasing or decreasing emissions. The overall picture for Europe is a slight increase in the sum of the above elements.

Na and Cl forms a very distinct geographical pattern for Europe with large amounts of fallout along the marine shore lines. This picture is equivalent for US, and the relation of these elements to marine salts is wellknown. There is no trend in the data but maybe a periodic variation with a periodicity of 8 years.

THE CHANGING ACIDITY IN PRECIPITATION

pH in precipitation has decreased considerably at almost every station in Europe. Figure 4 gives two examples of the values month by month. The Figures illustrate three phenomena rather common in this type of data.

1. The occasional occurance of higher to much higher pH values in relation to the general bulk of data. Such values appear mostly in the summer time and are likely due to local deposition of alkaline dust. The lack of covariance between nearby stations excludes a more large-scale cause to the high pH-values. A regional effect, however, is that the summer values are slightly higher. This is illustrated by the years 1958, -59, -60, -64, -65, -66 and 1969 at Tystofte.

2. A long-term periodicity appears at Tystofte but not at Forshult. The length of the period is approximately 12 years. The correlation with nearby stations is fairly low. This indicates, that the variation at Tystofte is local or at least less than the grid of the network. For other stations a covariance may appear for certain years (cf. Figure 5).

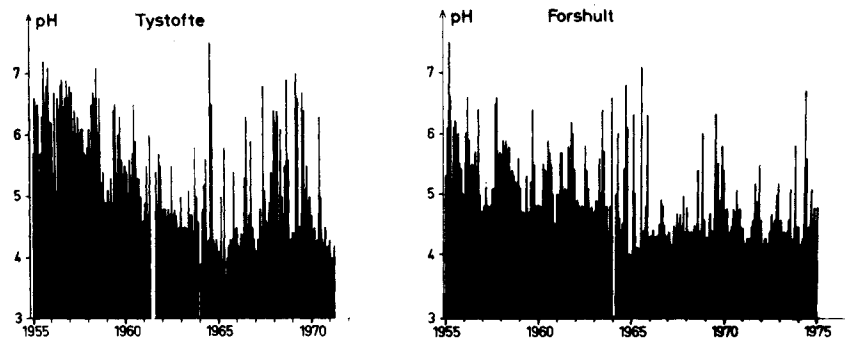


Figure 4. Monthly pH-values from Tystofte in Denmark from 1955 to 1971 and from Forshult in Sweden from 1955 to 1974. See Figure 1 for location of the stations.

3. Generalized for the period, a negative trend takes place at both stations. The pH-values drop from approximately 6.5 to slightly above 4. The same takes place at almost every station in Europe. Due to the large scatter of the data, the regression line for pH with time is not easy to determine.

The large variation in the data on a monthly basis is somewhat reduced when yearly average values are computed. Examples from 6 stations are given in Figure 5. The sequence of the yearly data nevertheless show a large variation. The fulldrawn regression line for each station was drawn (by eye) in 1970. The additional data show that such trends are sometimes not always justified. The trend at Flahult and Plönninge is overestimated, at Smedby underestimated. For the other stations the previous trends are fairly correct. A straight-line relationship means that the acidity has increased exponentially from 1955 to 1974. This is not likely to take place in the long run and the most probable trends are curves tending to a limiting value somewhat below pH 4. The data in Figure 5 illustrate the difficulty in evaluating much atmospheric chemical data. They also show the need for much more research in atmospheric chemistry and related sciences.

To my knowledge, as yet there is no method to eliminate or reduce the variation between years. This should be possible, however, since the co-variance between stations must be related to some factors of physical reality. As shown, the curves for Kise and Ås are very similar. For long periods this is also the case at Flahult, Plönninge and Smedby.

The geographical distribution of the yearly mean pH values of the precipitation are shown in Figure 6. In 1956 a center of acidity (pH 5.0 - 4.5) appears over southeastern England, Northern France and the Benelux countries. Three years later the central area has become

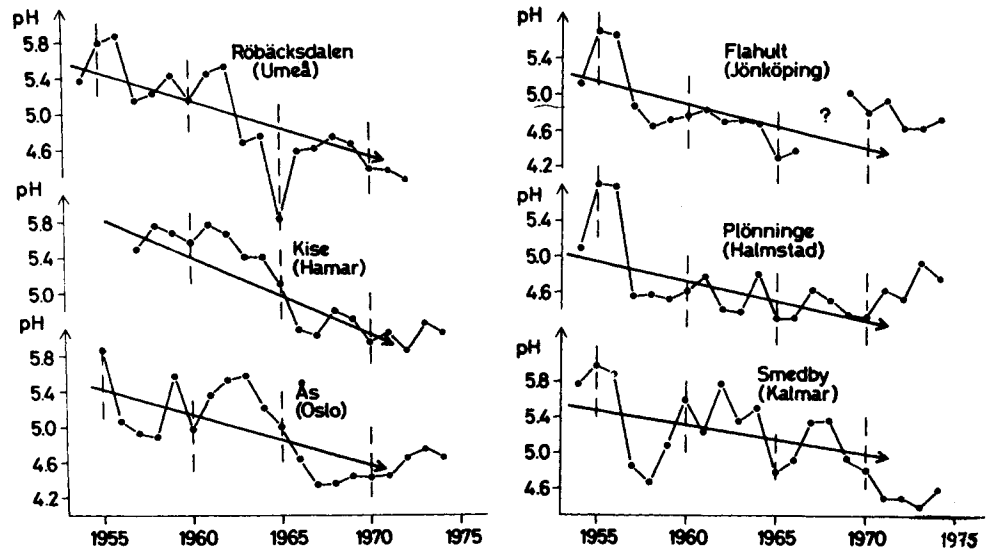


Figure 5. Yearly average pH-values for 2 stations in Norway and 4 in Sweden. The straight trend lines were drawn in 1970. Note the effect of additional data. The station at Flahult was operating only part-time in 1967 and 1968. Stations are localized in Figure 1.

more acidic (by 0.5 pH-units) and the area affected is spreading outwards. Data from the USSR in 1959 make it possible to show that the acidification in northern Europe is regional and mainly isolated from the rest of the Continent.

In 1966 the situation of increasing acidity was still more pronounced. In small areas (Benelux countries) the yearly average pH-values were below pH 4. The areas receiving rain of pH 4.5 - 4.0 were very large in 1966. The maps indicate that the increasing acidity is spreading to the east with the prevailing easterly winds. On the other hand, it can not be excluded that a second center of acidity in the USSR and the Eastern European countries also has been intensified and enlarged, forming a combined area of increased acidity with that of Central Europe.

There is no doubt that sulfur plays a major but complex role of the acidity of precipitation. At almost every station, the sulfur content is steadily increasing while pH is decreasing. Four examples are given in Figure 7 to illustrate this relationship. When examined in detail, however, the correlation is not too good. Changes in the fallout of bases like NH_4, Ca, Mg and K as well as acids like HNO_3 and HCl will also contribute to the acidity or the alkalinity of a sample. Actually, when all ions are taken into account, the pH-values can be

Figure 6. pH-maps for Europe for four years. Isolines differ by 0.5 pH-units. The maps are based on the yearly average of 12 monthly samples.

computed from the balance of ions when the acidity is low enough. This has been proposed by Granat (10) and successfully applied by Cogbill & Likens (11).

Lack of a high correlation between pH and sulfur in precipitation may in part be due to interactions between the mineral acids H_2SO_4, HNO_3 and HCl within the water droplets, when precipitation is formed. When appreciable amounts of H_2SO_4 occur in the water phase, the other acids will diffuse into the air phase. This effect of phase equilibria has not yet been studied to my knowledge. However, we have found substantial amounts of acids in filtered air.

When the maps for the fallout of sulfur are plotted year by year the pattern is very irregular. In some years the fallout is markedly higher in central Europe and USSR, in other years this pattern more or less disappears. The fallout of sulfur obviously is very sensitive to other factors than just the amount of emissions. Sulfur emissions have continuously increased by 2 to 5% per year during the last 15 years, but there is no smooth response in the fallout. There are a multitude

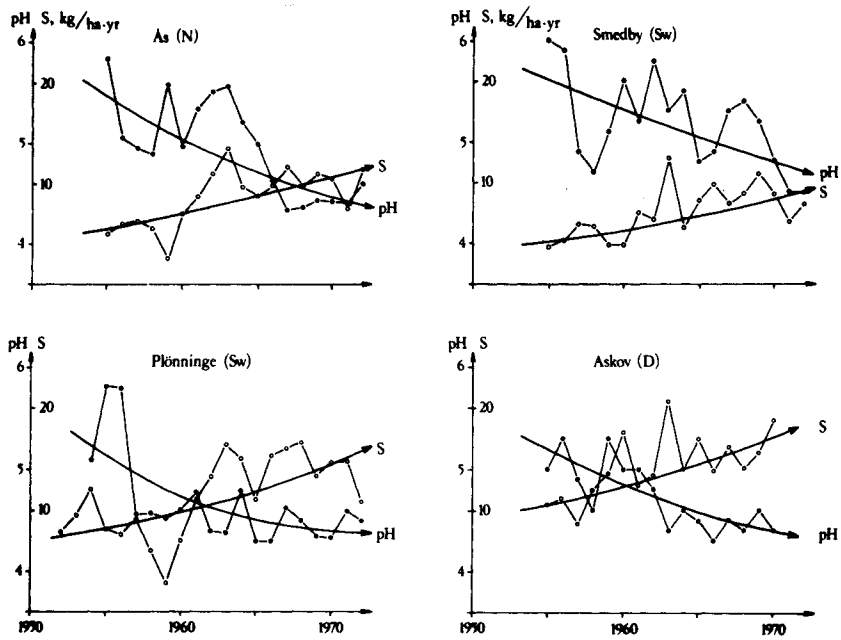


Figure 7. Sulfur and pH as yearly average figures at four stations in Scandinavia. For location, see Figure 1.

of causes for this related to atmospheric chemistry, meteorology and exchange processes with soils and surface waters. Some are listed below.

1. The formation of H_2SO_4 depends on the rate of photochemical oxidation of SO_2 along with

2. a chemical effect of ozone and

3. an enhanced effect due to catalytic dust particles and

4. of NH_3 or other bases in the air.

5. Furthermore, the different products formed will have different life times in the atmosphere and consequently influence their distance of dispersal. Unlike other elements,

6. the mixing of air-masses with different chemical composition may enhance or retard the oxidation of SO_2 at great distances from the point of emission. Finally,

7. sulfur takes part in exchange processes with soils, vegetation and surface waters. Small changes in this exchange may strongly influence the fallout and consequently the dispersal of sulfur.

As yet, the effect of the complex sulfur chemistry has not been worked out taking all these factors into account. Conflicting statements are quite common. When the regional effect of the sulfur-acidity problem have been discussed, various objections against the idea of long-range transport were presented. Among others it was stated that the life time of SO_2 was only a couple of hours before it was transformed to sulfuric acid. Since sulfuric acid is very hygroscopic it will fall out rapidly after its formation. Consequently the emissions of S in the United Kingdom or central Europe could not possibly reach Scandinavia neither in the form of SO_2 or H_2SO_4. SO_2-data from a cruise from Gothenburg to Tillbury to Gothenburg in March 1969 has also been interpreted in favor of this opinion (Figure 8).

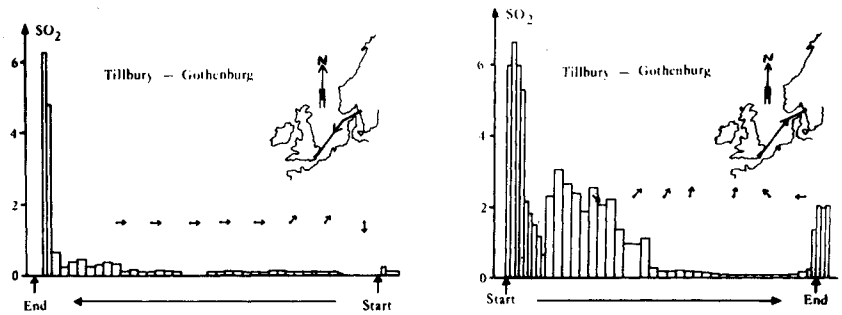


Figure 8. SO_2-data at "sea level" from a cruise by M/S Saga. The route is shown on the small map. The arrows indicate the wind direction. Measurements made by C. Brosset.

The low figures far out in the North Sea were interpreted to indicate that SO_2 is transported in the atmosphere only over very short distances. We now know that the life-time of SO_2 may be up to a week or more. The low but constant figures over the North Sea most likely are a result of turbulent diffusion from a large pool of SO_2 at high altitudes down to the ocean surface, which is an effective sink for SO_2 due to its high pH. Such pools of continental SO_2 at high altitudes has lately been found by flight studies in Sweden (12) and through the OECD project: Long distance transport of air pollutants.

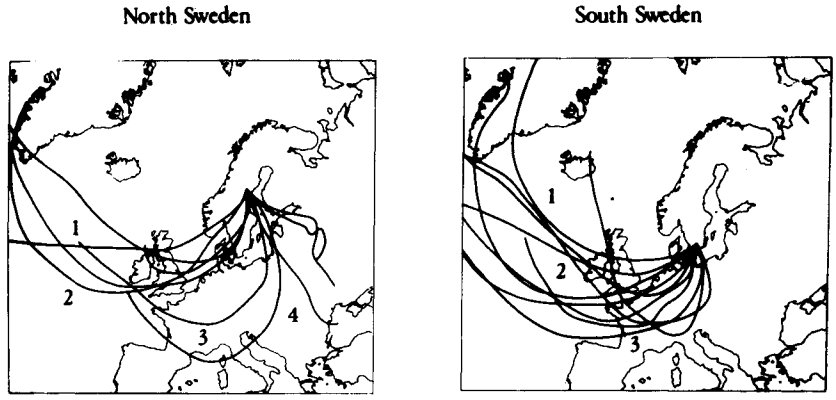
The emission of sulfur varies considerably between different countries in Europe. The figures below are computed from the Swedish Case Study: *Air pollution across national boundaries. The impact on the environment of sulfur in air and precipitation,* (13), which was presented at the UN Conference on the human environment in 1972.

Emissions of sulfur in kg S/ha/year from some countries in Europe in 1965.

Norway	2.5	France	20
Sweden	6.7	U. K.	131
Denmark	30	Holland	152
W. Germany	65		

These figures show a very large variation between the countries. High figures indicate that the atmospheric export is high too. A considerable transport of sulfur takes place from the United Kingdom and central Europe to the Scandinavian countries. This is shown especially by the fact that the discharge of S by Swedish rivers far exceeds the total emission of S within Sweden (cf. below).

In 1961-62 I made a study of the chemistry of individual rain storms at several stations in Sweden along with simultaneous determinations of the wind trajectories. Applied to the present problem some results are given in Figure 9. The fulldrawn curves on the maps show



Trajectories at rain	pH	S	Tot-N	Cl
1. N Great Britain and Denmark	5.2	0.8	0.2	2.3
2. S Great Britain and Benelux	4.9	1.1	0.3	1.1
3 & 4. Central and E Europe	4.7	2.6	0.7	0.6

Figure 9. Wind trajectories to Sweden for occasions of general precipitation. The chemistry of the precipitation reflects the degree of pollution from different parts of Europe. Sampling period: October and November 1962.

the trajectories three days prior to intense precipitation in North and South Sweden respectively. All occasions with general precipitation during a period of two months are included. The air masses are

obviously passing over different emission areas in Europe, and will consequently be polluted accordingly. The least contaminated air (trajectory 1) leads to precipitation with the highest pH-values and lowest figures of S and total N. At trajectories 2, 3 and 4 the pH drops and S and total N increase substantially. The situation for Cl is the reverse; this is logical since the ocean is the main source for Cl.

The trajectories in Figure 9 show that the winds at precipitation periods are mainly from the west and south with respect to Scandinavia. Under dry conditions this is not equally well pronounced. Figure 10

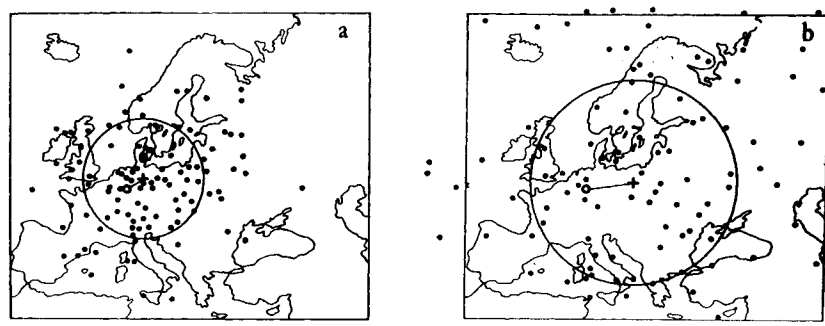


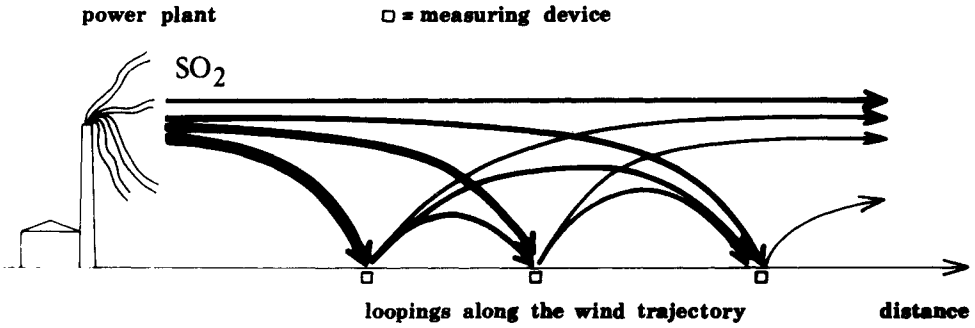
Figure 10. End points of trajectories at a height of 1.5 km from a point (marked by a circle) in northern central Europe for a) 24 hours and b) 60 hours calculated every third day for a period of about one year. 50% of the points are to be found within the circle which are centred around the mean position of all points (marked with a cross).

shows (by dots) the endpoints 24 and 60 hours respectively from a starting point denoted by a circle (13). The spread of the endpoints is almost circular. This means that the pattern of the dry fallout, which may be equally large or larger than the wet fallout, also is circular. The mean position of all points (denoted by a cross) shows that a slight mean wind to the east takes place. This is evident also on the maps for total-N and for pH (cf. Figure 3 and 6).

Figure 9 and 10 show clearly that there is a substantial possibility for interactions between different countries in Europe through the movements of air masses. There is no agreement, however, as regards either the amounts or the effects of this international transport of substances. As long as this state of matter persists, reductions of emissions is not likely to be made.

Several studies have been made in Sweden and elsewhere to determine the spreading distances from an isolated city or a point source like smelters, power plants or paper mills. Theoretically this distance is indefinite. However, measurements in this respect are limited not only to the sensitivity of instruments but also to the difficulties to define a proper base-line or background value. High noise level and periodic fluctuations will lead to an underestimation of spreading distances. The spreading tail will thus be incorporated into the background. At a place remote from cities and industries many such tails may add up anonymously leading to a change in the chemical climate. This is what has taken place in Europe and large parts of North America.

Another natural process that will give the same result is "looping". The process is illustrated in Figure 11. Elements which may form volatile compounds like water, H_2S, $(CH_3)_2S$, NH_3, N_2O, $(CH_3)_2Hg$, DDT etc., and which are added to soils in one form or the other, will start to diffuse into the atmosphere. Scavenging processes lead to fallout and the process starts again. The rate of looping increases with decreasing figures for the residence time of the compound in the two reservoirs.



Effects of looping of sulphur

1. Fallout data are overestimated
2. Spreading distances are underestimated

Figure 11. The arrows illustrate the principle of looping. Measurements of fallout or concentration will give the indicated effects. Measurements in a recipient are free from the artefacts of looping.

At average wind conditions, increased atmospheric transport will take place due to looping. As an example, evapotranspiration of water

is a looping process; without this most areas of the Continents would be deserts. Or to state it in other words: the fallout (in time) along a wind trajectory is always greater (or sometimes several times greater) than the differential flux between the endpoints related to that period of time. Thus, the fallout from a given source will be overestimated due to the repeated measurement of fractional parts of a given fallout quanta. This means that spreading distances are underestimated to a degree proportional to the intensity of the looping process. In spreading studies or when global or regional budgets have been computed, the effect of looping has not been accounted for.

CONCEPTS OF ATMOSPHERIC ACIDITY

The amount of acids in a sample of precipitation is uniquely defined by the pH-value at unbuffered conditions. When the sample contains weak acids, the buffering capacity of these acids has to be taken into account. Some reports from the United States claim that weak acids make up a major part of the acids in precipitation (37). This is rarely the case either in Europe or in the United States. Weak acids like acetic acid, amino acids, other organic acids or salts of iron or aluminum may appear occasionally but their quantitative part in relation to the total acidity is only a few percent (14, 38).

From a pure chemical point of view the amount of acids in precipitation can be computed from the pH of the sample with due regard to pH 5.6, which is the pH for distilled water in equilibrium with atmospheric CO_2. In my original approach (1) alkaline samples were not considered. This was criticized by Eriksson (15) who introduced the concept of "excess acids". This quantity is computed by subtracting the sum of alkalinity for those months with pH>5.6 from the sum of acids in monthly samples with pH<5.6. The procedure is illustrated in Figure 12. For the most, however, local contamination by dust, lime, ashes etc is the cause to the high alkalinity values (cf. Figure 4). Such monthly values may be correct for the immediate place of the sampling station but may be incorrect for a place 100 meters away. The almost nonexistent correlation between stations for those months with high pH-values, shows that such values are not representative in a regional sense and should consequently be omitted. The concept of excess acids leads to a fairly large underestimation of the fallout of acids.

The fallout of local, alkaline dust--irrelevant for the regional acidification--interferes also with the monthly samples, which are collected by an open sampler. Since this is the case with the European network, the true pH-values from this network are consequently lower than those measured. Internal weathering of silicate minerals may also take place during a storage time of more than a month, which

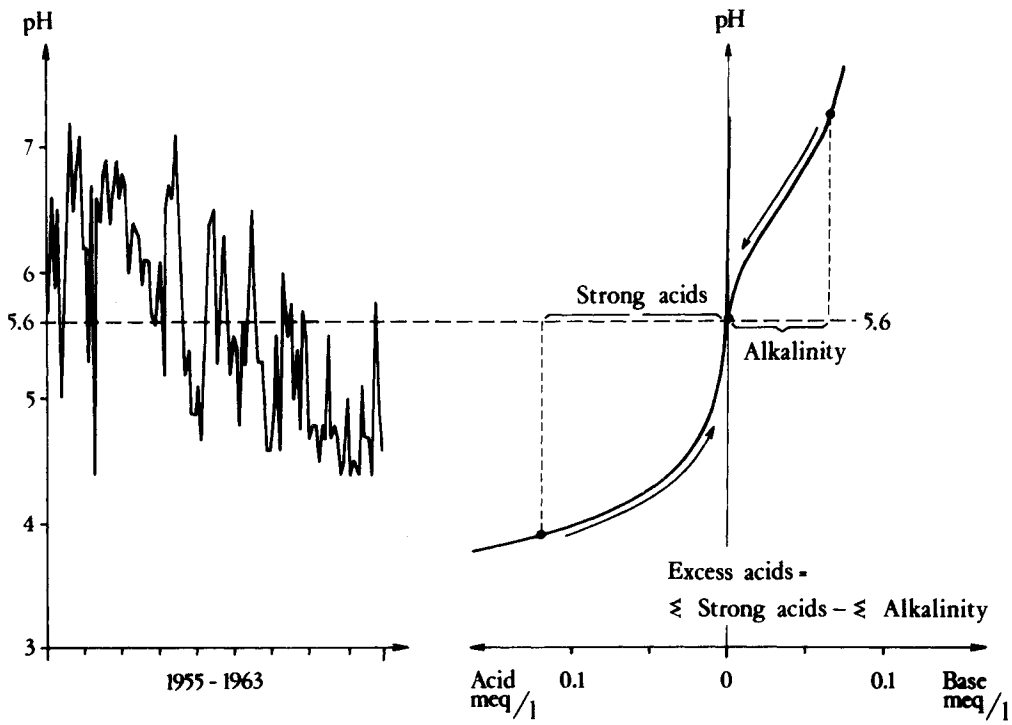


Figure 12. Left: Actual record of monthly pH-values. Right: Analytical and computational procedure of "excess acids".

further reduces the measurable acidity of the sample. Alltogether this may partly explain the discrepancy that excists between measured atmospheric acidity and observed effects in water systems.

Acidification is a dynamic phenomenon. Thus, the term is used to describe a process by which a given environment is made more acidic. The extent of acidification can be expressed as a change in pH from one state to another state. In order to quantify changes in the amount of acids or bases which cause acidification, we also have to compare one state with another reference state. In natural systems, the most appropriate reference state is one that is free of interference by man. Other reference states have no meaning (physically or chemically), but may be useful or even necessary from a computational point of view.

The amount of 'excess acids' in precipitation (or any other similar unit) can be properly computed, but a figure resulting from such a computation has no chemical meaning in any other system than the one for which it was derived. It does not give a figure for the impact of acids on e.g. soils or surface waters. This is due to the introduction of an artificial state of reference, pH 5.6 When Δ-values (time or space) are computed, however, this artificial state of reference will be cancelled and the Δ-values will have a chemical

meaning, e.g. the increase in the fallout of acids between two times or between two places.

However, the *total acidifying effect of precipitation* can be computed if a proper state of reference is introduced. With respect to the present problem, such a natural reference is of course the pH of non-polluted precipitation. The European data suggest that such a pH is above 7, say 7.2. Using such a reference we can calculate the extent of acidification in quantitive terms that are chemically meaningful with respect to affected systems. An example of such data are tabulated below.

Conditions		Acidity(+)/Alkalinity(-)
$pH_{ref_{natural}}$	= 7.2	- 94 ueq/l
pH_{1955}	= 6.4	- 15 "
$pH_{ref_{analytical}}$	= 5.6	state of analytical reference
pH_{1970}	= 4.3	+ 48 "

Results:

"Excess acids" for the year 1970	= 48 ueq/l
Increase of acidifying substances up to 1970 (or decrease of alkaline substances)	=142 "
Increase of acidifying substances up to 1955 (or decrease of alkaline substances)	= 79 "
Changes in the "excess acids" 1970 - 1955.	= 63 "

By this example the figure for "excess acids" in 1970 underestimates the true impact of acid precipitation that year by a factor of 3.

Since the natural state of reference is rather uncertain both in Europe and the U. S. we can not, for the present, compute reliable figures for the total acidifying effect of precipitation. Our computations are restricted to determinations of changes.

THE ACID IMPACT ON SURFACE WATERS

In order to study the biological effects of changes in the chemical climate, a water quality network was set up in 1961-62 in Finland and Sweden. In the beginning, the Swedish network operated with a limited number of determinations but since 1965, when Dr. T. Ahl took over the responsibility, 18 elements or other conditions were measured on every monthly sample (Figure 13). Since the water flow

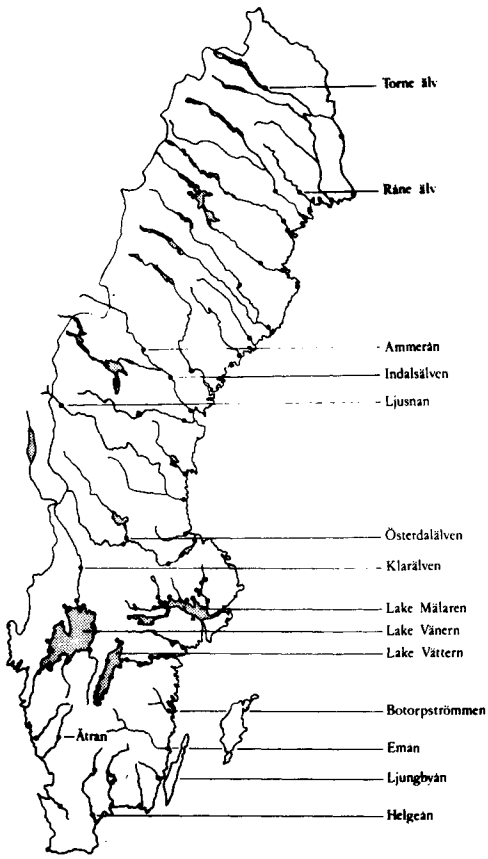


Figure 13. The major lakes and rivers in Sweden. The dots denote the location of the sampling stations. The network is administrated by the Limnological Laboratory, Uppsala, Environmental Protection Board of Sweden.

also was determined, the discharge can be computed for every element. By comparing the atmospheric fallout with the river discharge, the effect of changes in the chemical climate can be determined. The influence of farming, water pollution or other wide-spread or intense activities may, however, distort such computations.

Changes in the acidity of air (dry fallout) and precipitation (wet fallout) will have an impact on natural reservoirs (as well as technical systems). Through the water quality network and parallel

studies on soils, a substantial amount of data have now accumulated to show the various effects of this fall out.

Figure 14 shows the monthly pH-values from three out of the 15 sampling stations, which started in 1965. These records (along with

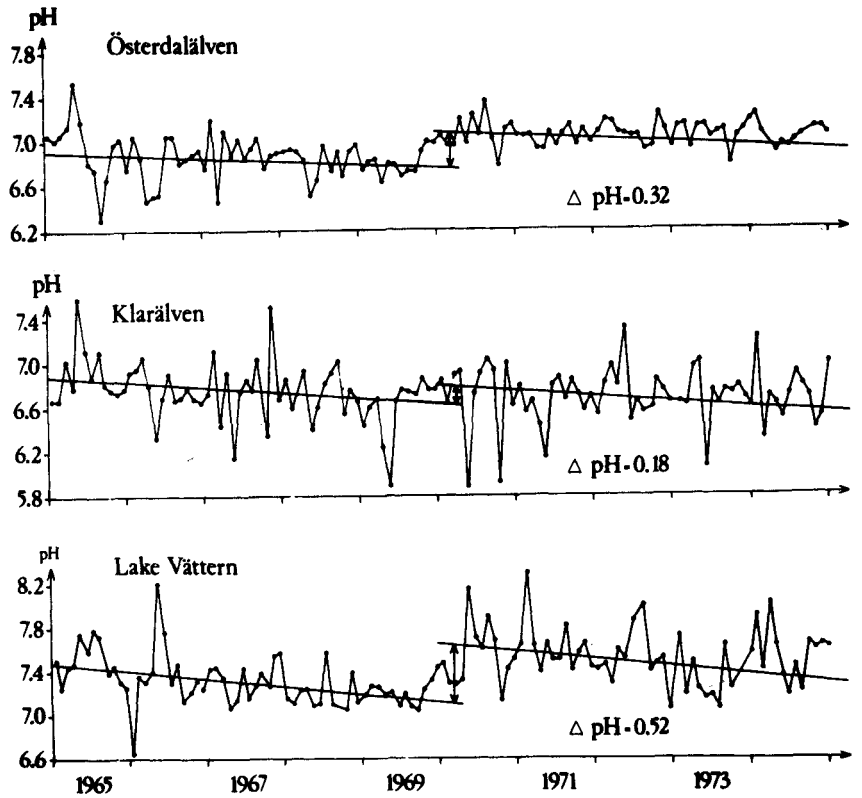


Figure 14. pH-records from 3 sampling stations of the Swedish water quality network during 1965 to 1974. ΔpH refers to the discontinuity denoted by an arrow in the beginning of 1970.

the other 12) show 1) random variations, 2) seasonal variations, 3) yearly variations, 4) time trends and 5) a singular discontinuity. Some of these points will be discussed in some detail.

A seasonal decrease in the pH-values takes place almost every spring. The effect is most pronounced in small water sheds, at high altitudes, and at northern latitudes. Sometimes the drop in pH occured simultaneously with other changes like increasing colour and the content of oxidizable material as measured by the consumption of $KMnO_4$

(cf. Figure 15). These effects proved to be related to the melting of

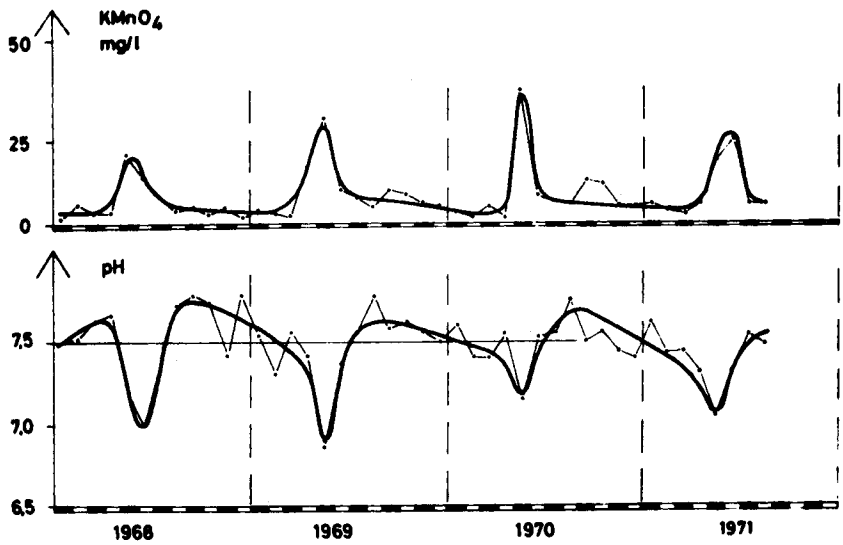


Figure 15. Records of pH and the consumption of $KMnO_4$ from the sampling station at river Ljusnan. See Figure 13 for location of this river.

the snow cover (16). In the first phase of the melting period most ions separate from the package of snow (17). The meltwater is salty and much more acid than the bulk of snow and will drain on top or in the upper layer of the otherwise frozen soil. A rapid flow to the tributaries of the river gives rise to drastic changes in the chemistry of the river water. Such changes may have a profound influence on fish life as a kind of shock-effect.

During the second phase of snow melting, almost pure water infiltrates the soil. If the ground water reservoir is filled at that time the equivalent amount of more or less alkaline ground water is extruded into the surface waters. pH is then rapidly restored. This model has been applied and verified by others in Scandinavia (18, 19). The effect on thermally statified lakes has been shown to be of special interest (20).

The discontinuity in the pH-records in 1970, denoted by an arrow in Figure 14, is also related to snow. The storage of snow was especially large during the winter 1969/70. The soil, however, was almost unfrozen that winter and at snow melting, most of the melt-water infiltrated the soil leading to the alkaline ground water effect discussed previously. The ΔpH at the point of discontinuity is well

related to the amount of calcareous materials in soils and the bedrock within the different river basins. Where calcareous materials do not exist in the drainage area of a river the pH-discontinuity is not noticable (21).

The pH-trends in all Swedish rivers investigated since 1965 (some from 1963) are all negative. The regression lines seem to be straight within the investigated period and the discontinuity in 1970 does apparently not lead to a change in the slope. If the slopes are extended to pH 5.5, which is supposed to be a biologically critical pH-value a "life-time of health" is obtained. On the average 60% of the investigated rivers in Sweden will reach this critical point in 40 years and as much as 90% in 80 years (13). Each discontinuity will extend these ages by 4 years on the average. The frequency of such jumps, however, is not known but is likely to be very rare in Scandinavia.

In 1965 and 1970 we made a synoptic water quality study of Scandinavian surface waters by roughly a 1000-point network (16). Several regions proved to have much lower pH-values than surrounding areas. Such regions were the southwestern part of Norway, the western part of Sweden, and some areas in the interior of middle and south Sweden. The low pH in these regions are mainly a consequence of the increasing acidity of air and precipitation along with soil conditions of low buffering or neutralizing capacity.

By now, numerous investigations have been made by others in Sweden, Norway, Canada and U. S. on the acidity of lakes and rivers. Almost all give the same results showing a decrease in pH. Small lakes at higher altitudes may actually have pH-values close to that of the precipitation, i.e. around 4.

Natural waters are normally buffered by soluble substances (PO_4, organic acids, amino acids etc), colloidal organic matter (humus, seston) and bicarbonate. A set of buffering curves for waters from the Swedish water quality network is shown in Figure 16. The rivers designated SE, SF and SL have obviously low buffering capacity and are consequently sensitive to additions of acids. The shape of the curves makes it clear that all waters are very pH-sensitive in the range pH 6.5 - 4.5. Small additions of acids to such rivers may thus cause a rapid drop from pH 6.5 to pH 4.5. Above pH 7.0 the waters may be highly pH-stable due to bicarbonate (cf. SA and SB in Figure 16).

At present the content of bicarbonate steadily decreases in almost all lakes and rivers within the water quality network. As such this has no direct biological consequences but it is a measure of increasing acidity within the water shed area. The only acid of any importance in this respect is sulfuric acid or the trans-form of its ammoniumsulfate salt. The ratio HCO_3/SO_4 is a very sensitive index (besides pH) of the continuing acidification of natural waters. Four examples are given

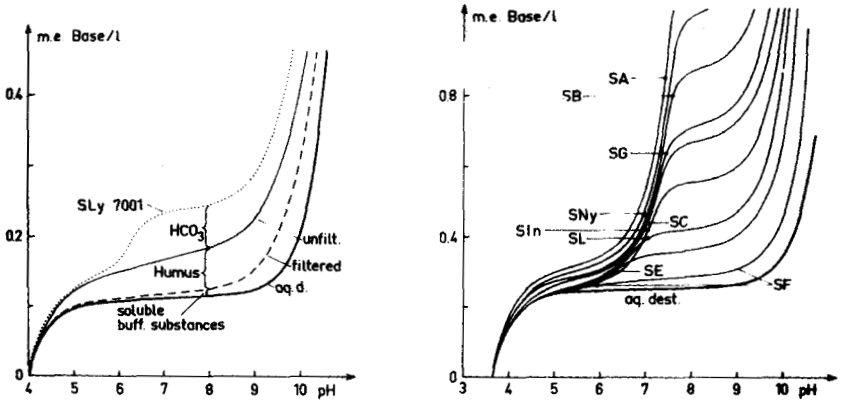


Figure 16. Left: The total buffering capacity of surface water (SLy 7001) is made up by HCO_3, humus and soluble substances. Right: Buffering curves of river waters from the Swedish water quality network. The dot on each curve denotes the pH-value at the time of sampling.

in Figure 17. All rivers show a continuous decrease of this ratio.

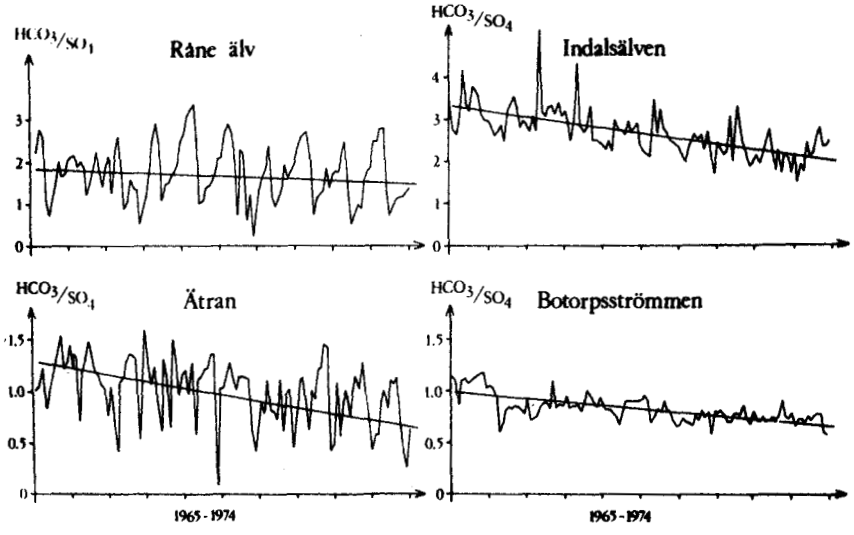


Figure 17. The ratio of bicarbonate to sulfate on an equivalent basis for four rivers of the Swedish water quality network. For location of the sampling stations, see Figure 13.

The slope is steepest for rivers in the south and west of Sweden; this is in accordance with the greater fallout of acids in these areas.

When the HCO_3/SO_4 ratio is zero, bicarbonate has disappeared. pH is then about 5.5, i.e. the pH-value previously discussed as a critical value. When the slope of this ratio vs. year is extended to its zero value, figures for the life time of a healthy state will be obtained. Such computations from all long-term stations give a spectrum of ages, which is almost identical with that based on the pH-trends (cf. Figure 14).

The chemical changes of the Swedish river waters, illustrated by our data from 1965 to 1974, started of course much earlier. This can be shown by comparing the discharge of Ca and HCO_3 at three different periods. Each line in Figure 18 represents the regression line for a

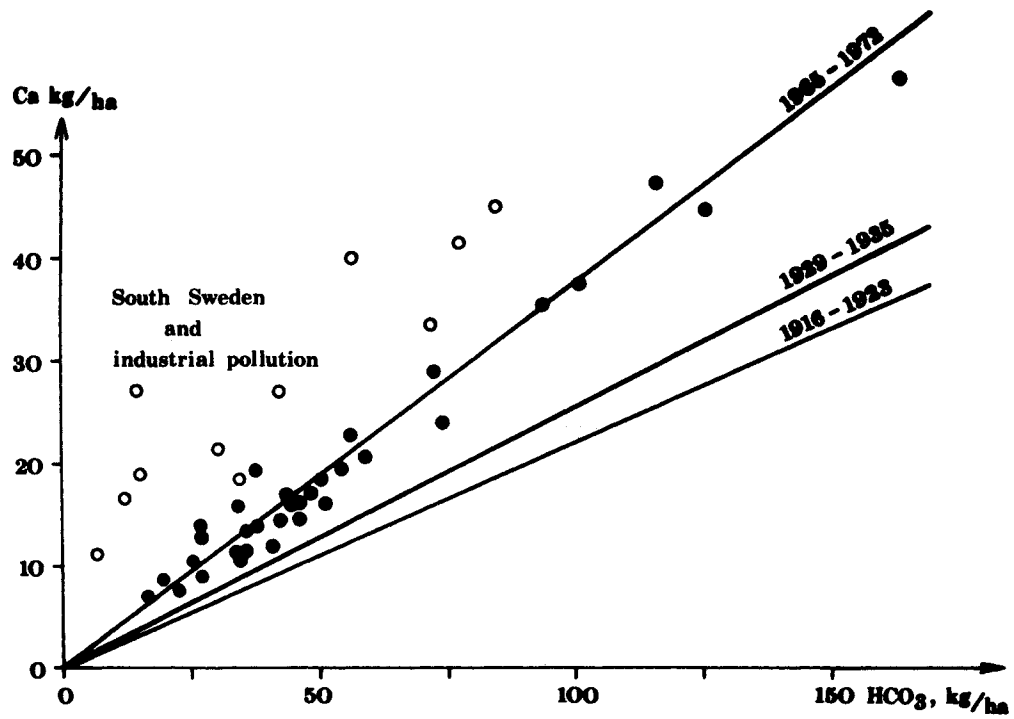


Figure 18. The discharge of Ca and HCO_3 by Swedish rivers at different time intervals. The circles refer to rivers in south Sweden and those polluted by calcium sulfate.

large number of data from lakes and rivers at indicated time intervals Obviously, the slope is gradually increasing with time. This indicate that the discharge of a given amount of Ca will take place with

successively lesser and lesser amount of HCO_3. This is only possible if HCO_3 is exchanged by another anion, as e.g. sulfate. The figures below show that the discharge of sulfate by Swedish rivers actually has increased considerably since the beginning of this century.

Discharge of SO_4-S, kg/ha/year

Region		1909 - 1923	1965 - 1972
North Sweden ,	> 65°N	2.3	6.3
Central Sweden ,	60°N - 65°N	4.4	9.1
South Sweden ,	< 60°N	10.3	21.0
Skåne - Blekinge		12.5	31.0

The discharge of sulfate is now more than twice as large as in the past. When only the anthropogenic part of sulfur is taken into account (corrections are made for cyclic salts) the increase is three to five times between the different periods. In the southeast part of Sweden (Skåne-Blekinge) the increase of anthropogenic sulfur is about 20 kg S/ha/year within a period of 50 years. In the form of sulfuric acid this equals 60 kg H_2SO_4/ha/year or approximately 1500 kg for the whole period.

The total discharge of sulfur by Swedish rivers, corrected for cyclic salts and sulfur in fertilizers is much greater than the Swedish emission of sulfur. Thus a considerable atmospheric import takes place. Our data makes it possible to compute, that the impact of Continental sulfur in Sweden amounts to about 70% (22).

THE ACID IMPACT ON SOILS

The chemical conditions in lakes and rivers reflect in a more or less complicated way reactions and changes in the soil system and occasionally in the bed rock. When the lake area is small in relation to the drainage area, neither sink mechanisms in bottom sediments nor the effect of precipitation or dry fallout directly at the surface of lakes and rivers has to be taken into account. In Sweden 80 to 95% of the surface waters is actually a mixture of shallow soil water and groundwater, and consequently, changes in the water chemistry is almost totally related to transformations within the pedosphere of acid precipitation in a wide sense.

As a model, the relationship between precipitation (and dry fallout), infiltration, ground water runoff, surface water runoff and the mixing of different categories of water in lakes and rivers is

illustrated in Figure 19. When the precipitation is acidified, a

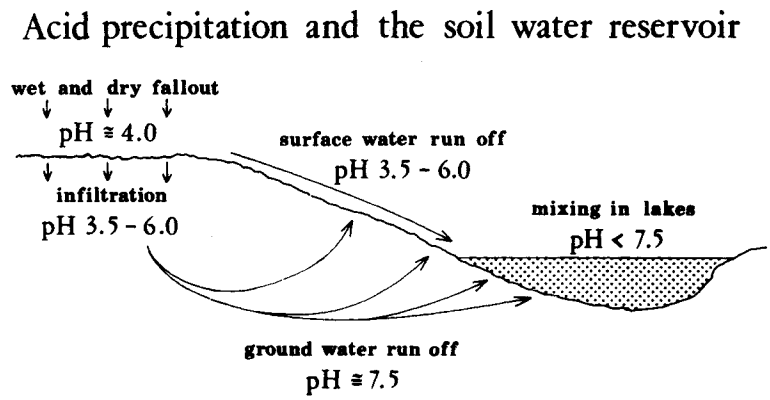


Figure 19. Part of the hydrological cycle related to soils and surface waters with respect to pH-changes along different pathways.

multitude of reactions will take place at the soil surface and the zone of infiltration.

A soil is normally in dynamic equilibrium with its surroundings including vegetation; alternatively it may be drifting slowly towards new equilibrium conditions, for example due to farming, lumbering or fertilization. The impact of changes in the chemical climate causing acidification (decrease in alkalinity, increase in acidity, or increase of elements causing biological acidification) will also tend to create new equilibrium conditions for many different reactions in the soil system. For example, an increase in the acidity of the soil solution may be a primary effect. However small, this will lead to an exchange of adsorbed cations on the soil colloids. The desorbed ions will be leached out of the soil and the degree of base saturation will be reduced. These processes will extend downward in the profile with time. A more acidic and a diminished nutritive status will interfere with plant growth and will change the composition of the plant community in the long run. Such biological changes are likely to induce increased acidification. Furthermore, the rate of mineralization of litter and humus will be retarded. Until a new equilibrium is obtained, the cycling of nutrients in the ecosystem will be retarded too. Some of these effects will tend to be counterbalanced by increased dissolution of carbonates, and increased weathering of silicate minerals. When a soil type with accumulation horizons is affected, large amounts of ions, i.e. heavy metals, may start to dissolve. Processes of soil formation will be enhanced, and less productive soil types will be formed, for example, because of decreased fixation of atmospheric nitrogen.

Some of the above reaction mechanisms have been verified by us or by others. Other mechanisms have been formulated as postulates since they are derived from common knowledge in Soil Science or Soil Biology. The knowledge of these reaction mechanisms is necessary to evaluate biological effects and to understand *why and how* but they are extremely difficult to integrate to obtain the total impact of acidification in quantitative terms. Due to the assumptions made for such an integration procedure or to the incompatibility of laboratory results to conditions in nature, different quantitative answers will be obtained. Studies at the physical boundaries (soil-atmosphere interface or soil-surface water interface) make it possible to obtain quantitative answers of changes of the impact of acidification (cf. below) or, when a proper state of reference is introduced, the corresponding effect in absolute terms (cf. discussion on page 16-17).

In 1970 we made a survey of forest soils in Sweden and Norway in order to study the impact of acidification (23, 24, 13, 25). Sites similar with respect to soil type and vegetation (185 places) were selected and profiles were sampled down to a soil depth of 50 cm. The maps for pH and the degree of base saturation are given in Figure 20. As shown, there is a large continuous zone in the southwestern part of Scandinavia with lowest figures both in pH and in the degree of base saturation. This part is also closest (with respect to wind conditions) to the center of acidity in Europe. A small area of similar soil changes occurs west of Stockholm. At a place within that area alum shale has been burnt for decades giving rise to large emissions of SO_2. The effects on the soils, however, are only local.

As indicated in Figure 20 the soils in southwestern Scandinavia are considerably depleted of cations. In comparision with a normal podsol these soils have lost between 55 to 70% of their normal content of cations; the latter figure refers to the subsoil. With central Sweden as a reference the losses of cations down to 0.5 m in the profile amounts to around 80 keq/ha. A large part of these losses may be accounted for by the integrated atmospheric acidification during the last hundred years. Our computations point to 70 keq/ha excluding nontransient processes. The remaining part is due to natural differences between the SW part and the interior part of Scandinavia. The underlaying data and the details in these computations will be presented in ref. 26.

In order to establish that the soil conditions in southwest Scandinavia are due to anthropogenic effects (the opposite has been argued), a study around a copper smelter at Falun has been made. This smelter has been operating for about 500 years and the total emission of SO_2 amounts to some 5 million tons of SO_2 over this period. Some results are shown in Figure 21 and 22.

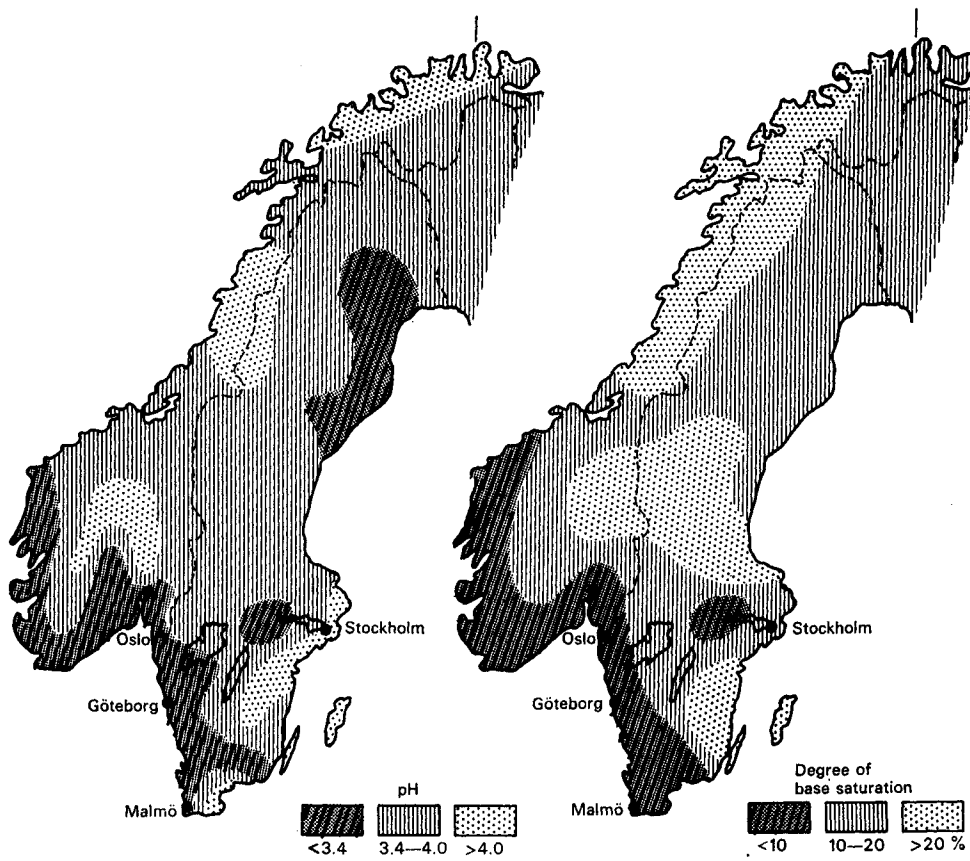


Figure 20. pH and the degree of base saturation in the upper 5 cm of podsolized forest soils in Scandinavia.

pH has been considerably reduced in all soil horizons even down to a depth of 40-50 cm. Close to Falun the pH at that depth has dropped by approximately one unit with respect to reference values outside the map. In fact, the whole of the investigated area is influenced by increased acidity at this depth. The degree of base saturation is also considerably decreased.

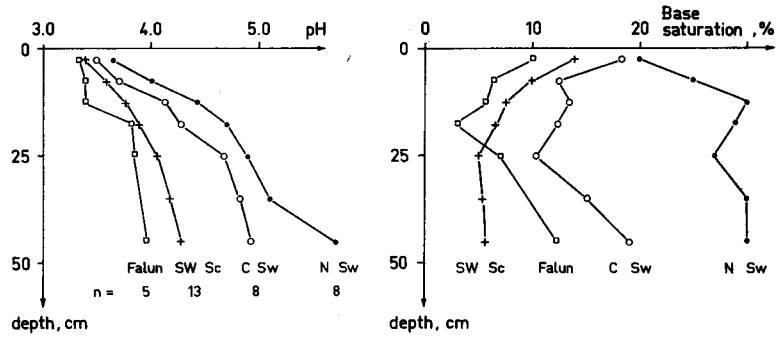


Figure 21. Profile data on pH and the degree of base saturation from the following parts of Scandinavia: South-West part of Scandinavia, Central Sweden and North Sweden. The Falu-area is also included. Data are averaged for the indicated number of profiles.

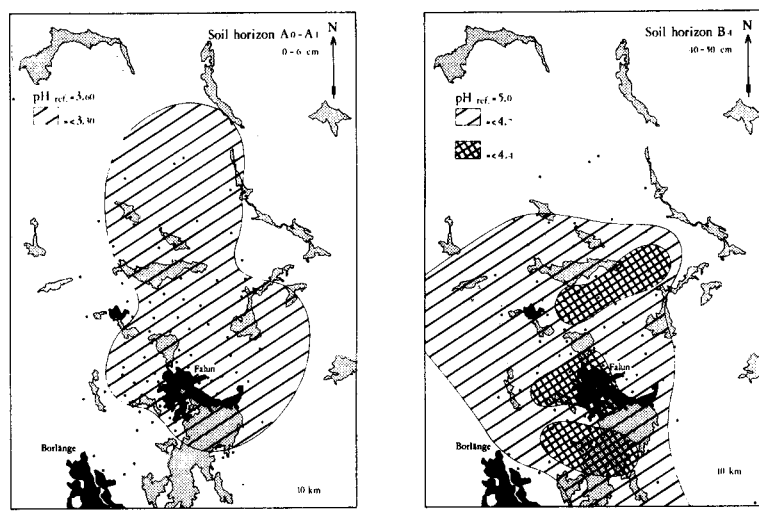


Figure 22. The maps show the pH-depression at horizon A_0-A_1 and B_4 in the Falu area. Reference values refer to sites outside the map.

Outside the investigated area the degree of base saturation is about 25%, but close to Falun the value has dropped to 10% at deeper depth.

The spreading of acidifying substances from Falun has an impact on surrounding soils very similar to that in the Southwestern part of Scandinavia. The effect on forest growth, however, has not yet been measured in any of these areas. According to other studies on forest growth, a reduced growth rate is to be expected (27, 28). The productivity of both pine and spruce has proved to be much less for plant communities of low calcium status than for other communities at high calcium status (29, 30).

For the present, the atmospheric acidity has been related only to mineral acids like sulfuric acid, hydrochloric acid and nitric acid. Biological processes, however, may also cause acidification in soils and surface waters by means of different reaction mechanisms. I have called these processes "biological acidification". When the production of organic matter is balanced by the corresponding decomposition of organic matter, there will be only a small net effect of such processes. Those denoted in Figure 23 will cause acidification due to a phase-shift in time of the different mechanisms related to the biological turn over of ions either on a yearly or a longterm basis.

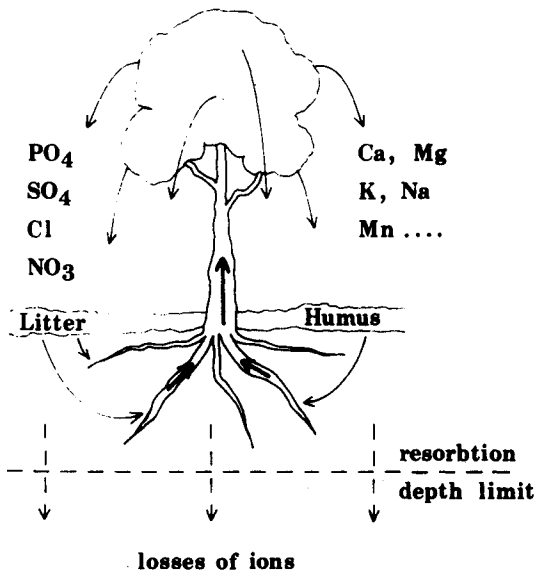
Biological acidification will be considerably enhanced when the production of organic matter is larger than the decomposition. This takes place in nature when peat bogs or forest peats are formed, and these systems are also very acid. However, the same applies to systems influenced by man. The harvest of crops on agricultural or forest land often causes a large difference between production and decomposition of organic matter within a given area.

Biological acidification consists mainly of two processes: an increase of excess alkalinity in plants and the effect of nitrogen metabolism (31). Our studies on the excess alkalinity (ΣNa, K, Ca, Mg, Fe, Al ..... minus ΣSO_4, Cl, PO_4 .....) on a variety of plant tissues show figures varying from 8 meq/100 g dry matter up to 300 meq/100 g dry matter. By means of the following figures (meq/100 g d.w.)

Pine,	trunk	8	Podsol, F+H layers	35
"	bark	34	Peat bog	23
"	litter	45		

we can compute, that a pine forest induces acidification of the soil by 340 eq/ha every year and that the increase of organic matter in the F + H layer during the life time of a forest rotation adds another 55 eq to that figure. As another example, a peat bog, with a growth rate of 1.1 mm a year, acidifies the system by 260 eq/ha/year.

The biological turn over of ions



Yearly effects

1. **Pulses of losses of ions in spring and autumn**
2. **Fluctuations in pH and exchange capacity**

Longterm effects

1. **Increase of net bases in standing crop and humus**
2. **Accumulated losses at cutting**

Figure 23. Principal effects of mineral cycling due to biological turn over interfering with the acid-base status of the soil.

Following the original work by Pierre (32) the uptake of NH_4^+ or NO_3^- will make the soil more acid (-) or more alkaline (+) depending on the pathway of the nitrogen metabolism. The following may be given:

Uptake of	1 eq	NO_3-N	leads to +	0.5 eq alkalinity
" "	"	NH_4-N	"	- 1.0 "
Nitrification of	"	NH_4-N	"	- 2.0 "

Applied to the examples above, nitrogen metabolism at irreversible conditions may acidify a pine forest ecosystem by 475 eq/ha/year and a peat bog by 320 eq/ha/year. Part of the mechanisms above have been verified quantitatively in a field test (33). The elegant studies of induced acidification of a water course ("oligotrophication") by Gran et al (34) may also be formulated quantitatively in chemical terms related to mechanisms of biological acidification.

Changes in the chemical climate may be expressed in the same terms as biological acidification. Results for the southwestern part of Scandinavia during the period 1955-1971, are shown in Figure 24. The background values for the fallout of NO_3-N and NH_4-N (cf. Figure 2) gives rise to a constant background value of the biological

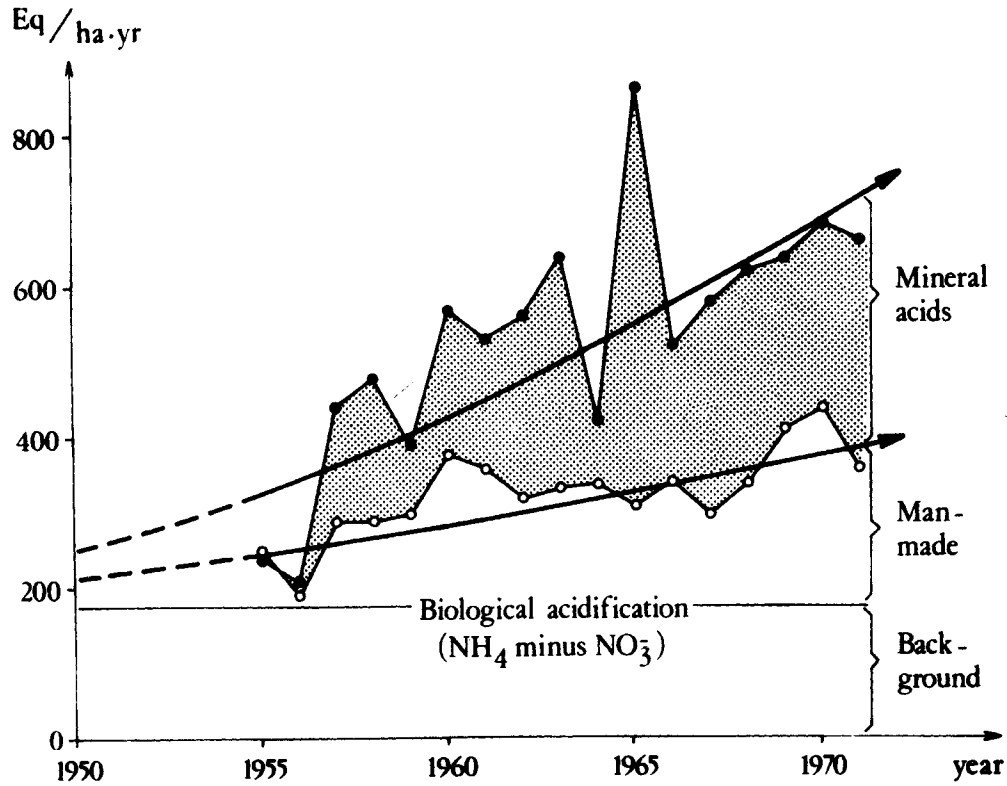


Figure 24. The curves show the time sequence of acidification due to mineral acids (= excess acids) and to biological processes. The background figure is computed from data in Figure 2. The computation is relevant for the southwestern part of Scandinavia and is based on data from the International Meteorological Institute.

acidification. The change in time of nitrogen in precipitation adds a man-made part of the biological acidification. When excess acids are added (without taking the errors of this concept into account) we may obtain figures for the total change in the acidifying effect on soils and waters due to precipitation.

A MODEL TOWARDS QUANTITATIVE SOLUTIONS

As demonstrated, there are several limitations in computing quantitative data for the atmospheric impact causing acidification of soils. It is equally difficult to obtain such data directly from studies on soils due to the many reaction mechanisms involved, the very high heterogeneity in soil characteristics, and the lack of a proper

reference state. As a third alternative, solutions may be obtained by a proper evaluation of the chemistry of surface waters. An example of this approach will be given by utilizing data from the river Ätran, Figure 25.

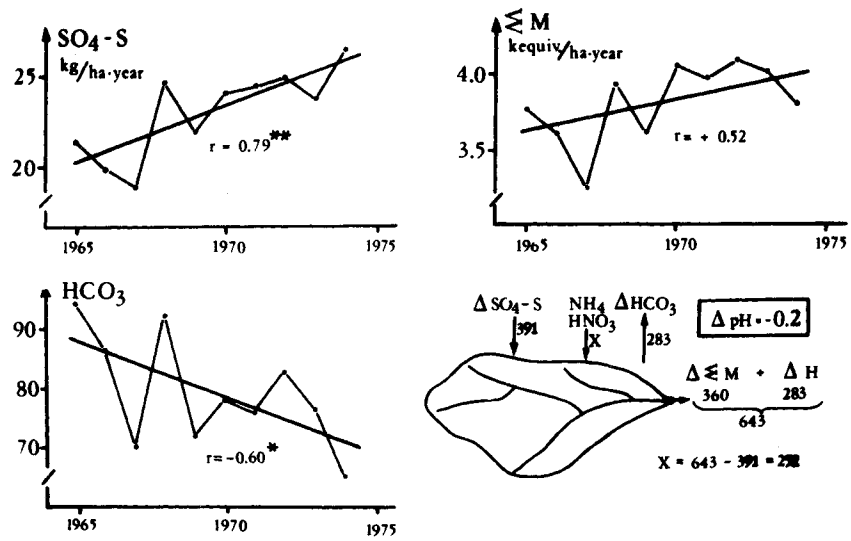


Figure 25. Discharge of SO_4-S, HCO_3 and the sum of cations (ΣM) from the drainage area of river Ätran. Changes of these quantities during the last ten years are given in eq/ha. X denotes the magnitude of processes due to biological acidification. Original data are recomputed to cancel the variations in the discharge of water between years.

The increase of acidification over a ten year period is given by the sum of the changes in alkalinity ($\Delta H + \Delta HCO_3 \rightarrow CO_2$; $\Delta H = 283$ eq/ha) and the amount of cations ($\Delta H \rightleftarrows \Delta\Sigma M$; $\Delta H = 360$ eq/ha). This means that only 56% of the increased acid impact is counterbalanced by ion exchange and weathering. The remaining 44% suppresses the dissociation of bicarbonate. This leads to a decrease in pH according to the buffer curve (cf. Figure 16). The change in total acidification consists of two parts: atmospheric fallout and biological acidification. The atmospheric part may, at maximum, be estimated from the ΔSO_4-S (= 391 eq/ha) in the river water with due regard to terrestrial sources. Consequently, the increase of biological acidification amounts to at least 252 eq/ha.

The partition between weathering and ion exchange may be computed from the change of silicon in the river water and knowledge of the chemical composition of the weathering products. Our data in these

respects show, that ion exchange accounts for about 10% of the increased losses of cations in the soil system during the investigated period. 90% is not explained by ion exchange.

When a relevant state of references is introduced (if that is possible), the above computations may be given as absolute figures for approximately the last 100 years. At present, however, no reliable method can be offered for that purpose.

Part of this paper was presented as a plenary lecture at the 19th Congress of the International Association of Limnology in Winnipeg 1974 (35). The Congress adopted the following resolution:

> "Whereas, the increased introduction of man-made pollutants to the atmosphere is seriously contaminating the earth's airsheds, often remote from local sources, and
>
> Whereas, the fallout of these materials is contributing to acidification and other pollution of lakes, rivers, and ground waters of large geographic regions, and,
>
> Whereas, the recently observed, and projected changes in acidity of waters represent a serious stress for natural aquatic ecosystems,
>
> Therefore, this Congress deplores such degradation of aquatic ecosystems, and urges governments, scientists, engineers, and layman every where to investigate thoroughly the ecological magnitude of these changes, and to undertake prompt and ecologically sound remedial action."

I accept these statements as a suitable guide-line for our future work on the acidity problem.

Part of the work presented in this paper has been sponsored from time to time by the Research Council of the Swedish Environmental Protection Board. The Swedish Case Study was supported by the Swedish government. The author is much indebted to the staff of our Department and to Dr. T. Ahl for many years of valuable cooperation.

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A PRESENTATION OF THE NORWEGIAN PROJECT "ACID PRECIPITATION - EFFECTS ON FOREST AND FISH"

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INTRODUCTION

Air pollution is an international problem of the greatest dimensions. The continuous expansion of production and consumption in modern society is accompanied by the steadily increasing emission of air pollutants of different types. It is generally recognized that air pollutants can be transported in substantial amounts over distances of 1000 - 2000 km. This phenomenon has been studied with special attention being focused on acid sulphur compounds, which are the main cause of acid precipitation.

The Norwegian research program entitled "Acid Precipitation -- Effects on Forest and Fish" (or the SNSF - Project) was undertaken to study such problems. The present paper discusses the evolution of that project and some of the research areas in which it is now involved.

THE SNSF - PROJECT

The long range transport of air pollution in Europe has caused many problems. Through the Organization for Economic Cooperation and Development (OECD)-Project, "Long Range Transport of Air Pollutants," considerable progress has been made in establishing the connection between emissions of air pollutants, weather conditions and concentrations in precipitation areas in Europe. Southern Norway is especially exposed to increased precipitation from winds between the southeast and southwest. These air streams almost inevitably have passed over important emission regions within the industrialized belt across Europe. The precipitation that is caused by the mountain ranges in southern Norway will, therefore, often contain high concentrations of pollutants from remote sources. The severity of the air pollution problem, particularly acid precipitation, becomes obvious when we recognize that 80% of the productive forest land in Norway is dominated by acid podzolic soil, and that thousands of lakes are located on acid granite bedrock.

Long range transported air pollutants are recognized as the most acute environmental problem in Norway today; the problem is of sufficient importance to justify extensive studies. Therefore, in 1972 the nationwide joint research project, "Acid Precipitation - Effects on Forest and Fish" was initiated as a result of action taken by the Government and two Norwegian Research Councils. This modern research effort is organized strictly as a project-oriented, cross-institutional, self-governing entity. More than ten Norwegian research institutes participate in this project, involving nearly 50 scientists and a large supporting technical staff. The Norwegian government has recently increased its budget allocation for this project by a significant amount, thereby indicating the importance and reality of the acid precipitation problem to Norway. The government has clearly shown its intention and willingness to do something about the problem.

The main objective of the SNSF - Project is two-pronged:

1) To establish as precisely as possible the effects of acid precipitation on forest and fresh water fish, and

2) To investigate the effects of air pollutants on soil, vegetation and water, (to the extent required for paragraph 1).

The data from this research project will be used as a scientific contribution to the forthcoming international negotiations aiming at control of the overall emission of air pollutants.

SNSF RESEARCH PROGRAMS

AIR POLLUTION DEPOSITION

Air pollution occurs primarily in the central mountain region of southern Norway. Close cooperation with the OECD - Project, in which the Norwegian Institute of Air Research acts as the Central Coordinating Unit, gives the SNSF - Project the possibility to utilize forecasts of polluted air streams, their origin and time of arrival. This allows our research teams the time necessary to reach various field stations prior to the arrival of the precipitation that carries air pollutants. All of Norway is used as our field of operation.

Two examples of such pollution are: 1) During the period 5-13 January 1974, the southernmost part of Norway received precipitation as snow containing 850 kg sulphate per km^2 , of which approximately 90% was sulphuric acid. The precipitation arrived on southeasterly winds with contributions both from eastern and western Europe, 2) During an 8-day period in January 1974, the southwestern parts of the country received over 20,000 km^2 precipitation from Great Britain amounting to 4,000 tons

of sulphate corresponding to 100% sulphuric acid.

In addition to the deposition by precipitation, air pollutants may also be absorbed and adsorbed by vegetation and by the ground. This dry deposition accounts for the removal of a substantial amount of pollutants from the air. In some cases the concentrations of various pollutants in precipitation under exposed trees have been found to be 2-3 times higher than in open terrain. The degree of dry deposition is closely associated with the total active surface exposed to the polluted airstream. Figure 1 shows the tip of a single spruce needle as seen by

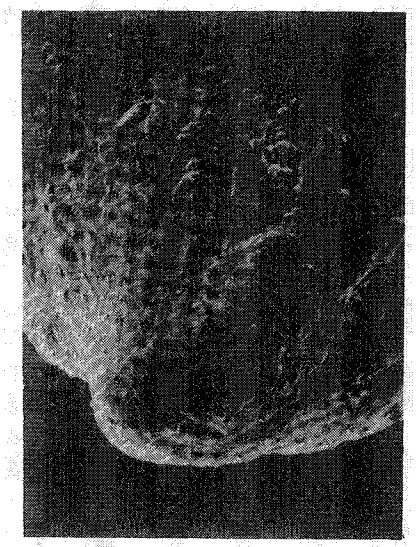

Figure 1. Tip of a single spruce needle photographed by an electron microscope.

an electron microscope and demonstrates the scale on which this deposition phenomenon occurs.

In addition to the acid forming compounds, polluted air and precipitation also contain heavy metals, soots and tar products from combustion processes. The presence of organic micro-pollutants has also been demonstrated both in precipitation and as dry deposition. Great efforts will be made to quantify the total deposition of the various air pollutants, particularly within the most heavily exposed areas of Norway, especially southern Norway.

EFFECTS ON THE FOREST ENVIRONMENT

The effect of pollutants on the forest environment is one of the

most important questions within the SNSF - Project. The growth response is a result of interacting physico-chemical and biochemical processes. Intensive studies are being carried out to quantify the damage caused by the long-range transported air pollutants with regard to forest growth. However, at present, it is not possible to draw any definite conclusions.

Extensive experiments with spruce, pine and birch are also underway in phytotrons, nurseries and under field conditions where air pollutants at various concentrations and compositions are added. On the basis of existing knowledge, it is possible to assume that the total production potential will be reduced and that some plant communities will disappear almost completely as a result of gradual acidification of the soil in the more susceptible regions of the country.

EFFECTS ON AQUATIC ECOSYSTEMS

An increasing acidification of the water in watercourses in southern Norway has been observed in recent years. There are many examples which indicate that streams, rivers and lakes can be exposed to heavily polluted loads of acidifying components and other air pollutants, particularly in connection with episodes of strongly polluted precipitation. The topography and the geological conditions are of great significance in this connection. There are clear indications that the chemical composition of water within a precipitation area is altered as a result of the pollutants which are added through precipitation and possibly through dry deposition.

When precipitation falls in the form of snow in the winter, pollutants are accumulated over a long period of time in mountainous snowfields and then transmitted to watercourses when the snow melts. During the winter a vertical transport of pollution occurs. A resultant accumulation of pollutants in snow has been demonstrated, which means that the pollutants collect in the lower layers and are then released in more concentrated form at an early stage in the melting process, at a time when the water level in watercourses is still low. This can lead to sudden and acute increases in water pollution levels. Measurements taken during the spring thawings of 1974 and 1975 have shown pH levels in the vicinity of 3.0 in run-off water from snowfields. In addition, substantial amounts of heavy metals and also organic micropollutants have been found in the run-off water. These problems are undergoing intensive study through the SNSF - Project.

INLAND FISHING

Inland fishing in southern Norway has suffered severe setbacks in recent years, caused mainly by acidification of the water. The majority of these waters are extremely poor in organisms and have completely lost

their fish populations. This is the present state of affairs in thousands of localities, particularly in the southern part of the country. Intensive studies are being undertaken to gain more scientific knowledge about the effect of air pollutants on fish and important fish food organisms.

As an illustration, when fish, collected from the field, are immediately exposed to water from some of the highland rivers during the spring snow melting, they most likely die after a few hours. In studies of this type, great attention is paid to the physiological effects of pollutants. In modern mobile field laboratories, details about blood chemistry, ionic exchange mechanisms, respiration and neuromuscular response are studied.

Field experiments on spawning and hatching have also revealed a dramatic effect of high acidity. Oligotrophication, a self-accelerating process, is apparently underway in many of our lakes and rivers. Acid precipitation affects the aquatic ecosystem in such a manner that it becomes controlled primarily by physiochemical factors rather than by biological mechanisms.

Where does this end? We may be approaching "the silent spring" which may be an appropriate term to refer to the outlook for many lakes and rivers in Scandinavia as the linking of these effects along trajectories from major emission sources in Europe becomes more and more apparent.

SUMMARY

The severe and continuing depletion of fish stocks in Norwegian lakes and rivers provides ample justification for our grave concern over this problem. Even more so, the project is seriously concerned with the long-term impact on the environmental systems of the forest and mountain regions.

On the international scale, total emissions in the years to come are expected to increase. For this reason, Norwegian governmental officials have asked me to express their appreciation to the United States of America for initiating this conference hosted by this great State of Ohio. The Chairman, on behalf of the Technical Program Committee, has expressed hope for effective communications among concerned scientists. In the very same spirit, I have been personally asked by the Norwegian Ministry of Environment to announce plans for an international conference on the effects of acid precipitation to be held in Norway in June of 1976. This conference is expected to cover topics related to effects of acid precipitation on soils, vegetation, water, materials, and human health.

Such conferences as the First International Symposium on Acid Precipitation and the Forest Ecosystem and the one planned for 1976 convey the magnitude and complexity of the air pollution problem, which in turn reveals the need for better scientific understanding. In trying to protect the environment today, we shall take into account the great responsibility that each of us shares with respect to the generations to come.

THE MORE THINGS CHANGE

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It is a truism for the living environment that life cannot sustain itself on its own wastes. The environment has self-cleansing properties which permit the dilution, reconstitution, and reuse by other natural processes of waste. These self-operative properties are what produces the flow of dynamic change that renews what is renewable within nature. The forces for renewal are powerful but they are not infinite. Already mankind has found the means to disrupt them in part and, unless steps are promptly taken to counteract the present trends, mankind will inadvertently and indifferently risk their total disruption.

In this light, the Air Conservation Commission of the American Association for the Advancement of Science in 1965 made a dramatic announcement about what they considered a necessary limitation upon human conduct.

> "Any environment must be self-cleansing in order to sustain life. Unless the environment can dispose of life's by-products, life will cease."[1]

What prompted this utterance and turned a truism into melodrama was the condition of the metropolitan atmosphere as the result of pollution emanating from four sources in high energy culture: motor vehicles, thermoelectric power generating stations, industry, and households because of their space heating and trash incineration.[2] The atmosphere had been turned into a sink by all of this and conditions, previously known only indoors, had been made a commonality outside in the general air supply for urban regions.

Much of this air contamination had been due to the efforts of urban-industrial civilization to introduce amenities within the home and factory by displacing objectionable substances into the outside air. At first the effect on the outside air, similar to a small amount of pollution discharged into a flowing stream, was not noticed. But as industrial development and urban concentrations progressed, the outdoor conditions acquired noticeably deteriorated characteristics that had once been known only in tightly confined spaces.[3] Such amenities as indoor comfort and the luxury of private motor cars had been purchased at the price of polluting the formerly common air supply.

Through most of man's own biological history, his environment has been "characterized by the virtually unlimited availability of what we now refer to as 'pure air'. Only after humanity learned how to release the energy stored in plants and fossil fuel was this sort of environment modified by emitted waste. However, for thousands of years this energy conversion took place in low energy culture. Whatever the case of air pollution at the advent of fire's discovery by man, it was not until high energy culture that the products of combustion, along with other by-products of human activity, formed that massive pool of substances in the atmosphere to which man must now genetically adapt himself.[4] The significance of this is as yet unknown. The time to accumulate a perhaps fatal experience has been insufficient. Furthermore, the atmosphere still possesses a truly formidable capacity to dilute, disperse, and destroy an enormous list of substances man chooses to indifferently discharge into it. The renewing environment's powers have till now indulged man in his use of them as sinks, but the time of that indulgence is drawing rapidly to a close, if it has not done so already.

The AALS Air Conservation Commission certainly did not take a position favoring environmental purity. So far from being advocates of atmospheric purity were they, that they defined pollution as the condition which

> ". . . occurs when these processes cannot keep up with the rate of discharge, and when . . . [there] is . . . a susceptible receptor, such as man."[5]

Very little shrift was extended to other life organisms. Air was viewed by them in terms of its physical properties and these had importance to the commission only insofar as they had bearing upon human well-being. Pollution was not something emitted into the atmosphere. Pollution was the result of the aerial processes being unable to keep up with the pace of the emissions. Nature had to the commission rather the value of a caged canary in a mephitic mine.

This attitude concerning the acitvities of high energy culture in its atmospheric emissions was underscored in the commission's six-point air pollution control and air conservation program. Even it would be regarded as too extreme, of course, by those zealous advocates of all the "benefits" and "amenities" of high energy culture who delight in denouncing all critics of those individuated pleasures as "doom-writers".[6] The proposals, though, were really minimal, being intended to

> ". . . take into account (i) the volume and mobility of the air mass overlying the area where emissions occur; (ii) the interaction of pollutants and the self-cleansing attributes of the atmosphere; (iii) the topography of the region and any effects it may have on dispersing pollutants; (iv) the variables of meteorology; (v) the existing pattern of industrial practices, transportation, use of land, production of energy,

> and all matters that pertain to their further development; and (vi) the range of sensitivity of human beings, plants, and animals in the region."[7]

Helpful as all these might be -- and, since the Air Quality Amendments Act of 1970 with its subsequent state enabling acts, may have become -- they call for no basic change in high energy culture. Instead, what they urge is a determination of nature's full ability to serve as a sink for waste. Every suggestion is cast in the form of using nature's resources to the fullest extent possible and of exploring the full range of the sensitivity of all living things, other than man, rather than making hard questions about the necessity internal to the maintenance of high energy culture of its present undifferentiated and open-ended demand structure.

It is a long-established demand structure and sometimes ancient documents are dug out of the files that impose a powerful sense of deja vu upon their readers. It is as if there is no new knowledge about man's responsibility to nature. They leave one with the sense that all that has been needed to be known was known long ago, and that man has chosen simply not to act upon the basis of that knowledge. Nature is exploited; the living and renewing environments are used as waste sinks; ecosystems are broken; and all of this is done with the knowledge of what is happening. But the knowledge, when contrasted with the demand for the individuated profits, becomes a matter of indifference. Such a document was uncovered in the records of the city of Cleveland in 1972 and concerned a report prepared in 1891 on the condition, effect, and treatment of air pollution in that city -- and all of the reasons given then as to why nothing could be done. As reading for a late 20th century reader, it is enlightening and disheartening in about equal parts.

In that year, J. E. Arthur, Professor of Botany at Purdue University and a consultant on the report, could say that the trees in Cleveland, the Forest City, were in "really deplorable condition". He insisted,

> "I am fully convinced that the chief difficulty with these trees arises from the be-fouled condition of the atmosphere. The great amount of soft coal used for heating and in the production of power by the large manufacturing establishments and of crude petroleum burned at the refineries . . . covers trees, buildings, and other objects with a thick coating . . ."[8]

From the coal and oil being burned at that time, he reported that great quantities of oxides of sulphur were being emitted. It was his conclusion that ". . . the sulfurous acid forms when sulfur oxides produced during combustion combine with water vapor in the air". He was as unconfused about the reaction of water with oxides of sulphur in 1891 as he could have been in the 1970's.

The views of this consultant were supported contemporaneously by the chief of forestry of the United States Department of Agriculture, B. E. Fernow. This official informed Cleveland that its problems were not different than those of Pittsburgh and St. Louis. For all of them, the problems of air pollution were largely the result of particulate ash and oxides of sulphur. What gives Fernow's remarks an even more modern ring were his recommendations as to how the problem could be dealt with in order to reduce the effects of the pollution or to prevent the emission of the pollutants. It was his suggestion that this be done by the erection of high stacks, or by "smoke washing devices", or by the use of such a binding agent as lime for trapping the pollutants. In 1891 this federal official already had recommended in principle the same sort of control measures that had the United States Environmental Protection Administration in a quandary almost nine decades later: intermittant high stack policy, or precipitants, or the use of a limestone sludge.[9] Truly, one could fervently say that the more there is change, the less change is made.

And if this could be said about air pollution conditions and suggestions for controlling them as between 1891 and the 1970's, the truth holds even stronger for the industry reaction to the report at that time. Industries' reasons then for not doing anything were no different than they were to be nearly nine decades later. What were they? First of all, industry, with a pious concern for air conditions, claimed high stacks would offer no solution since they could only spread the pollution by deteriorating whole air sheds. Environmentalists in the 1970's would agree with that, although by now industry would seemingly be pleased to settle for an intermittant high stack policy as the primary reliance in the battle to control air pollution. But that was only the opener in industry's 1891 defense. More importantly, industry insisted that there were no methods for removing sulphur oxides from air emissions. And more significantly, there was nothing "economically reasonable" or "technically feasible" for cleaning up the air in Cleveland.[10] For those who have listened to industry spokesmen in the 1970's, the 1891 arguments almost seem like a rehearsal, a preview surviving from another age.

Certainly when this old report was re-read by Cleveland's commissioner for shade trees in 1972, he could only tell an interviewer the problems were no less severe than they had been in 1891 when the report had been filed with the old municipal division of public works. The major changes in the interval had been the substantial stoppage in the use of coal as a means of home heating and the arrival of the motor vehicle, burning gasoline and other distillates. What the city had attempted to do had been to "plant against pollution". It had found that the pine, the spruce, and the sugar maple had been the best indicators of severe air pollution. These, consequently, had been the most vulnerable to eventual elimination in a metropolitan area where the Cleveland Flats daily provide an exhibition in what an urban-industrial civilization means to nature. The Cleveland municipal government has for years planted only those trees which would best resist air pollution

on the assumption that air pollution is not going to stop. No one familiar with Cleveland would find that conclusion at all unpredictive in its accuracy.[11]

Yet, realistic as the "plant against pollution" slogan sounds, it is not economically reasonable or technically feasible itself in the long run. It means that severe and worsening air pollution conditions are accepted as an unchangeable state of affairs so that the vulnerable species are eliminated first by the impact of the aerial pollutants and then by the decision not to replace them. Ultimately, though, all species have vulnerability to the air conditions when pollution reaches severe enough levels. One has to admit the value of trees in lowering certain pollution levels. The illusory appearance of forestation that many American cities have when viewed from a high building is a valuable resource for counteracting many of the varieties of pollution. To say that "planting against pollution" is inadequate is not to say that there has been no worth to nature in the program. But it is to say that, in the face of high energy culture wishing to use nature as a waste sink, it is doomed to failure. Eventually, at some point, the rise in pollution levels must become intolerable to all varieties of urban plant life. The necessity for the New York penthouse dwellers to wash their plant leaves each week indicates the limits for plant life under the imposition of massive air pollution.

The attitude of industry since 1891 has scarcely changed. Now as then the industrial managers insist that all known methods for eliminating sulphur oxides are "too expensive and too unreliable". Suggestions for pretreating fuels for the chemical removal of sulphur are given little higher priority than the cleaning of the emissions themselves. In the years of the mid-1970's, many have taken to their hearts the energy crisis as the ideal excuse for making no change at all in the accepted ways of converting fossil fuels to energy. They can agree that there is no extensive possibility of converting all energy sources from high sulphur coal to low sulphur coal, oil, or natural gas because either of the relative scarcity of the latter, or because of the environmental problems of ground restoration in the arid regions where the low sulphur coal is located, or because of the difficulty in handling the increase in particulate waste which the use of low sulphur coal would produce. Beyond this, however, there is little agreement.

The men who watched the trees dying in Cleveland from the sulphur content in the coal and oil during the late 1880's and early 1890's could return from their graves in the mid-1970's with a minimum of shock insofar as any overall improvement in air pollution would be concerned. They would find less particulate matter but they could still stand on Fair Hill, look to the horizon of the lake, and watch the pyrotechnical display over the Flats. The violence of it would still come home to them the way the concept of violence is brought vividly to the attention of a man who receives his first direct blow to the pit of his soft belly.

There have been changes, of course. There are pollutants in quantities from the automobiles which were not present then. A hugely larger metropolitan area suffers from the conditions of air pollution than was the case ninety years in the past and a much larger number of people have been brought under the influence of this severe air pollution. But the leaders of industry are still saying that very little is at all feasible or economically reasonable about removing sulphur from either the fuel or the smoke emissions when the fuel is burned; nor will there be anything much possible for a good many years.[12] For them, as for their predecessors in 1891, what is needed is a blanket delay and the pious expression of hope that someday some different course of action might be possible. Those who came back from their graves to the mid-1970's, with the 1891 report still in their minds, could really wonder if anything at all different had happened: urban industrial growth still insistent in how the resources of nature must be used to serve that growth and government still pliable in the presence of that insistence.

To behave in such a way over so long a period of time, when knowledge was available for further pursuing, is a datum. To watch the quality of the atmosphere deteriorate, to perceive the harm done to certain species of trees, to observe the biophysical bases of the urban environment decline decade after decade, to see so little change in nature while the rhetoric of the environmental revolution rolled on, serve to accumulate additional data of equal significance. For anyone who looks at the relationship between high energy culture and the environment that surrounds its demand structure, there has to be grave doubt as to whether a fairly long-run stability is possible.

One might be pleased about the strength of the current insistence on environmental protection in the presence of the demand levels of high energy culture. Still, the old attitudes exert a pervasive influence on behavior, even behavior that superficially is not exploitative of the environment. It is an influence that is felt in the way data is gathered for declared purposes of environmental protection. This is due to the fragmented character of all that relates to the living and renewing environment under the present demand structure of high energy culture. The result is that more current production of nature presents a Janus-face. One side is turned toward methods that would reflect the unity in nature; the other remains facing nature as something to be processed into human units of production and consumption. It is the latter direction that continues to serve as a contribution to the problem rather than as any sort of solution.

Much of the work being done by public authorities is not done for the forward-looking purpose of producing integrated action. It is carried on simply as a reflection of past needs and traditions.

In bureaucracy, archaisms stay on because no one seems able to find the bases to change them. Such decisions for change are more often political acts than technological ones; and this is often lost to sight by those making the criticisms. The fragmentary character of high energy

culture has created a political organization which justifies bureaucracies accumulating avalanches of disordered data. The result is a governmental action-reaction pattern that gives very limited significance to the data being taken and recorded by government, as pointed out with asperity by a Rutgers University study. As they note with technocratic disdain,

> "Budgetary fluctuations and crash sampling efforts in response to crises . . . [produce] a vast avalanche of data in varying states of order and disarray. Taken together, these data do not add up to a congruent body of information . . . "[13]

What has made the encysted bureaucratic conduct a survivable possibility is that technology often passes by and makes comfortably irrelevant the data being so scrupulously collected by the supporters of the old ways.

However, this is more political than it is technocratic behavior; and the change has to be political. The pressure is growing politically in the late 20th century to adopt techniques that will reflect totally the extent of pollution and the sort of abatement of that pollution that might exist in any region where measurement is being conducted. There are so many interrelated connections that the inherited traditional way of considering them in a fragmented way is becoming less politically palatable. What might air abatement measures, for example, require? Possibly the use of cleaner fuels. If these are not available, then the collection of potential pollutants before their release to the atmosphere, or process changes meant to reduce emissions, or changes in transportation use systems that put a limitation on motor traffic in restricted zones. Manufacturers could be ordered to relocate either to prevent excessive build-up or to concentrate it. Activities could be temporarily suspended during emergency episodes; industries could be grouped geographically; or industry groups could be given relief from the anti-trust laws so that they could develop co-operative plans to jointly limit emissions. When the basic subject of the tests is the ambience of the air, these are all interlocked procedures because any one of them could be the means of relieving the pollution situation.

The demands which high energy culture will make upon nature must affect the bases and the subjects of measuring, monitoring, and model building by those charged with gathering data for environmental protection. Where the agencies charged with this function refuse to recognize the point of origin for the environment's difficulties and isolate themselves in technical exercises, any "solutions" they purport to offer can only intensify the problems. All decisions must be unraveled in order to show the extent of their effects. If an election is made to weight future decisions in favor of clean air users rather than waste emitters, the result of this election must affect the measurement studies in ways that would have had to be quite different if the opposite election had been made.

The renewable environment cannot continue to be treated as if it were a piece of machinery to be cannibalized and worked in as spare parts into other processes as needed by them. There is a collective worth in nature that constitutes a conferred value on humanity. In this sense, the value far transcends anything which mankind purports to confer through the employment of the price structure upon whatever is found in nature capable of reflection in price terms. Price simply cannot comprehend the worth of the life support mechanisms in nature. Any human action which does not rest upon this position lacks all practicality.

Treating nature in any of her systems as an inexhaustible source of supply or as sinks for wastes are practices that cannot continue as they have for so long. The political organizations that have been indifferent to the collective good, except as it could be made specific through granting contracts or making employment for waste treatment processes, must become more aware of the vital worth to mankind as a living species of the collectivity of nature. A competence must be created within the political and economic institutions of high energy culture capable of doing this; and stories of how difficult this must be shall have to be put in their proper perspective of survival versus a grave peril to survival.

Environmental protection, therefore, cannot be served by just creating another agency, or setting up another public measuring organization, or doing any of the discrete, isolating actions that have been considered solutions in the past. Solutions they are not. Instead, they are likely to perpetuate the fossilization of past practices in a fragmentary institutional setting incapable of being pulled together for integrated behavior and useful only as a clog to change, however badly the change might be needed.

But change of this sort needs no fettering. If mankind are to keep for themselves the major part of the values they have taken from nature, this realization is going to have to be acted upon very promptly. If mankind refuses, then the time will fatally go by in which positive action of any kind would have been possible.

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ATMOSPHERIC TRANSPORT, CHEMISTRY AND PRECIPITATION

Chairman, Thomas A. Seliga

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AN EVALUATION OF POSSIBLE MECHANISMS FOR CONVERSION OF SULFUR DIOXIDE TO SULFURIC ACID AND SULFATE AEROSOLS IN THE TROPOSPHERE

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ABSTRACT

The mechanisms and rates of conversion of sulfur dioxide to sulfur trioxide, sulfuric acid, and other "sulfate" aerosol precursors are considered in view of current knowledge related to atmospheric reactions and chemical kinetics. Several heterogeneous pathways exist for SO_2 oxidation promoted on solid catalyst particles and in aqueous aerosol solutions in ambient air. The rates of these processes are of questionable significance in SO_2-containing gases which are well removed from pollutant sources and highly diluted through turbulent diffusion and transport mechanisms. Computer simulations of the rates of SO_2 removal reactions show that several homogeneous pathways for SO_2 conversion to acid precursor are expected to be important in atmospheres containing even low levels of NO, NO_2, and oxidizable organic matter. Mechanistic considerations allow some reasonable speculation about the nature of the initial products of the SO_2 reactions which lead ultimately to acids and various sulfate salts.

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MODELING ATMOSPHERIC EFFECTS - AN ASSESSMENT OF THE PROBLEMS

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ABSTRACT

Our ability to simulate atmospheric processes that affect the life cycle of pollution is reviewed. The transport process is considered on three scales (a) the near-source or single-plume dispersion problem, (b) the multiple-source dispersion problem, and (c) the long-range transport. Modeling the first of these is shown to be well within the capability of generally available techniques, although determining the input parameters is often difficult. The second scale has been well studied within the context of urban diffusion and is a very productive area of current research. Finally, long-range transport is treated mainly as a meteorological problem. The state-of-the-art in modeling the various meteorological processes is reviewed. Removal of pollutants is discussed in the form of both dry deposition and precipitation scavenging. It is suggested that dry removal is especially effective in forested areas, and that the forests may enhance accumulation of pollutants.

An approximate transport model is developed which is used to calculate the ambient concentration of SO_2 throughout the United States. Associated calculations include dry deposition and the ratio of dry to wet removal for each State of the contiguous United States.

1. INTRODUCTION

It is generally accepted that precipitation in the Scandinavian countries may have values of pH sufficiently low to cause damage to terrestrial and aquatic ecosystems. The low pH is attributed to anthropogenic sources of SO_2. The location of these sources is somewhat open to discussion, although it is clear that Eastern and Western Europe and England are all contributors. The acidity of precipitation in the northeastern United States appears to be increasing.

A particularly insidious point about acid precipitation is the fact that the sources are not necessarily close to the most acid measurements. The U.S. has set maximum standards of groundlevel concentration of SO_2. A common method for achieving these standards is to release the SO_2 through tall stacks so that it will be dispersed and reduced to an acceptable level of concentration prior to reaching the ground. This has been a rather short-sighted solution, however, since it in no way reduces the amount of SO_2 emitted into the air.

In order to control increasing levels of SO_2 in the air, the U.S. Environmental Protection Agency has promulgated new source performance standards. These laws require that no more than a small amount of SO_2 may be emitted from any new sources. Nevertheless, there are so many new SO_2 sources proposed and under construction that these regulations will certainly be subject to a thorough review.

This paper will attempt to provide some background on how to relate source emissions to ambient concentrations. It will review some of the methodology for developing air quality models, present some of the existing models, and consider needed improvements. Finally, to provide some background to the conference, I have attempted to put the U.S. problem of SO_2 concentrations in perspective with some approximate calculations.

A major objective of this analysis is to point up the need to study the long-range transport of pollution. Dry and wet removal mechanisms as outlined in this paper suggest that forested areas may be a major recipient of air pollutants removed from the atmosphere. Thus the problem of acid precipitation, indeed the problems of long-range transport and of background air quality, may eventually affect the productivity and multiple uses of our forests.

In the next section, the general theory of air pollution modeling is reviewed. Section 3 deals with the single source and the methods developed for calculating dispersion from such a source. Section 4 on multiple source needs is largely a state-of-the-art review on urban modeling, since this represents the bulk of the work on this scale. Section 5 deals less with the methodology of evaluating long-range transport and more with the complexity of mesoscale meteorology. In Section 6, the dry deposition of air pollutants, particularly SO_2, is reviewed in depth, with some general discussion of wet removal processes. The paper concludes with an assessment of U.S. ambient SO_2 levels in Section 7.

2. THE GENERAL TRANSPORT PROBLEM

The behavior of the atmosphere determines in large part the transport of materials introduced into the air. Three elements of the

atmosphere which affect its behavior are the wind field, the temperature structure, and the various forms of the water substance. In dealing with problems of acid precipitation all three of these elements play a major contributing role. Wind fields exhibit a wide range of scales containing significant amounts of energy. The temperature field, in response to solar forcing, determines in large part the degree of mixing within an air mass. The occurrence and nature of the precipitation affect the cleaning of the atmosphere.

The problem of transport can be reduced to solving a complex equation representing the conservation of mass. Written in terms of the concentration of a particular chemical species, say C_α, this becomes

$$\frac{\partial}{\partial t} C_\alpha + \underset{\sim}{V} \cdot \underset{\sim}{\nabla} C_\alpha = S_\alpha - R_\alpha + \kappa_\alpha \nabla^2 C_\alpha \qquad (1)$$

where

$\underset{\sim}{V} = u, v, w$ = velocity vector

$\nabla = \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}$ = space differentiating operator

S_α = sources of species α

R_α = sink of species α

κ_α = molecular diffusivity of species α

It should be noted that the precise specification of $\underset{\sim}{V}$, S_α and R_α is a rather complex problem. Generally these terms are dependent on time, space, chemical reaction, and surface conditions, among other factors.

Physical transport is complicated by the fact that the atmospheric velocity field, separated into components (u, v, w) in each of three coordinate directions, is not a constant in either time or space. Velocity measured at a point varies with a very high frequency, indicating that significant motion changes occur on time scales shorter than one second. High frequency variations must be filtered from any trends of a long-term nature in order to access the effect of the velocity field on transport. This is done by introducing an average or filtering assumption, by which all the variables are redefined as a mean value $\bar{A}$ and a fluctuating component A'

$$A = \bar{A} + A'$$

The equation is then averaged using the mean value definition to give the following:

$$\frac{\partial}{\partial t} \bar{C}_\alpha + \underset{\sim}{\bar{V}} \cdot \underset{\sim}{\nabla} \bar{C}_\alpha = \bar{S}_\alpha - \bar{R}_\alpha + \kappa_\alpha \nabla^2 \bar{C}_\alpha - \underset{\sim}{\nabla} \cdot \overline{C'_\alpha \underset{\sim}{V'}} \qquad (2)$$

The equation is different because of the addition of a so-called "turbulent correlation" term. This changes the solvable problem of one equation for one unknown into an insolvable problem of one equation for two unknowns ($\bar{C}_\alpha$, $\overline{C'_\alpha \underset{\sim}{V}'}$). Additional information must be introduced in order to solve the equation. Generally, the turbulent correlation term is interpreted as a flux of species α across some surface due to the turbulent velocity $\underset{\sim}{V}'_\alpha$. As such, it is assumed that

$$\underset{\sim}{\nabla} \cdot \overline{C'_\alpha \underset{\sim}{V}'_\alpha} = - \underset{\sim}{\nabla} \cdot K_\alpha \, \underset{\sim}{\nabla} \bar{C}_\alpha \tag{3}$$

which formally defines K_α the eddy diffusivity of the α species. It is easily shown (Pasquill, 1962) that the eddy diffusivity K_α is much larger than the molecular diffusivity κ_α and that the latter term can be neglected in equation (2). Thus we result with

$$\frac{\partial}{\partial t} \bar{C}_\alpha + \underset{\sim}{\bar{V}} \cdot \underset{\sim}{\nabla} \bar{C}_\alpha = \bar{S}_\alpha - \bar{R}_\alpha + \underset{\sim}{\nabla} \cdot K_\alpha \, \underset{\sim}{\nabla} \bar{C}_\alpha \tag{4}$$

as a representation of the conservation of mass.

Significance has been attached to the difference between the second and the last terms in equation (4). The second term represents advection or bulk movement of the average concentration by the average velocity. The last term represents the diffusion of material by the turbulent velocity field. If we consider a spherical cluster of particles released in the atmosphere, for example, the advection term would transport these particles from their release point according to a trajectory determined by the mean velocity, while the diffusion term would spread the particles by mixing them with the atmosphere. Most considerations in atmospheric transport are based upon a simplification and idealization of either or both of these processes.

In general, the simplification which is most appropriate depends upon the scale of the mixing process under consideration. We will identify three scales and concentrate on them. The near-source diffusion problem is rather classically treated by neglecting advection. Some problems related to developing the parameters necessary to use the models are discussed in Section 3. The multiple-source diffusion problem deals with the mixing of individual plumes into each other. This problem has been treated by a wide variety of techniques with little consensus on any one proper approach. The details of the wind field variations in both time and space must be considered with regard to their mixing properties, but this may be accomodated in different ways as described in Section 4.

Perhaps the most difficult scale to deal with is the more regional scale ranging into thousands of kilometers. The methods for modeling on these scales are only just beginning to be developed.

While we will concern ourselves with the diffusion and advection terms of equation (4), the values of the source and sink terms S_α, R_α,

warrant discussion as well. The source term represents the input of α to the total amount of α, and the sink term represents the removal of α. These terms are complex because of both atmospheric reactions and physical removal mechanisms. The latter will be discussed in Section 6, but the former are beyond the scope of this paper. If, for example, α is sulfur dioxide, then the source term should consist of the emission of SO_2 from both point and area sources as well as atmospheric chemical processes, such as oxidation of H_2S, that produce SO_2. Chemical processes, also deplete SO_2 by various oxidation reactions requiring their consideration in the sink term.

The most common procedure for dealing with reactions is through chemical kinetics expressions for the rate of formation of a compound. Such equations in terms of concentrations may take the form

$$\frac{\partial}{\partial t} C_\alpha = - kC_\alpha C_\beta \qquad (5)$$

where k is a rate constant for the reaction

$$\alpha + \beta \rightarrow \gamma + \delta$$

Similar expressions can be written for C_β, C_γ, C_δ, so that all of the reaction components can be accounted for. Equation (5) represents a sink term for α and β and a source term for γ and δ~.

Arguments related to turbulence apply to equation (5) so that this equation can be rewritten as:

$$\frac{\partial}{\partial t} \bar{C}_\alpha = - k\bar{C}_\alpha \bar{C}_\beta - k\overline{C'_\alpha C'_\beta} \qquad (6)$$

which then introduces a coupling between the fluctuation of concentration (resulting from turbulence) and the fluid motion. From these equations it is obvious that the separation of transport phenomena from transformation phenomena is not strictly valid.

To understand the details of atmospheric transformations it is necessary to use the complete system of equations. Recently, Donaldson and Hilst (1972) have discussed the limitations of not considering turbulent correlations in equation (6). Their results illustrate two basic regimes; (a) where the transformation is fast and thus limited by the availability of reaction components, i.e., diffusion limited, and (b) where the chemistry is relatively slow and the turbulent correlation $\overline{C'_\alpha C'_\beta}$ becomes increasingly significant, i.e., mixedness limited. These added turbulence terms may be significant when dealing with relatively slow reactions in regions of high concentration although further information is needed on this point.

3. NEAR-SOURCE DIFFUSION

Consideration will be limited to diffusion of materials emitted from an elevated point source, since the vast majority of SO_2 emitted into the atmosphere is through this mechanism. The concentration of SO_2 emitted from such a source, while quite variable, is of the order of 10^9 $\mu g/m^3$. Generally, the emission is hotter than the surrounding air, and is moved away from the stack by both buoyancy forces and by momentum imparted by the exit velocity. The maximum height to which the plume rises depends upon a set of parameters including the exit velocity, exit diameter, temperature difference, and the atmospheric temperature profile.

The emission concentration can easily be reduced two or more orders of magnitude within the plume a short distance from the source as the plume spreads due to mixing with air. It has been both empirically observed and theoretically derived that, under certain ideal conditions, the spread of material in the plume will exhibit a gaussian shape. This distribution, for example, is a valid solution to equation (1) if one reduces it to:

$$\frac{\partial}{\partial t} C_\alpha = K_\alpha \left(\frac{\partial^2 C_\alpha}{\partial x^2} + \frac{\partial^2 C_\alpha}{\partial y^2} + \frac{\partial^2 C_\alpha}{\partial z^2}\right)$$

and considers the K a constant related to a spreading parameter of the gaussian plume. Sources of more detailed information include Slade (1968), Turner (1970) and Pasquill (1962) which provide a discussion on the validity of the gaussian model and further rationale for its use.

The generally accepted formula used to calculate diffusion from a point source is

$$\chi = \frac{Q}{\pi \sigma_y \sigma_z \bar{u}} \exp[-y^2/2\sigma_y^2 - h^2/2\sigma_z^2] \qquad (7)$$

where

χ = concentration, Q = emission rate

σ_y = standard deviation of the gaussian plume in the y horizontal coordinate direction transverse to the wind direction.

σ_z = standard deviation of the gaussian plume in the z vertical coordinate direction

$\bar{u}$ = mean wind speed in the x direction

h = effective stack height = $h_s + \Delta h$ = stack height + plume rise

The plume is assumed to be oriented with the mean wind, which for the duration of the calculation is assumed to be steady (not changing in direction) and constant (not changing in magnitude). Determination of the diffusion parameters σ_y and σ_z is by far the most difficult task in the computation. The difficulty is relating the values of σ_y and σ_z to other more conventional and easily measured meteorological parameters. The parameters are strong functions of turbulence in the atmospheric boundary layer. A number of methods are available to establish numerical relationships, largely based upon experimental studies performed in England and the United States. The most conventional systems include about six separate categories of atmospheric stability -- so called classes A, B, C, D, E, and F -- ranging from the most unstable and most highly turbulent (A) down to the most stable (F). For example, Briggs and Gifford at Oak Ridge National Laboratory (Gifford, 1974) have recently analyzed the various diffusion parameterizations and suggest that, for class A stability

$$\sigma_z = 0.2\bar{X}$$

where $\bar{X}$ is the horizontal distance from the source, while for the most stable class F

$$\sigma_z = 0.02\bar{X}/(1 + .0003\bar{X})$$

or roughly an order of magnitude decrease in the dispersion parameters. Curves of σ_y and σ_z as a function of stability class are presented by Turner (1970), and appear as figures 1a and 1b.

The next difficulty is relating measured atmospheric conditions to the various stability classes. Atmospheric turbulence is generated both mechanically and thermally. These two types of forces are governed by different parameters, and the resulting turbulence is at most times a combination of the two. The roughness, Z_o, and the friction velocity, $U_* = -\overline{u'w'}$, appear as parameters of the wind profile given by

$$\bar{u} = \frac{U_*}{k} \ln(Z/Z_o) \qquad (8)$$

where k=.4. These are the mechanical roughness parameters. Thermal turbulence is governed by the incoming solar radiation and surface characteristics, but is measured by such parameters as the amount of cloud cover and the temperature change with height. A convenient parameter is the Monin-Obukov length scale, L,

$$L = -\frac{U_*^3 \, T}{kg \, \overline{w'T'}}$$

(where T = reference temperature, g = acceleration of gravity and $\overline{w'T'}$ = vertical flux of heat) which represents the ratio of mechanical to thermal turbulence. The absolute value of this length scale is

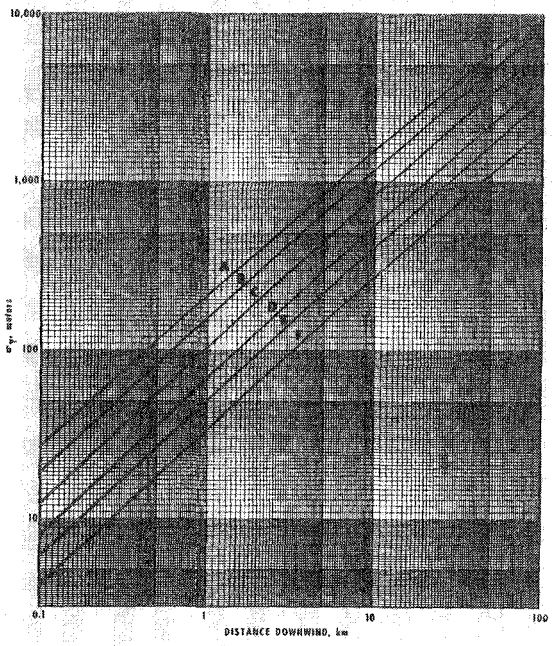

Figure 1a. Horizontal dispersion coefficient, σ_y, as a function of downwind distance from the source (Turner, 1970).

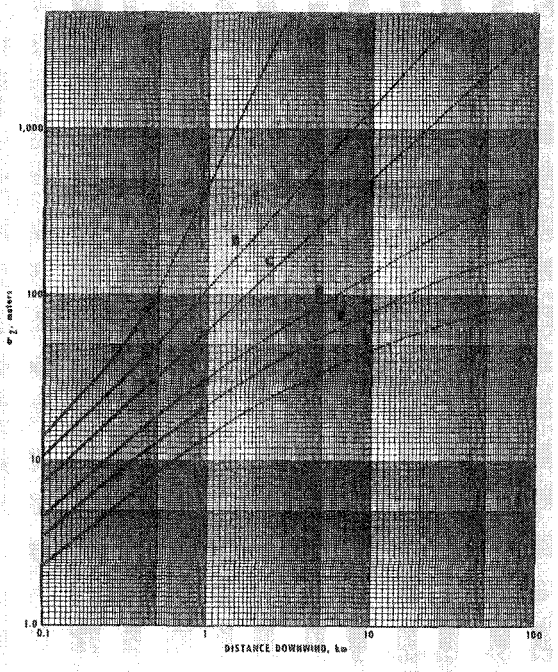

Figure 1b. Vertical dispersion coefficient, σ_z, as a function of downwind distance from the source (Turner, 1970).

proportional to the depth through which thermal turbulence is not significant. When $\overline{w'T'}$ is negative (heat is transported by turbulence toward the ground) L is positive and approaches infinity as the value of heat flux approaches zero. Smith, (1974) has recently related the various meteorological parameters namely incoming solar radiation, Z_o, U_*, $\bar{u}$ (10 meters) to the stability class. Figure 2 illustrates the relationships which result.

The remaining parameter in equation (7) is the plume rise Δh. Plume rise has been a subject of discussion for many years in the literature. The summary by Briggs (1969) is the generally accepted reference, although new data are appearing regularly. The formula which seems most appropriate for us here, valid for tall buoyant point sources, can be written as

$$\Delta h = \frac{1.6\ F^{1/3}\ x^{2/3}}{\bar{u}}$$

where

$$F = \frac{gQ_H}{\rho C_p \pi T_A}, \quad Q_H = \text{heat emission}, \quad T_A = \text{ambient temperature}$$

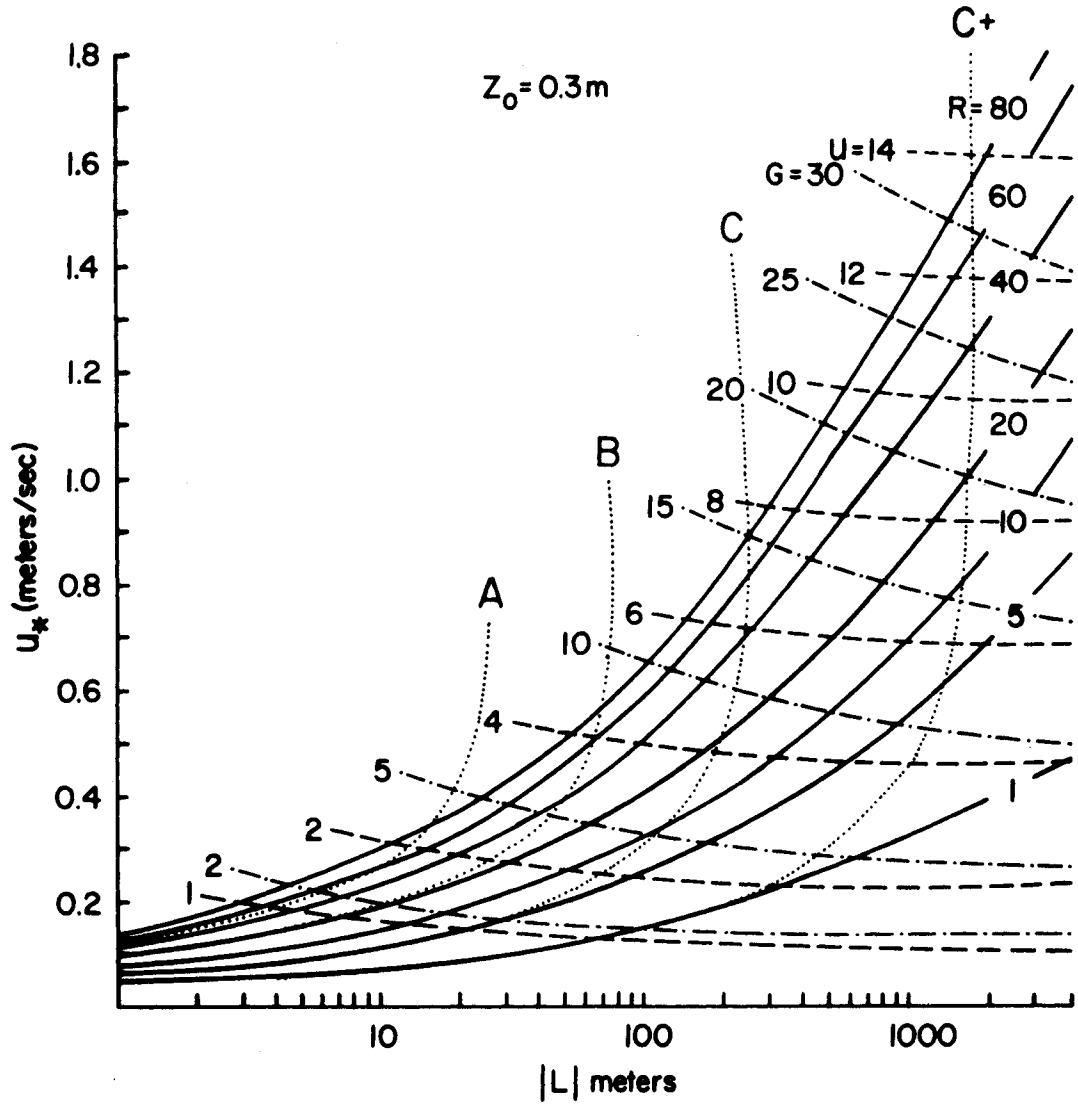

Figure 2. Relationship between solar radiation, R, Geostrophic gradient, G, wind at 10 meters, U, friction velocity, U_*, Monin-Obokov, length L and Pasquill stability classes, A-C, from a model of the boundary layer by F. B. Smith (1974).

The problem of estimating near-source diffusion has thus been reduced to relating meteorological parameters to source emission using various formulas presented here and other reference material. It is necessary to have meteorological information available, preferably from on-site measurements, in order to estimate the resultant diffusion.

4. MULTIPLE-SOURCE DIFFUSION

Multiple-source diffusion is generally studied in the context of an urban area. The approaches used range from distributing the emission uniformly through a volume defined by either arbitrary or natural boundaries, a so called box model, to a rather detailed solution of equation (2).

One logical method for calculating the diffusion from multiple sources is to advance the concept stated in equation (7). With a single direction strong wind persisting over the area, the summation of isolated point sources is mathematically straight forward and is a reasonable solution to the problem. When the wind is less pronounced, and the more variable, models have been developed which employ a gaussian distribution for a discrete set of sources. Such models have been discussed extensively in the Proceedings of the conference on urban diffusion models (Stern, 1970).

A simple material balance over a volume defined by cross sectional area, A(H) where H is the depth of the inversion which limits the area and h is the length would yield a concentration given by

$$\chi = Q/A(H)L \tag{9}$$

if there is no "ventilation". If, however, the rate of change of concentration within a time unit t is assumed to be small compared to the source strength and to advection by the mean velocity, $\bar{u}$, an expression of the form

$$\chi = Q/A(H)\ \bar{u}t \tag{9a}$$

results where t is a unit of time (Fox, 1975). Variations of equation (9) have been used extensively in the literature on urban diffusion. Gifford has been most persistent in comparing such a technique to much more sophisticated models with successful results (Gifford, 1973). It has been shown (Fox, 1974), however, by using a rather limited but highly detailed data set from St. Louis, Missouri, that the accuracy of a computation increases as the sophistication increases. A comparison with experimentally measured concentrations yields standard deviations of 0.35 for the multiple-source gaussian diffusion model (Geomet, 1972), 0.39 for a vertically stratified box model, and 0.53 for a very sophisticated numerical solution of a finite difference version of equation (2) (Shir and Shieh, 1974).

The more direct numerical solution of various forms of equation (2) has been pursued in many papers. Basically, two techniques have been employed, one which essentially follows a mean wind trajectory by assuming a coherent parcel of air and allowing diffusion within that parcel as well as any appropriate chemical reactions (Eschenroeder, et al., 1972). This method has been applied extensively in Los Angeles, California where some recent field experiments have tentatively suggested that the assumptions of a coherent parcel of air may be quite

reasonable (Angell, et al., 1974). Liu and Seinfeld (1974) have presented an extensive discussion of the errors involved and a critical comparison of the accuracy of the trajectory approach as compared to a more conventional finite difference solution of (2).

A few models attempt such a finite difference solution of equation (2). The successes of such models are rather remarkable (Roth, et al., 1974 and Shir and Shieh, 1974). There is little doubt that this approach will in time replace all others. However, there are a number of difficulties. Certainly, one major limitation is the need for a large computing budget and for a great deal of specific information about the area under study, about the sources of pollution in the area, and, of course, about the meteorology.

The need for meteorological information is particularly acute since it is required in very fine detail in space and time. Obtaining such data is extremely expensive, and as a result there is an increasing interest in calculating wind fields using a model of the urban atmosphere on these very fine scales.

5. LONG-RANGE TRANSPORT

Distances greater than the multiple source or urban scale present somewhat different and more difficult problems to the atmospheric scientist. It is more difficult on this scale to separate the diffusion process from the meteorology. It is more difficult to study, measure, or forecast the meteorological conditions on this range of scales. It is more difficult to identify and to model the chemical reactions occurring with less concentrated species over the longer times and distances involved. These problems exist in part because there has been relatively little work done on long-range transport and mesoscale meteorology.

A number of recent problems, however, have pointed attention to the need for knowledge of the interactions between long-range transport and chemical reactions. Among these is the observation of very high oxidant values in rural or semirural surroundings. The generation of fine particulate matter (sulfates) over long ranges, the observation of pollution from one country in another and of course the problem of acidic precipitation.

Among the various subdivisions of meteorology there are at least three which must be drawn together to study long-range transport of pollution in general, and acid precipitation in particular. The micrometeorologist must be able to provide the knowledge of turbulence, dispersion, and removal mechanisms, the cloud physicist must input detailed cloud behavior to determine the efficiency of precipitation in removing pollution and the large-scale dynamicist must provide a knowledge of the transporting mechanism. This is made somewhat more complicated by the fact that the micrometeorologist is not used to dealing on such large-scales, while the dynamicist must come down in scale from his usual activity.

Perhaps the most common method of dealing with long-range transport is through the use of trajectories. Classically, meteorologists have used the trajectory to determine the current or past location of an air mass. The concept is rather simple in that one assumes knowledge exists about the flow field, namely its structure and its intensity, and that a hypothetical "air mass" remains coherent and is moved according to the velocity field. This approach has been used rather extensively by the OECD project (Nordø, 1975) and by the Air Resources Laboratory of NOAA (Miller, et al. 1975), among others. It is appropriate, however, to point out some of the difficulties in applying a trajectory analysis.

A major complication of atmospheric circulation is that the air system does not move uniformly like the sloshing in a glass of water, but rather exhibits often totally different behavior as a function of elevation. The vast majority of atmospheric flow is horizontal or two dimensional (in terms, for example, of total kinetic energy of the circulation) but the horizontal flow is different from one layer to the next, giving rise to both direction and magnitude changes in wind with height, so called shears. After the sun has gone below the horizon, the layers of air nearest the ground may become totally disassociated from the larger scale flow aloft. This nonuniformity presents a tremendous problem in analyzing where pollution goes over a 24-hour period.

One would expect the trajectory method to be a fairly good representation of pollution transport for flat terrain where the only questions are, how deep is the pollution layer, i.e., what is the inversion height, and what is the distribution of pollution through this height. One complication of long-range transport is the vertical component of motion. Organized vertical motion fields associated with topography or with the presence of meteorological "fronts", while somewhat predictable, are difficult to include in a trajectory model. The random vertical motion associated with thermal convection (cumulus cloud buildup) is generally not considered in long-range transport. Another problem is the lack of specialized meteorological data for even a simple trajectory analysis. Collection of the proper amount of meteorological information is prohibitively expensive. Thus, one must proceed with what information is available, generally only the larger scale standard weather maps. Such data must be supplemented on scales of concern with some sort of meteorological model.

Modeling mesoscale meteorology -- the scale from say 10 to 200 km -- is currently one of the most active fields of meteorological research. The success of modeling large-scale general circulation problems (Smagorinsky 1962) and small-scale turbulence (Fox and Lilly, 1972) has led to attempts to bridge the gap between these two fields. A major problem beside the lack of data is the nonuniqueness of mesoscale situations. To deal successfully with mesoscale problems, a large degree of parameterization must be incorporated into any model. This parameterization is necessary to account for both larger and smaller scale phenomena which affect the mesoscale. The ever changing general circulation pattern must be imposed as large-scale boundary conditions.

Methods must be developed to allow the introduction of these changing boundary conditions into a running calculation.

One of the more fundamental difficulties in mesoscale meteorological modeling is knowing what equation to solve. The equations of fluid motion, the Navier-Stokes equations, are similar to equation (2) but with a velocity component $\underset{\sim}{V}$ replacing the C_α and the addition of a pressure gradient force $(1/\rho)(\partial P/\partial x_i)$ and a buoyancy force $\Delta\rho g/\rho$ (in direction of gravity). The equations also require the addition of an internal conservation of mass (density) statement in order to be solvable. Solutions, however, are unstable when the Reynolds number (equal to velocity times a relevant length scale divided by the kinematic viscosity, ν, where ν is the molecular diffusivity of momentum divided by the density of the fluid) is as large as it generally is in the atmosphere. This instability leads to an equation for a turbulent fluid requiring the same type of averaging process as that for concentrations. The proper specification of $\overline{u_i' u_j'}$ in terms of mean quantities (closure) is essential to calculation of proper mesoscale fields. A number of models have been proposed (Donaldson, 1973) but a great deal of work remains to determine which performs best under realistic conditions. These turbulence terms are also responsible for the vertical spreading of pollution, and as such are tied up in the determination of long-range transport even more directly.

While it is not our purpose to review all the current mesoscale modeling, we will briefly mention a few of the techniques. The most detailed work is that of Deardorff (1973) (cf. Fox and Deardorff, 1972) who, through the use of three-dimensional numerical solutions of equations for small regions of the boundary layer, has sought to understand the nature of small-scale atmospheric behavior and to verify various theoretical developments. Other modelers who have attempted to retain as much of the nonlinearity of the problem as possible are Anthes (1974), Kreitzberg (1975), Pielke (1973), Pandolfo and Jacobs (1973) and Liu et al. (1974), to mention only a few. They attempt to solve the motion equations themselves. Another approach is to assume a multiple-layered atmosphere but simplify each layer. The efforts of Lavoie (1972), Tingle and Dieterle (1975) are examples of this procedure which solves an altered set of motion equations. A useful approach is to interpolate between measurements, but in a mathematically efficient manner. Objective analysis techniques, as these are called, can be forced to strictly reproduce the exact data, or can be weakly constrained to enforce selected conservation criteria (Sasaki, 1970). Dickerson (1975) and Sherman (1975) have used this approach for pollution applications.

The presence of mountainous terrain presents great problems to long-range transport analysis. Wind in mountains is affected by the local surface conditions as well as by larger scale motions. A model based on data interpolation introduced by Anderson (1971) has been adopted and refined for application to mountains by Fosberg, et al. (1975). Figures 3 and 4 illustrate some of the results.

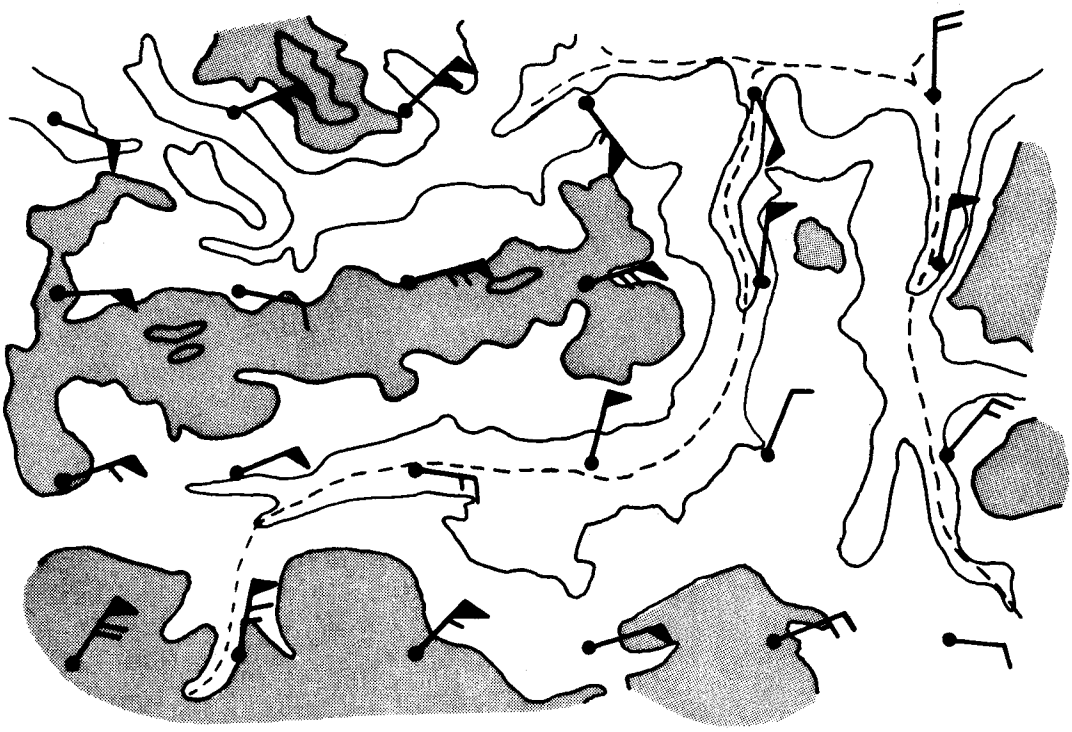

Figure 3. Windspeed and direction calculated for a mountainous area. Speeds are given by the sum of the barbs on the arrow tails. The arrow head points with the wind. Pennant is 5m/sec., full barb, 2m/sec., half barb, 1m/sec. (Fosberg, et al. 1975).

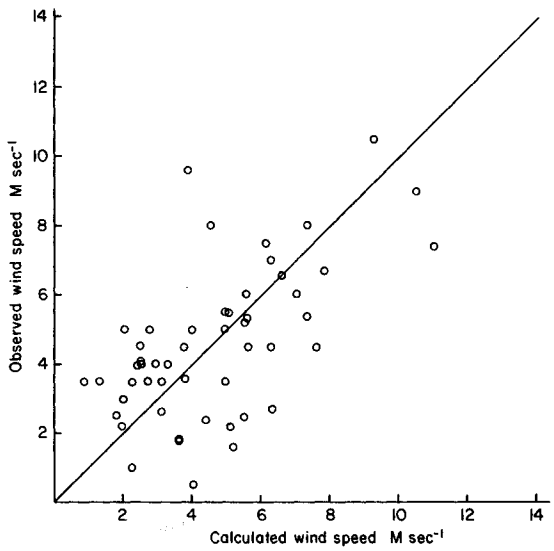

Figure 4a. Comparison of calculated windspeeds with observed windspeeds, (Fosberg, et al. 1975).

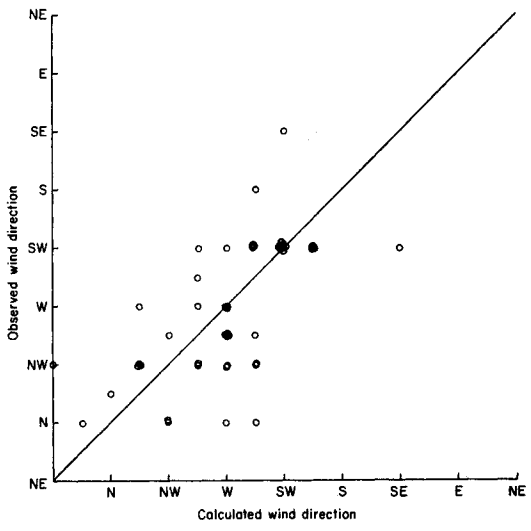

Figure 4b. Comparison of calculated wind directions with observed wind directions.

Finally, transport modeling was recently studied by Scriven and Fisher (1975). They present a simple moving box model which they show represents a good approximation of long-range transport. This technique is a basis for some calculations in the last section of this paper.

6. REMOVAL PROCESSES

It is difficult to deal with transport of air pollutants without considering removal. Removal occurs directly when the pollutant encounters the ground or any surface which has a sorbing capability for the pollutant, or indirectly when the pollutant becomes tied up in the precipitation cycle. Atmospheric chemistry plays a tremendous role in determining the nature of pollution removal alternatives.

Consider first the nonprecipitation or direct removal processes. Bolin, et al. (1974) and Chamberlain (1975) point out that deposition on a surface can be treated by considering a summation of resistances.

Resistance is defined as the inverse of the transport velocity (often called the deposition velocity) and is formally given by the expression

$$r = \frac{1}{V(Z_1, Z_2)} = \frac{\chi(Z_1) - \chi(Z_2)}{(F/\rho)} \tag{10}$$

where Z_1 and Z_2 represent the levels between which V and r are defined, χ is the concentration at each level, and F is the vertical flux (transport) of the concentration through $Z_1 - Z_2$.

Chamberlain (1975) suggests three separate resistances

$$r = r_a + r_b + r_c \tag{11}$$

where

r_a is a bulk aerodynamic resistance due to the structure of the air flow above the canopy,

r_b is due to the differences between mass and momentum transport,

r_c is the resistance due to the canopy.

r_a is determined from the velocity profile assumed as in Section 3 of the form $U = (U_*/k)\ln[(Z - d)/Z_o]$ where d is the displacement height required for the law to be used in the vicinity of large roughness elements such as trees. Analogous to equations (10) Bolin, et al.

(1974) considered the resistance to momentum transport as

$$V_m(Z_1,Z_2) = \tau/\rho\,[U(Z_1) - U(Z_2)] = U_*/[U(Z_1) - U(Z_2)] \quad (12)$$

where τ is the momentum flux or the stress, given by definition as ρU_*^2. The application of the logarithmic profile assumes $U(Z_2) = U(d) = 0$ so that

$$r_a = \frac{1}{V_m(Z_1,Z_2)} = \frac{U(Z_1)}{U_*} = \frac{1}{kU_*} \ln\left[\frac{(Z_1 - d)}{Z_o}\right] \quad (13)$$

Typical values for r_a over a forest can be determined by assuming $Z_1 = 10m$, $d = 7m$, $Z_o = .5m$, and $U_* \simeq .1 - .3$ m/sec. which yields $r_a \simeq 20 - 60$ sec./m.

The second resistance is to the transport of mass across the viscous surface layer. This resistance is expected to be dependent upon the viscosity of the fluid, the molecular diffusivity of the pollutant, and some shape factors of the surface. Chamberlain suggests:

$$r_b = B/U_* \quad (14)$$

where

$B \simeq 2(Re)^{\cdot 45}\, S_\alpha^{\cdot 8}$, for bluff resistance elements $Re = U_* Z_o/d$, $S_\alpha = \nu/\kappa_\alpha$

$B \simeq 7$ for SO_2 over fibrous roughness elements

The third resistance is due to the absorbing capability of the surface itself. There is some indication that r_c is related to stomatal resistance (Chamberlain, 1975; Kozlowski, 1974). Retention efficiency also seems to increase in the presence of high humidity. Experimentally determined values of r are listed in Table 1, from Chamberlain (1975). As Chamberlain points out, the values for $r_b + r_c$ are similar to the bulk surface resistance of crops to transpiration (minimum of 30 - 50 sec./m).

The removal of aerosol particles is a somewhat more complex problem, since the relative effects of Brownian motion, sedimentation, and particulate inertia must be assessed as a function of particle size. The impaction efficiency of the surface becomes highly important. The removal of aerosol particles must be assessed with a knowledge of both the physical and chemical nature of the aerosol and the surface configuration of the impactors. Chamberlain (1975) presents curves of particle size vs. deposition velocity and impaction coefficients (ratio of number of particles impacted to number of particles which would have passed through had the impaction surface not been there) as a function of cylinder diameter.

A forest canopy, however, creates a special flow field of its own.

Table 1. Resistances of canopies to uptake of SO_2 (from Chamberlain, 1975).

Method	No. of Expts.	Crop	u (1 m) m/s (mean)	u_* m/s (mean)	r $m^{-1}s$	$r_b + r_c$ $m^{-1}s$	Notes
Mass balance in crop		alfalfa	-	-	100	-	Growth chamber
		Rye-grass	-	-	160	-	Growth chamber
		Mustard	-	-	100	-	Glass-house (soil tagged with ^{35}S)
Mass balance in air	7	Alfalfa	3	0.4	40	-	Wind Tunnel, limited fetch over crop
Fumigation with $^{35}SO_2$	6	Grass	4.0	0.41	120	90	Field
Fumigation with $^{35}SO_2$	3	Grass	2.8	0.25	130	70	Field
Gradient	9	Grass	2.45	0.22	200	130	Field
Gradient	14	Short grass	3.0	0.18	360	-	Field
Gradient	19	Grass	3.0	0.29	220	180	Field
Gradient	13	Bare chalky soil	3.3	0.25	115	34	Field

Bergen (1975) has proposed a theory of momentum transfer through the forest canopy which suggests that the flow structure has a characteristic length scale on the order of the typical branch structure. Whether this branch structure (10-20 cm) or the actual needle structure (.1-1 cm) is the more significant for capturing small particulates, say below 10μ such as sulfate particles has not been determined. It is clear, however, that the increased roughness of forests compared to nonforested terrain will lead to an increased U_*, resulting in general with an increase in deposition velocity. Profiles of sulfate particles (Georgii, 1970) suggest, however, that the deposition velocity of such small particulate matter is at least an order of magnitude smaller than that of SO_2. Thus, most of the dry deposition of S comes in the form of SO_2 while sulfate particles are removed largely by precipitation processes.

As a final statement regarding dry removal, it should be emphasized that such a mechanism is operative whenever pollutants are present in the atmosphere. Wherever the surface wind shear stress is increased, deposition generally increases. Thus, forests should be expected to receive relatively larger amounts of pollutants from the atmosphere for two reasons: they create higher shear stresses because of both the trees and the general presence of elevated topography, and they present substantial amount of surface areas of sorbing material. Observation of this phenomenon has been presented in a number of papers in this symposium, including Knabe and Günther (1975) and Nyborg and Hocking (1975).

Removal by precipitation must be recognized as an intermittent process. A precise theory of the mechanics of removal is only part of the answer to precipitation removal. The other part is the occurrence or nonoccurrence of the precipitation itself, and of course the nature of that precipitation. Although a complete discussion of precipitation scavenging techniques is far beyond the scope of this review, we will briefly raise some comments. Recent meetings on the subject have been held (USAEC, 1974), volumes have been published that deal specifically with it (USAEC, 1970), and much work is still on going.

Pollution is removed by precipitation in two basic ways. Removal is generally termed "rain out" when the pollutant becomes involved in the precipitation-formation processes and "wash out" when it is simply caught by a falling drop. Rain out requires the aerosol to either act as a cloud condensation nucleus (CCN) or to be agglomerated into a CCN. Within the cloud, the condensation nucleus grows by a process of condensation and coalessence. Pollutants could well be introduced during this collisional buildup process. The relative importance of each process depends upon both the individual cloud and the cloud type. Wash out is a somewhat more straightforward process involving the simple collision of falling precipitation with the pollutant particles.

Dana, et al. (1973) have developed a model capable of determining the direct removal of SO_2 from plumes. This model indicates that even low background levels of SO_2 can significantly decrease wash out from a concentration plume, and that pH of rain has a strong effect on SO_2 scavenging. Indeed, the authors found situations where SO_2 in rain was decreased after passing through a plume. An additional observation of these studies is that sulfate was about five times more susceptible to wash out than was SO_2.

Rodhe and Grandell (1972) have used rainfall occurrence statistics to determine the removal rates of pollutants. Their study was oriented toward a calculation of the mean atmospheric residence time of aerosols in the troposphere, which they proved to be 100-300 hr. in summer and 35-80 hr. in winter. Their study was based upon the precipitation climatology of Sweden, and has not been applied to different precipitation regimes. Bolin, et al. (1974) calculated residence times by using the Rodhe and Grandell numbers in precipitation-scavenging and dry-deposition formulations in a simplified mass balance equation. They found that the ground parameters U_* and Z_o were most significant in determining residue times of pollutants emitted from tall stacks. Scriven and Fisher (1974), using an adaptation of a method suggested by Calder (1973), found a somewhat shorter residence time for SO_2 for approximately 24 hours. Any of these times, however, are probably sufficient to generate a good deal of $SO_4^=$, which contributes to the acidity of rain.

7. THE U.S. PROBLEM IN PERSPECTIVE

A number of the papers at this conference are oriented toward local problems or, at best, regional problems. The European work, however, does include significant considerations of the longer ranges of transport. To develop a base of understanding, it seems appropriate to consider the problem in the United States as a whole. To attempt such a broad and nonspecific inquiry we have purposely chosen rather broad and nonspecific modeling techniques. One of the basic principles of modeling is that no one component of the model is any more detailed and precise than any other component. We have made a number of gross assumptions which we will explain and attempt to justify in the next few paragraphs.

First, we have limited our consideration to SO_2 alone, although nitrogen-based anthropogenic emissions are responsible for as much as 30-40% of the strong-acid anion found in low pH samples in the U.S. However, characterization of NO_x emission is more complex than SO_2. Of the approximately 24 million tons of NO_x emitted annually, 45% is from industrial and power-generation point sources, while 36% is from transportation sources (U.S. EPA, 1974). In comparison, of the 32 million tons of SO_2 emitted, 87% are emitted through stationary point sources with the remaining 13% from stationary area sources. The complication of both active photochemical reactions and mobile sources make an analysis of NO_x pollution levels very difficult.

The chemical reactions which change SO_2 to $SO_4^=$ are complex. Calvert (1975), in this symposium, has raised a number of points regarding the relative importance of homogeneous (gas phase) reactions and heterogeneous oxidation occurring on solid particulate catalysts and in aqueous solution. The gas phase reactions apparently may be significant in low-concentration background atmospheres which have some NO_x and oxidizable organics available. One might speculate that a straightforward correlation between SO_2, NH_3, and water vapor could lead to an acceptable prediction of pH. Indeed in Scandinavia where extremely low pH is routinely found to be due to sulfates in solution (about 90% of the excess hydrogen ion is due to sulfuric acid) this approach works reasonably well, (Nordø, personal communication). In the U.S., however, this correlation does not seem to be as useful an approach because of elevated NO_x concentrations and the implications of NO_x involvement in both generation of $SO_4^=$ and direct formation of HNO_3. Thus, we have decided to calculate SO_2 concentrations assuming no chemical depletion, but accounting for dry and wet removal in an approximate manner.

Figure 5 is a map of the contiguous United States with the emission of SO_2 according to U.S. Environmental Protection Agency data (U.S. EPA, 1974), in each State. The choice of the political boundary of a State rather than the more reasonable air quality control region boundaries was based upon a desire to put no more precision into the calculation than it is worth. In considering a State such as New York, for example,

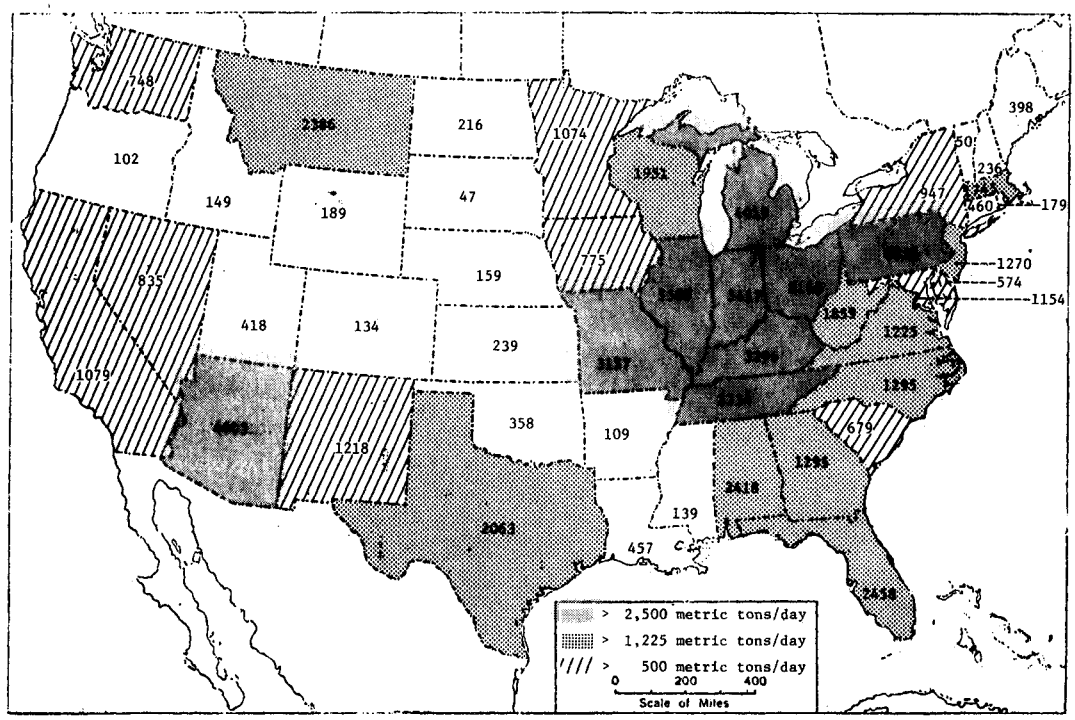

Figure 5. Emission of SO_2 in metric tons (10^3kg) per day from U.S. EPA, 1974.

it is obvious that the air quality of the New York metropolitan area is substantially different from the general background value for the State. If we had broken down the analysis to individual air quality control districts, the gross box modeling techniques we use would have to be improved to consider spatial variations, and the climatological data would need to be substantially improved.

To calculate the concentration, we will assume a uniform ventilated box model. The question is, what volume of air should be assumed to mix with the emission to determine a meaningful concentration? Assuming a mass balance, the flux of material entering a State is given by

$$\chi_i \, U_i \, H_i \, L_i$$

where χ_i is the entering concentration, U_i is the average velocity through the mixing layer, H_i is the height of the mixing layer, and L_i is the length scale over which these values are operating. Assuming the emission within the State is zero, and the flux out of the State on the downwind side is

$$\chi_o \, U_o \, H_o \, L_o$$

then the concentration leaving the State would be, assuming no internal removal mechanisms,

$$\chi_o = \chi_i \left(\frac{U_i H_i L_i}{U_o H_o L_o} \right) + Q/U_o H_o L_o$$

or if assume $\chi_i = 0$,

$$\chi = Q/U_o H_o L_o \qquad (15)$$

which we will use as an estimate of the ambient concentration. L_o is a length scale we assume is the square root of the surface area. The mean velocity is taken from Visher's climatology (Visher, 1954) as an interpolation over the State. The mixing depth from Holzworth (1972) is the interpolated summer afternoon mixing depth. Figure 6 shows the results of this analysis.

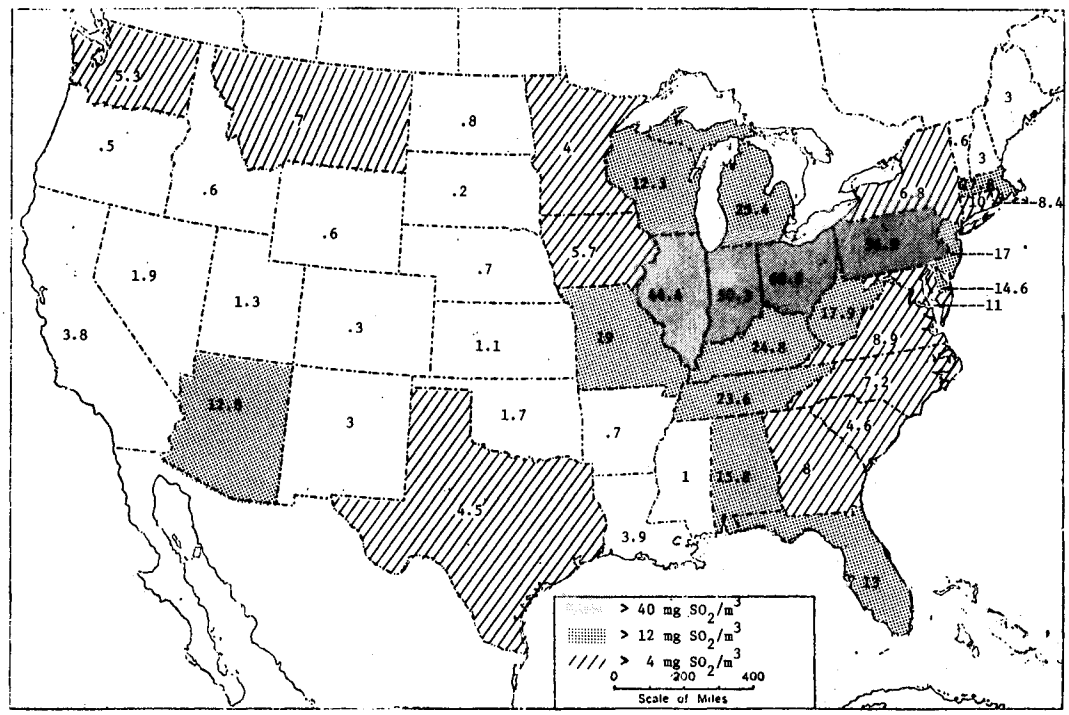

Figure 6. Concentration of SO_2 in $\mu g/m^3$ calculated using a simple ventilated box model, equation (15).

By assuming a mass balance between ambient concentration and dry deposition, Scriven and Fisher (1975) show that dry deposition, D is given by

$$D = \frac{V_g Q_o}{UHL_o} \exp\left(\frac{-Vgx}{UH}\right) = \frac{Q_o}{L_o x} \beta e^{-\beta}$$

which exhibits a maximum when $\beta = 1$ given by

$$D_{max} = Q_o / x_o L_o e$$

To estimate the maximum dry deposition over a State we have integrated this maximum over the entire State resulting in

$$D_{max} = [2\ Q_o / eL_o]\ \ln(L_o/2) \qquad (16)$$

Figure 7 shows the maximum dry deposition over each State, calculated from this equation.

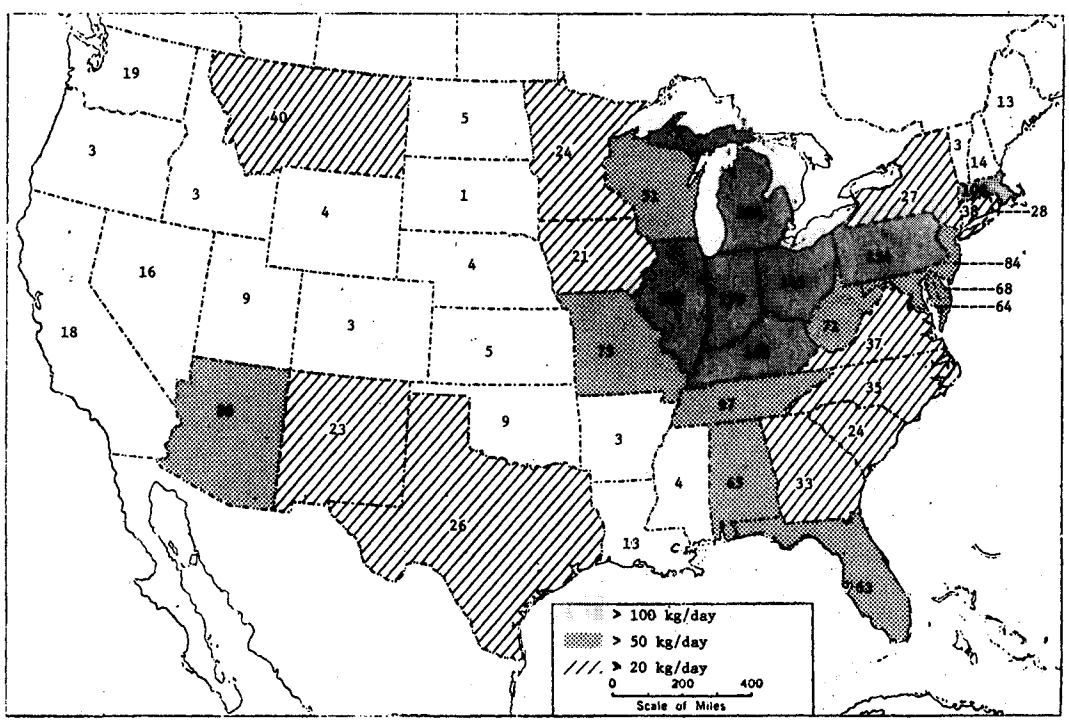

Figure 7. Maximum dry deposition in kilograms per day, calculated using equation (16).

To estimate the ratio of wet to dry deposition, we can again use the analysis of Scriven and Fisher (1975). They assume that removal by dry deposition is achieved by a deposition velocity Vg times the concentration χ, while precipitation removal is achieved by a "wash out factor" Λ related to the rainfall intensity. The removal term in a mass balance element under these assumptions becomes

$$(Vg + f\Lambda H)\ L_o\ \chi$$

One can then calculate the ratio of dry to wet removal r_{dw} by simply dividing the two components of this term, namely

$$r_{dw} = Vg/f\Lambda H \qquad (17)$$

where f is from Visher (1954) and represents the amount of time a rainfall of intensity i occurs, and Λ is the Langmur removal coefficient calculated according to Scriven and Fisher (1975) as

$$\Lambda \simeq 10^{-4}\ \sqrt{i}\ ;$$

where i has units of mm/hr. Figure 8 shows the results of the ratio of dry to wet removal, assuming that the deposition velocity is 1 cm/sec.

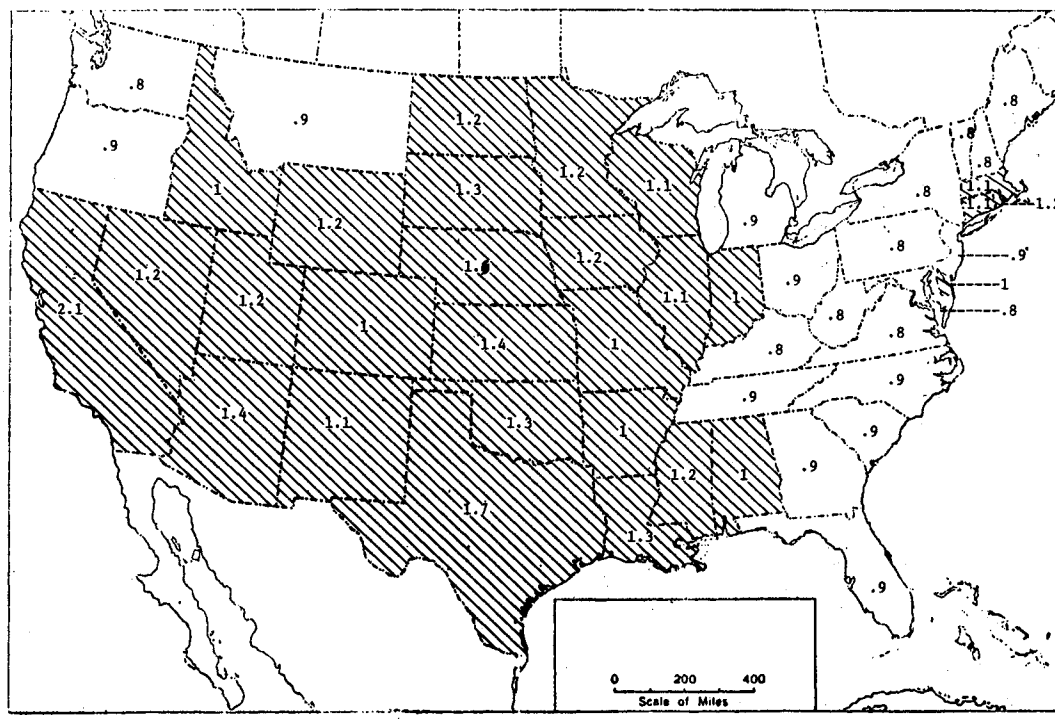

Figure 8. Ratio of dry to wet deposition, using equation (17) and assuming a deposition velocity of -1 cm/sec.

To improve the estimates of ambient concentration, we can use a mass balance model similar to Scriven and Fisher but including the contribution of sources within the transport distance. Considering a mass balance for a volume of width ∂x and length L_o, with the removal term as written above and the sources distributed as a general area source gives:

$$UL_o H \frac{d\chi}{dX} = -(Vg - f\Lambda H)\ L_o \chi\ Q_o/L_o$$

which is integrated to give

$$\chi(x) = \chi_o \exp[-(\frac{Vg}{H} + f\Lambda)\frac{x}{u}] + Q_o/HA(\frac{Vg}{H} + f\Lambda) \qquad (18)$$

where χ_o is the concentration at x = 0, the upwind edge of the area A. By assuming that $x = L_o/2$, an average distance to the center of the State, and that χ_o is an average of the concentrations in adjacent States, the ambient concentrations factoring in dry and wet removal and transport from other States can be calculated. Figure 9 shows the results of these computations. The significance of removal processes

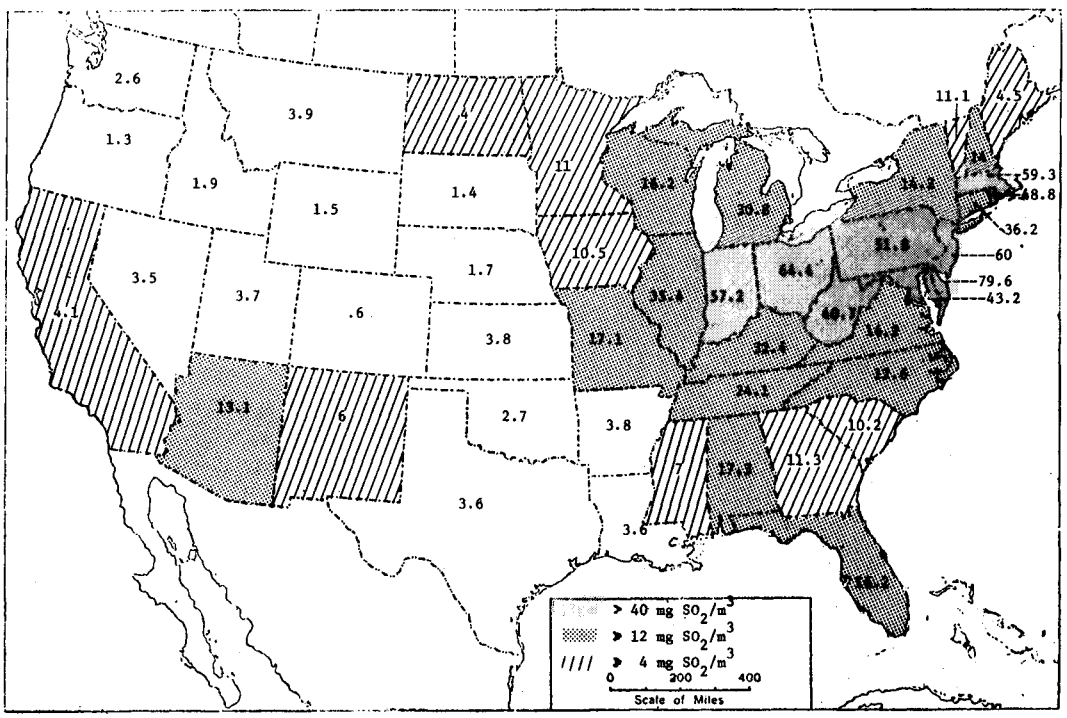

Figure 9. Concentration of SO_2 in $\mu g/m^3$ by considering effects of wet and dry deposition and transport from adjacent states, using equation (18).

and transport processes can be seen by comparing Figure 6 and Figure 9. Figure 6 estimates concentration assuming no removal and no out of state transport. Larger states removed from strong inflow of polluted air tend to show deposition processes are significant in reducing the concentrations. States in more heavily polluted areas are strongly affected by an influx of polluted air from adjacent areas.

It should be reiterated that these computations represent a gross estimate of the levels of SO_2 present in air over the United States. That they appear to present reasonable numbers is most likely due to the size of the area chosen for the analysis, and the fact that climatology is really not strongly variable from location to location. Furthermore, the computations point out that, except for some limited areas of the United States, particularly the Northeast, the vast majority of a State's ambient SO_2 comes from sources within the State.

Of concern, however, is the proposed coal development and utilization within the northern Great Plains. Recent estimates put the source strength at 2.5×10^6 tons SO_2/year which, emitted over an area of 5×10^{11} square meters, leads to a concentration increment of 14.8 $\mu g/m^3$. The impact of such an increase is certainly going to be significant to an area which currently has the cleanest air in the United States.

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LONG RANGE TRANSPORT OF AIR POLLUTANTS IN EUROPE AND ACID PRECIPITATION IN NORWAY

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ABSTRACT

Observations show that pollutants from large emission sources may cause significant air concentrations 500 to 1000 miles away. Very acid precipitation occurs in such periods. The scavenging is often intensified by the topography. Case studies will be presented, with special emphasis on acid precipitation in Scandinavia.

Large scale dispersion models have been developed recently in order to estimate the long range transport of air pollutants. The models take into account chemical transformations as well as deposition of pollutants. The calculations will be compared with observations from aeroplanes and surface stations.

A simple model has been integrated over a long period of time in order to derive the best value for the decay rate of SO_2. This best value is based on a day-by-day comparison with surface observations.

INTRODUCTION

It was suggested many years ago that the acidification of lakes and rivers in Scandinavia was caused mainly by increased transport of air pollutants from the United Kingdom and the European continent.

Since the end of the 1960's daily observations have been collected and acid precipitation episodes have been studied in detail, using back trajectories to trace the origin of pollution. In 1971 this work was intensified and a first version of a large-scale dispersion model was established. During 1972 and 1973 various model studies were carried

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*The views expressed in this paper are those of the author only.

out in Scandinavia. A short review is given by Nordø et al. (1974 I) and by Nordø (1974 II). A number of acid precipitation episodes are also described in the same papers. The calculations are based on observed 850 mb and surface winds, analysed every six hours.

EPISODES OF ACID PRECIPITATION

Acid precipitation episodes are usually most clearcut in southern Norway because of enhanced (orographical) precipitation for winds between SW and SE, see Figure 1.

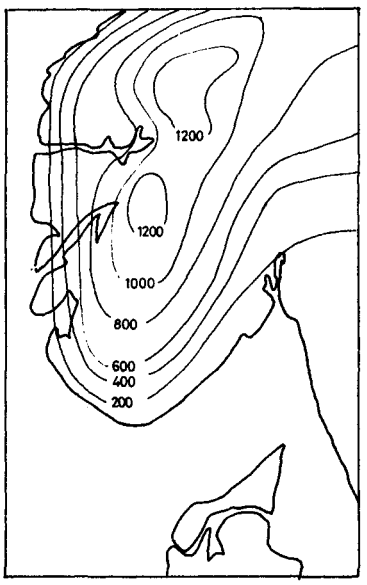

Figure 1. Topography of southern Norway. Heights are in meters

Figure 2, taken from Eliassen and Saltbones (1975 I), shows that winds from the sector SE - SW will often pass large emission centres. When the polluted air masses approach the mountain slopes, the cooling due to uphill motion may result in an intense scavenging of air pollutants. In winter the monsoonal high often resides over USSR. When Atlantic lows move into the Norwegian Sea converging air streams may at times transport air pollutants from most of western and central Europe towards the Norwegian mountains. Figure 3 shows such a case from January 1972. In fall, winter and early spring the condensation level is usually low and the maximum precipitation intensity is observed on the slopes of the large-scale mountains. The scavenging patterns of

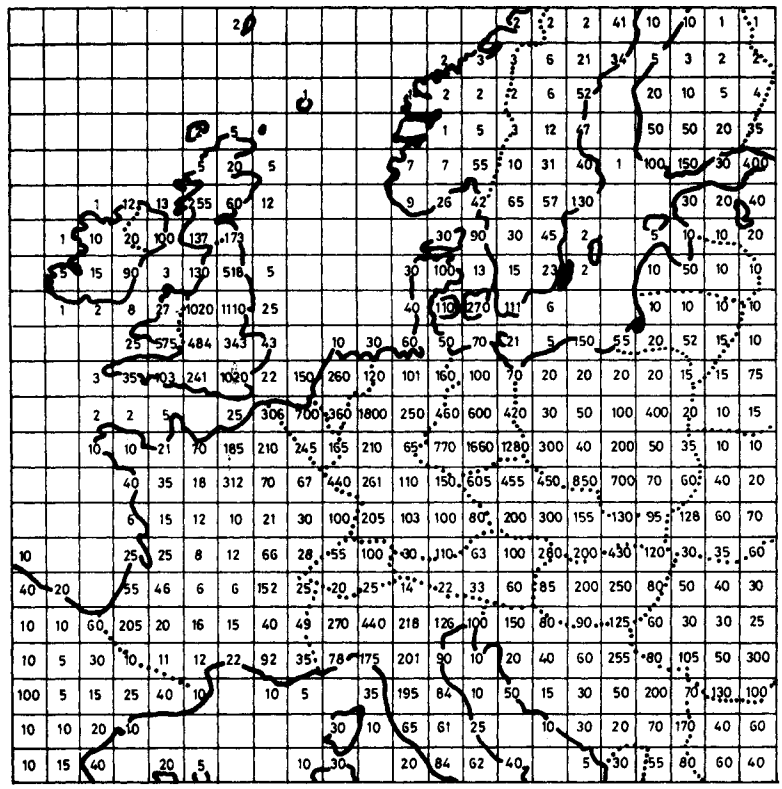

Figure 2. European SO_2-emission 1972. Unit: 10^3 metric tons y^{-1}. Better information has now been received for many countries. For instance, total 1973 emissions of SO_2 for the U.K. were about 5.7 million metric tonnes which is 12.3 per cent less than the 6.5 million tonnes indicated.

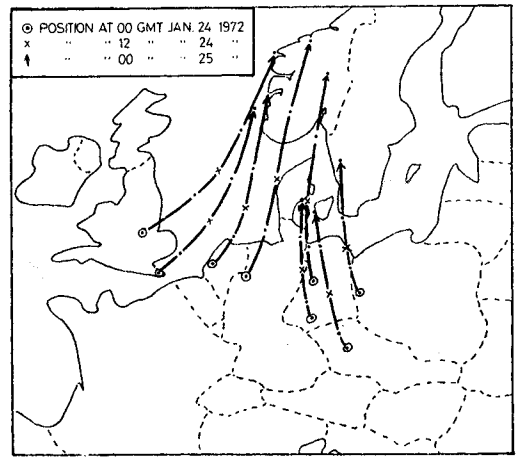

Figure 3. Forward trajectories for January 24th-25th 1972, using observed 850 mb winds.

Figure 4 are typical for a period with winds prevailing between SE and SSW. The period occurred in January 1974 and is described in a paper by Nordø (1974 III). The precipitated amounts of sulphur are plotted as mg/m^2 and the corresponding precipitation amounts are given in brackets as mm. Figure 4 shows that the concentrations are highest

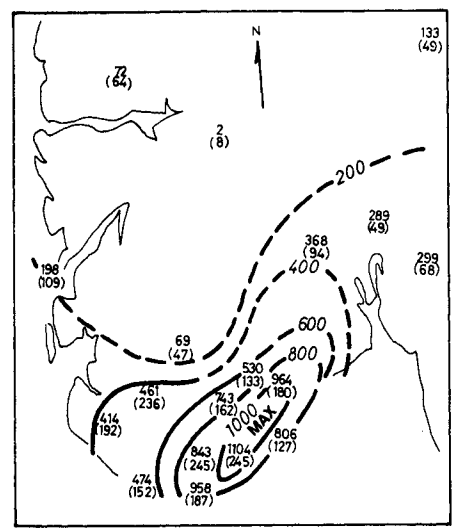

Figure 4. Precipitated SO_4 as mg/m^2 during the days January 5th-13th and January 23rd-31st, 1974. Precipitation amounts (mm) in brackets.

near the coast (line of inflow). The chemical analysis revealed that together with the sulphate significant amounts of nitrate and ammonia were precipitated to the ground. Figure 5 shows the ion concentrations of sulphate (solid line), ammonia (broken line) and nitrate (dotted line). The concentrations of ammonia and nitrate seem to follow each other. On Figure 6 the algebraic sum is plotted as a solid line and the corresponding measured H^+ concentration is given as a broken line. The agreement is reasonably good.

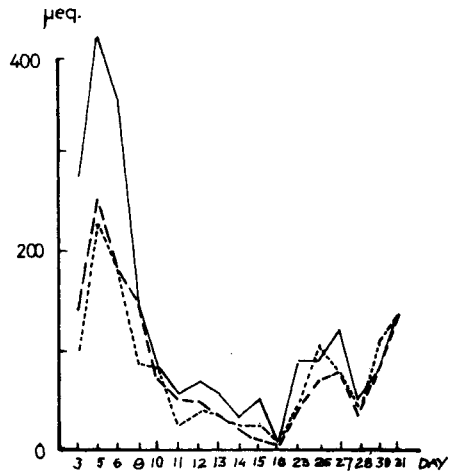

Figure 5. Daily January 1974 data on the ion concentrations of SO_4 (full line), NH_4 (broken line), and NO_3 (dotted line). All concentrations are given as microequivalents per litre.

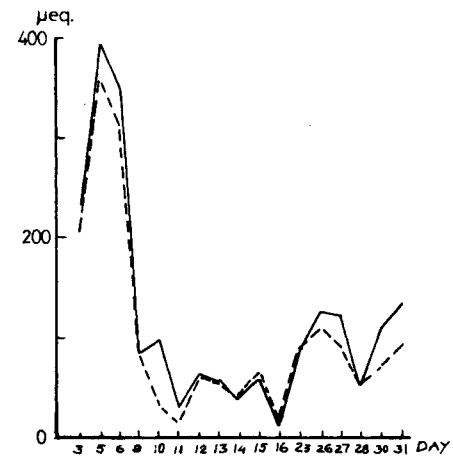

Figure 6. Daily January 1974 data. Full line shows algebraic sum of SO_4, NO_3, and NH_4 ion concentrations. Broken curve gives the observed H^+ concentrations.

In summer convective instability may cause a variety of episodes. We shall here restrict ourselves to an episode which occurred on 26th-27th August, 1974. Southerly winds prevailed then over the North Sea and Skagerak, see Figure 7.

This episode was predicted, and the NILU* aircraft was scheduled to take samples of a continental "plume" which was predicted to reach Norway later on August 26th. The aircraft measurements were carried out near noon, and are encircled on Figures 8 and 9. The routine calculations of SO_2 and SO_4 (on filters) are reproduced in Figures 8 and 9. The model used is discussed below. The sharp gradients along the

*Norwegian Institute for Air Research.

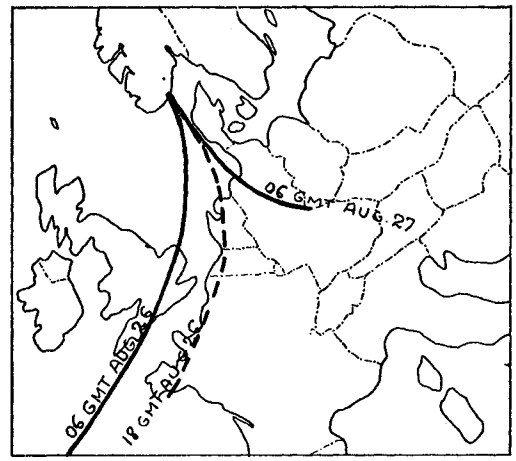

Figure 7. Back trajectories for a point in southern Norway, using observed 850 mb winds.

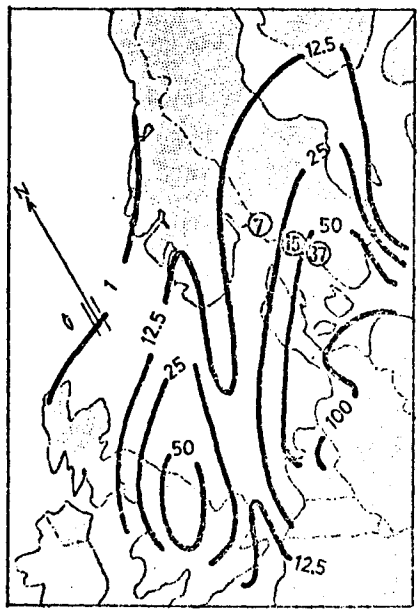

Figure 8. Model estimates of the SO_2 concentrations at 12 GMT on August 26th 1974. Aircraft measurements are encircled.

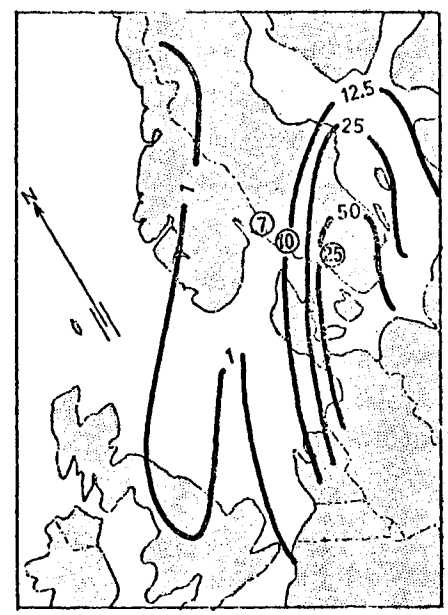

Figure 9. Model estimates of the SO_4 concentrations at 12 GMT on August 26th 1974. Aircraft measurements are encircled.

western coast of Sweden are verified by the aircraft data, but the sulphate concentrations are somewhat overestimated.

A frontal zone was established along southern Norway, and vertical displacements in connection with the front and the topography released convective instability. Heavy thunderstorm activity occurred along the slopes and the top of the mountain range. The 24 hour rainfall figures are given in Figure 10. We notice one maximum zone along the

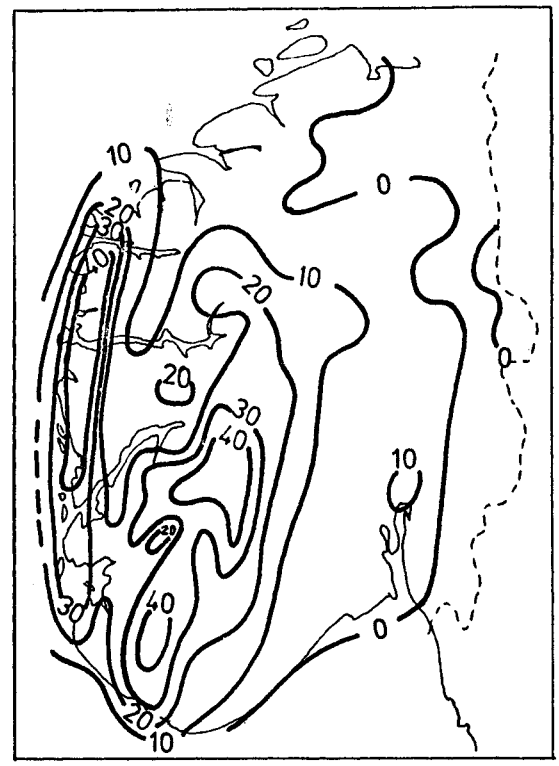

Figure 10. 24 hours rainfall (mm) in southern Norway during August 26th-27th 1974.

steep mountain slopes of western Norway. The other maximum zone lies along the divide. The rainfall is modest near the coast of southeastern Norway, and the precipitation distribution deviates much from the patterns which are typical for the winter season. The acidity was high with pH less than 4.0 along the divide, cf. Figure 11. The corresponding scavenging of strong acid is shown in Figure 12. Values of 3 milliequivalences per m^2 are found along the most elevated part of southern Norway. Another maximum is found on the west coast. The wet

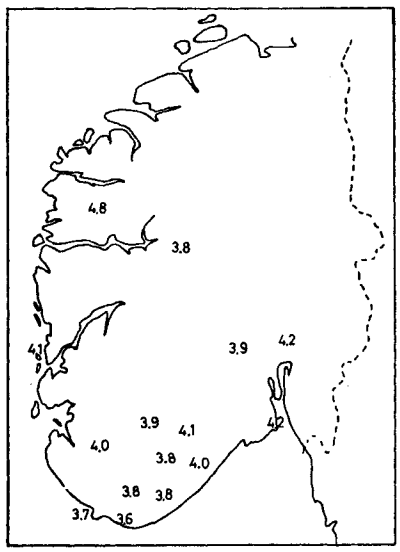

Figure 11. Acidity of rainfall (pH) on August 26th-27th 1974.

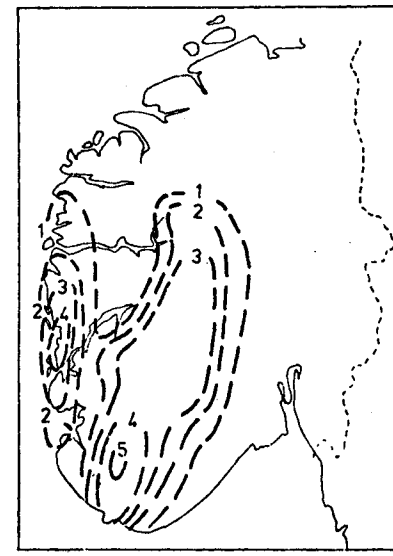

Figure 12. Wet deposition of H^+ as meq/m^2 during August 26th-27th 1974.

deposition of sulphate is given on Figure 13. The major maximum lies again along the divide, but a secondary maximum is indicated along the west coast.

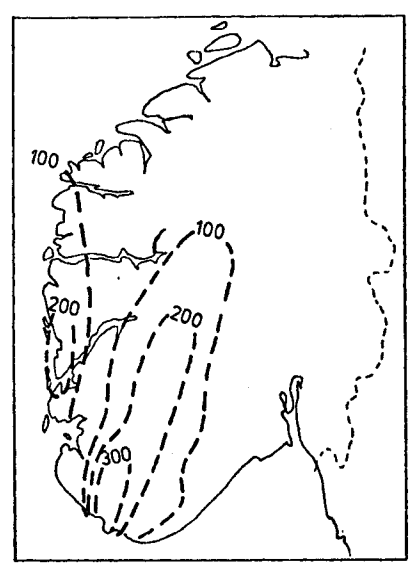

Figure 13. Wet deposition of SO_4 as mg/m^2during August 26th-27th 1974.

LARGE-SCALE DISPERSION MODELS

Knowing the wind distribution in time and space, it is possible to estimate the air pollution concentrations from the equation of continuity. The mass of a pollutant is then conserved as the air parcel moves along. Sources, sinks and chemical transformations must be taken into account during the transport. The SO_2 emissions are coming from low sources as well as high stacks. Using a two-layer model it is possible to simulate the effects due to low and high emission. Preliminary studies of this kind have recently been undertaken by Eliassen and Saltbones (1975 II). In a one-layer model no differentiation may take place after the initial mixing of the pollutants within the grid box. Transport out of the considered layer gives sink terms. The loss through the lower boundary depends on the "resistance" of the actual surface in addition to the turbulence in the boundary layer. Chemical transformations may act as sources or sinks depending on the pollutants being present.

Some applications of one-layer dispersion models are described in a paper by Nordø (1974 II). The model computations below are derived by using an improved version of the one-layer Lagrangian model of Eliassen and Saltbones (1973).

TRAJECTORY MODELS

In addition to the dispersion models discussed above, we shall present some results derived from a simple "trajectory" model. This model is extremely economical with respect to computing time. A number of simulations may therefore be carried out in order to see which parameter values give the best fit to the actual data.

In order to study the possible effects of precipitation on the concentration of sulphur as an air parcel moves along its trajectory, the following relations are used:

$$\frac{\delta q}{\delta t} = \frac{Q}{H} - (k_0 + k_1 + \delta_N k_2 N)q \qquad (1)$$

$$\frac{\delta r}{\delta t} = 1.5 k_1 q - Kr \qquad (2)$$

where q is the mixing ratio for SO_2, r is the mixing ratio for SO_4 (on filter), H is the height of the layer and is equal to 1 km in the preliminary studies, Q is the emission of SO_2, k_0 the dry deposition rate, k_1 the chemical transformation rate of SO_2 to SO_4, N the precipitation intensity in mm/hour, $\delta_N = 1$ when $N \geq 0.2$ mm/hour and equal to zero for

lower intensities, k_2 a factor between 0 and $8 \times 10^{-5}s^{-1}$, and K is the deposition rate of SO_4 to the ground.

Zero concentrations are assumed at the starting point of each trajectory. Back trajectories are computed every 6 hours, and the mean of four consecutive concentrations gives daily means. The precipitation amounts in each 12 hour interval are analysed and hourly amounts are derived by interpolation. A series of calculations are carried out for the period December 15th 1973 - March 31st 1974, varying the parameters of equations (1) and (2).

The precipitation intensities were rather weak during the period considered, and the correlation analysis showed no preference of k_2 in the region $0.5 \times 10^{-4}s^{-1}$ to $0.8 \times 10^{-4}s^{-1}$ when k_1 was put equal to $2 \times 10^{-6}s^{-1}$. k_0 was chosen as $0.6 \times 10^{-6}s^{-1}$. Similar correlations were found using $k_2 = 0$ and $k_0 + k_1 = 3 \times 10^{-5}s^{-1}$ when precipitation occurred. This value was derived from previous statistical studies by Jensen and Nordø (1975). When there was no precipitation k_1 and K were both put equal to $2 \times 10^{-6}s^{-1}$.

A correlation analysis showed that it might be slightly better to increase k_1 and K somewhat during precipitation, but the preliminary results are not conclusive on this point.

In order to derive optimal results one should use a transport wind near the level of the highest concentrations of the actual pollutant. Near the large emission sources low level winds should be used. At some distance downstream the pollutants are spread within the mixing layer, and the 900 mb or 850 mb winds may become good approximations.

A CASE STUDY

At the end of March 1974 easterly winds prevailed over the northern parts of the continent and the North Sea. On March 27th NILU was asked to fly their aircraft from southern Norway towards the British Channel in order to take a cross-section of an anticipated plume of sulphur pollutants. The solid lines of Figure 14 show the SO_2 concentrations according to the one-layer Lagrangian model. The computations are based on the 850 mb winds. The aircraft data are plotted within squares. Daily means of surface observations are encircled. The strong gradient between southern Norway and the British Channel is verified by the aircraft data. But west of the Netherlands the aircraft measured significantly higher concentrations. The upwind surface data over the Netherlands are, however, much lower than the computed concentrations. In this situation the lower troposphere was very stable and deposition to the ground has probably drained the lowest layer of most of its SO_2. The corresponding (aerosol) SO_4 concentrations are reproduced on Figure 15. We notice a much better correspondence between surface and

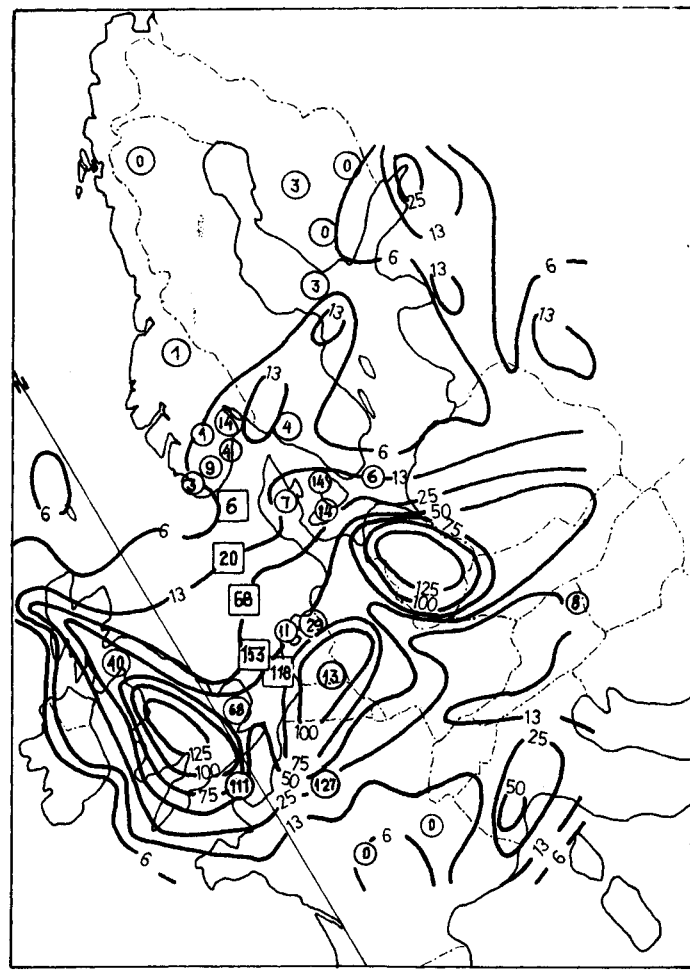

Figure 14. Calculated concentrations of SO_2 as microgrammes per m^3. Aircraft measurements are put in squares, surface records are encircled. Date: March 27th, 1974.

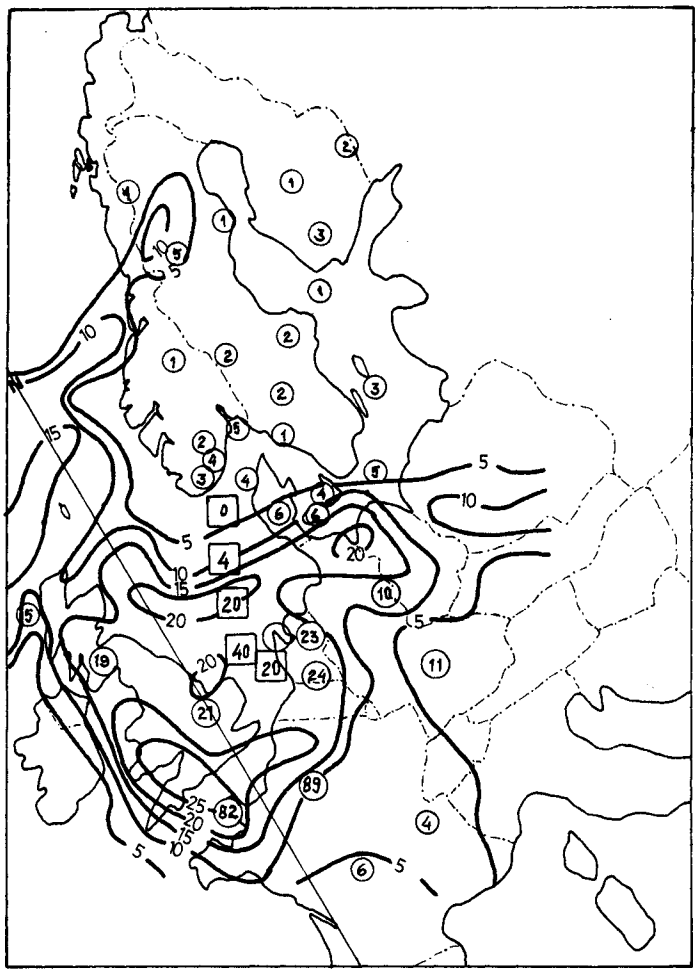

Figure 15. Calculated aerosol concentrations of SO_4 as microgrammes per m^3. Aircraft measurements are put into squares, surface data are encircled. Date: March 27th, 1974.

aircraft data. This result should be expected as the deposition of SO_4 aerosols is much slower than that of SO_2. SO_4 is therefore a good tracer and the model score is considerably higher for this quantity than for SO_2.

Some 48-hour back trajectories for 27th-28th March are shown on Figure 16. The computed daily means according to the trajectory model are given in brackets on Figure 17. The left-hand estimate is based on

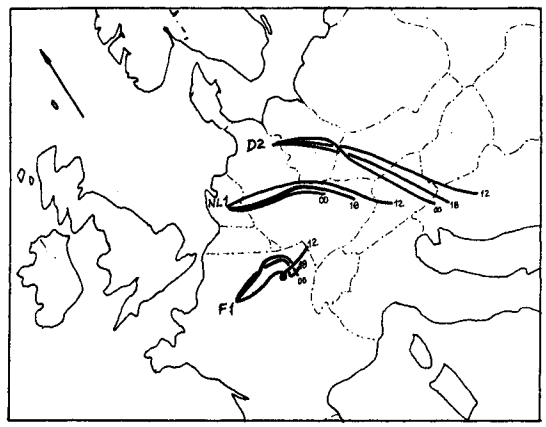

Figure 16. 48 hours back trajectories with arrivals between 12 GMT March 27th and 00 GMT March 28th, 1974, 850 mb winds.

$k_0 + k_1 = 3 \times 10^{-5}\ s^{-1}$ and $k_2 = 0$ when precipitation occurred. The right-hand estimate is computed by using $k_1 = 2 \times 10^{-6} s^{-1}$ and $k_2 = 4 \times 10^{-5} s^{-1}$ if precipitation did not occur.

The estimates correspond reasonably well with the aircraft values, but the stations in the Netherlands report rather low values. UK 1 does the same, but another station nearby reports high concentrations. The computations gave high estimates at D 2 and low estimates at F 1, quite the opposite of the observations.

Figures 16 and 18 show the back trajectories every six hours for 850 mb and surface. At the station F 1 the 850 mb transport is from the east, i.e. from regions with relatively weak emission sources. Near the surface transport is from the north and northeast, resulting in significant pollution from nearby and remote sources. At the station D 2 850 mb transport is from southeast, across some large emission sources. But the low level transport is due east and the result is a moderate pollution level.

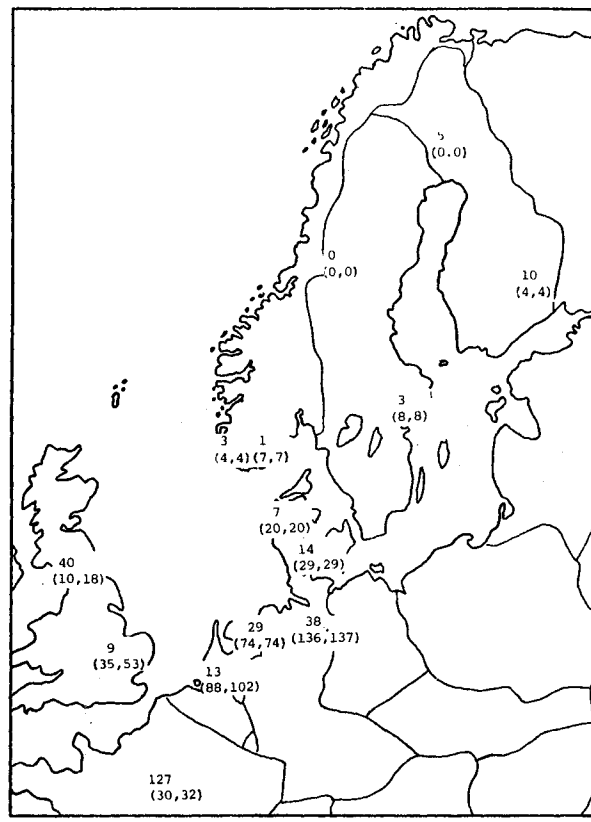

Figure 17. Episode on March 27th, 1974. Observed daily means of SO_2 compared to 850 mb trajectory estimates of SO_2 in brackets.

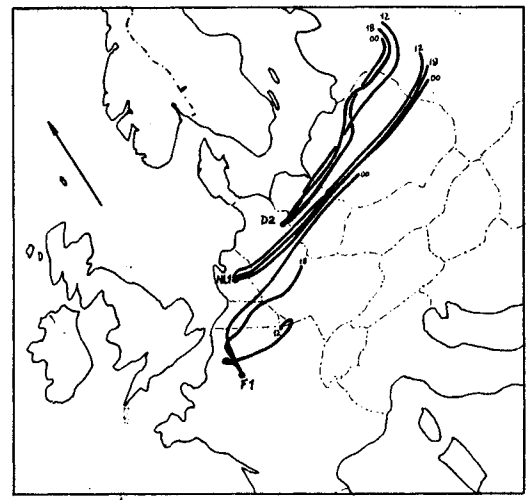

Figure 18. 96 hours back trajectories with arrivals between 12 GMT March 27th and 00 GMT March 28th, 1974. Surface winds.

The surface trajectory estimates are reproduced in Figure 19. The correspondence is now rather good at F 1 and D 2, showing once again that low level winds are preferable near the sources. But the station NL 1 has still high estimates, which agree well with the concentrations aloft. This result demonstrates that sharp vertical gradients may last for days in stable stratifications.

BUDGET STUDIES

The trajectory models cited above have been integrated over a longer time period, in order to estimate how much pollution a given location is receiving from specified local and distant sources. Preliminary budgets are already available for certain regions of Europe.

A one-layer dispersion model has also been integrated over 2-3 years in order to derive pollution statistics for wet and dry deposition of sulphur.

The computations indicate that most of the acidity is caused by anthropogenic emission within Europe itself. Europe "exports" also significant quantities of sulphur pollutants to the "background" atmosphere.

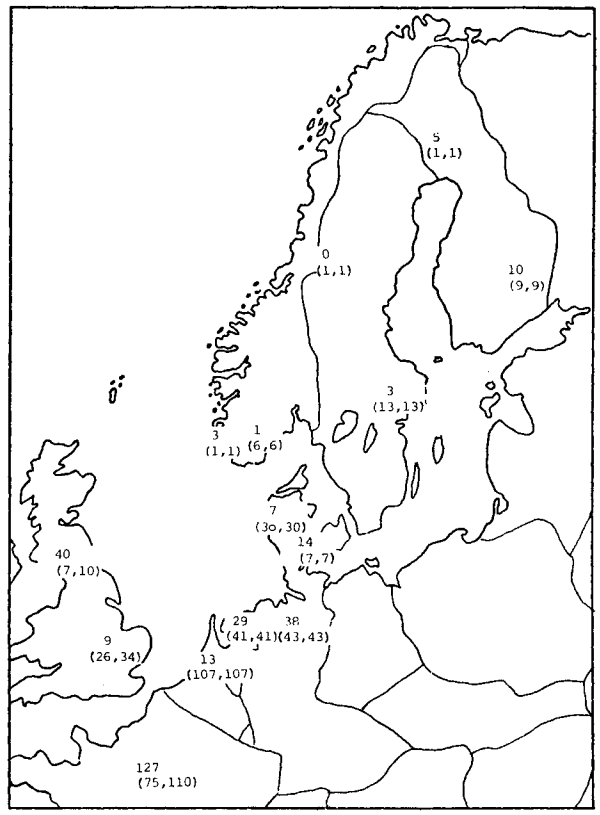

Figure 19. Episode on March 27th, 1974. Observed daily means of SO_2 compared to surface trajectory estimates of SO_2.

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ORGANIZATION OF LONG RANGE TRANSPORT OF AIR POLLUTION MONITORING IN EUROPE

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ABSTRACT

In the 1950's a network of stations for observation of the chemical composition of air and precipitation was established in Europe. Analysing these data, Odén in 1968, was able to show that a central area in Europe with highly acid precipitation was expanding from year to year. This was further substantiated by Granat in 1972, and the explanation is the increasing use of fossil fuels in Europe. In 1969, the problem was examined by OECD, and on the initiative of the Scandinavian countries, a joint research programme to study the long range transport of air pollutants was started in 1972. The Programme will be completed with a final report in 1976.

In this programme, atmospheric dispersion models are used to describe emission, dispersion and deposition of sulphur dioxide and sulphate with particular emphasis on the acidification of the precipitation. An emission field has been constructed for Europe, and data from the European weather forecasting system are used for the dispersion calculations. Calculated concentrations and deposition are compared with data from about 70 ground stations and measurements from aircraft.

Results show that the main cause for acidification of precipitation is the increasing use of fossil fuels. Large amounts of sulphuric acid can be transported over distances up to a few thousand kilometers.

In Southern Scandinavia where the soil is highly acid (podsol), this has caused severe damage to life in rivers and lakes, and it is feared that in the future, there will be serious damage to forestry. In the Alps, where the soil has a high carbonate content, such effects are not expected. The long range transport of air pollutants has also been shown to increase the corrosion of materials.

Work is now in progress to establish a more permanent system for the monitoring of air pollutants in Europe. The first plans for such a system were presented at the meeting in Oslo

in December 1974, where countries from both Eastern and Western Europe participated. The work is supported by the Economic Commission for Europe, UN, in cooperation with other international organizations such as the World Meteorological Organization and the GEMS programme of the United Nations Environment Programme.

In this connection, studies have also been taken up in several countries concerning the effects of the long range transport of air pollutants. In the future monitoring system, a coordination of these efforts is envisaged.

INTRODUCTION

In the middle of the 1950's, a network of stations for observation of the chemical composition of air and precipitation was established in Europe on the initiative of Professor Rossby at the International Meteorological Institute, Stockholm University.

After about 10 years, the observations indicated that the precipitation at several stations was becoming more and more acid. In an analysis of the data, Odén showed that in Europe a central area with highly acid precipitation (pH 3 - 4) was expanding from year to year (Odén 1968). The only explanation possible seemed to be the increasing use of fossil fuels, a more recent compilation by Granat shown in figure 1, confirms this (Granat 1972, Bolin 1971).

This was connected with the acidification of rivers and lakes in Scandinavia. Odén also pointed out that in the long run, this development could have an effect on the forestry.

In the Scandinavian countries Odén's report caused much alarm, and in 1969, an expert meeting was called in OECD to examine the evidence for the acidification of the precipitation. The meeting concluded that the precipitation in large parts of Europe evidently was becoming more and more acid and recommended that OECD investigated the situation. Shortly afterwards, the Air Management Sector Group of OECD asked the Scandinavian countries to work out a plan for such a study. In February 1970, scientists from the Scandinavian countries came together in Copenhagen to discuss the various approaches. The Scandinavian Council for Applied and Fundamental Research (NORDFORSK) was asked to coordinate the planning of the project, and a coordinating group consisting of representatives for the leading laboratories dealing with air pollution in the Scandinavian countries was established.

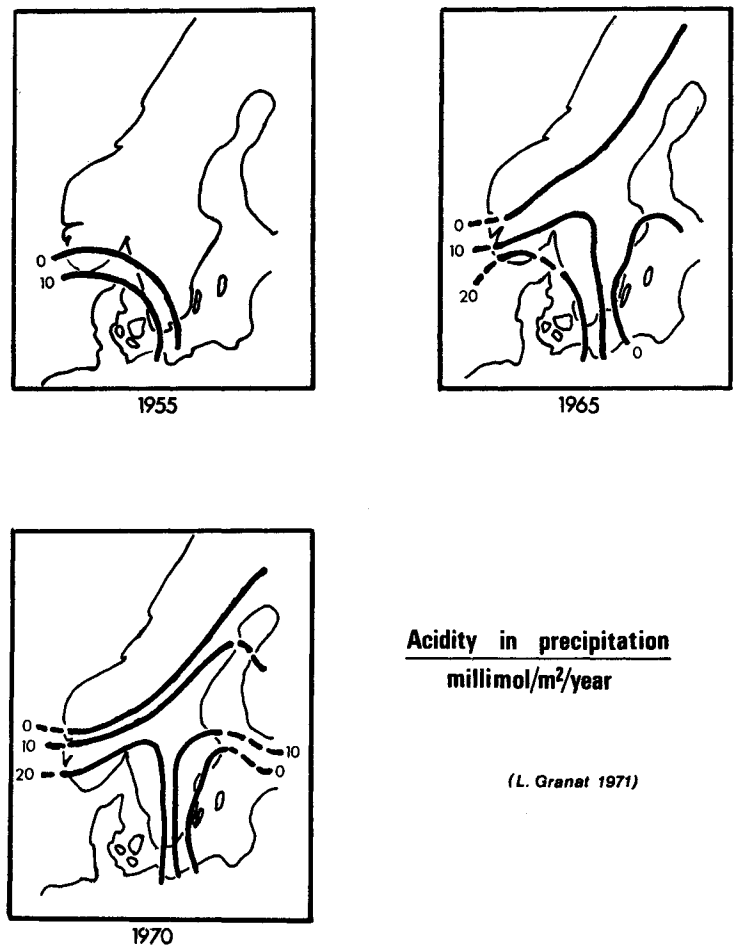

Figure 1. Acidity in precipitation, meqv/m • year.

This group was given two tasks: to organize a European study of the acidification of the precipitation, and to collect information for an early evaluation of the situation in Scandinavia.

In May 1970, the first project plan from NORDFORSK was presented in OECD, and in June an OECD planning committee was called together to examine the suggested project during the summer. This plan which called for a three year study, was ready in the autumn, but it soon became evident that several countries hesitated to tie themselves for several years to a plan which, to some, seemed very complicated, while others doubted that any significant long range transport of sulphur compounds would be found. In order to resolve these problems, the plan was divi divided into separate phases: a preparatory phase based on voluntary participation, a first measurement phase of an orientational character, and a second measurement phase to collect the data needed for

a full evaluation of the problems. This approach was accepted by the countries, and the voluntary preparatory phase was immediately launched. In the spring of 1972, the project was finally accepted by OECD. In all 10 countries agreed to participate actively in the project, (Austria, Denmark, Finland, France, Germany (West), Netherlands, Norway, Sweden, Switzerland, United Kingdom). Canada participated as an observer and special agreements concerning data collection were made with Italy and Iceland. Later also Belgium joined the programme. The programme was based on national measurement programmes, and a Central Coordinating Unit was established at the Norwegian Institute for Air Research.

The first measurement phase, which was to last one year, started in July 1972, but due to a late start of the measurement programme in some countries, it was later extended until January 1973, when the second measurement phase was initiated. The observation programme terminated 31 March this year, and the report from the Central Coordinating Unit will be sent out by the end of this year for examination by the participating countries. The final conclusions probably will be ready by summer 1976.

TECHNICAL APPROACH

The project plan was based on the assumption that a source oriented atmospheric dispersion model could be developed, which would describe the relationship between emissions and depositions of sulphur compounds, as dependent on the daily weather conditions. In this scheme, see figure 2, data from the emission field, and data from the meteorological field (wind and mixing height) are fed into an atmospheric dispersion model containing parameters describing the chemical transformations in the atmosphere and the deposition processes. Out of the model comes the concentration field, which is subsequently used to calculate the depositions. The various fields were described in a grid system with side length 100 - 150 km. The system is handled by solving the mass continuity equation in this grid system.

Several schemes for handling the data have been devised, (J. Nordø ibid). In principle, the air takes up a certain amount of pollutants while passing over one grid square. This amount is given by the emission field. The air is then moved with the wind to the next grid element, where a new amount of pollution is added to the air. At the same time, some of the pollution is deposited, and chemical transformations take place in the air. To calculate the concentration field, data from the WMO weather forecasting service were used. Using precipitation data and assuming various rates for dry deposition and gas absorption by vegetation, (Meetham, 1950), the total deposition of sulphur compounds may be calculated.

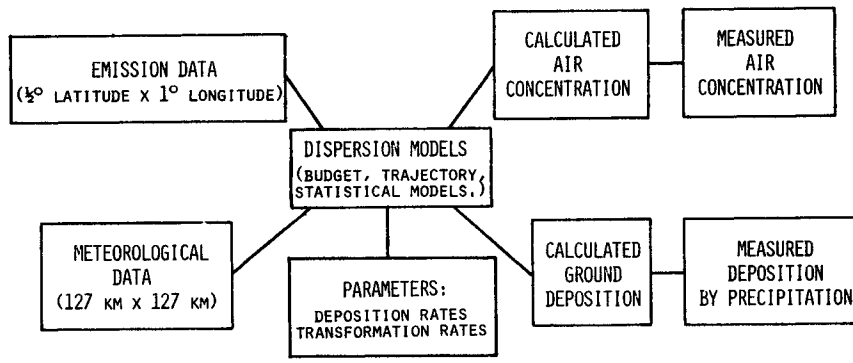

Figure 2. Block diagram representing operations in the LRTAP modelling of sulphur dioxide advection and deposition.

In order to check the calculations, altogether about 60 ground stations were established in the participating countries, (figure 3). At these stations, 24 hourly samples of air and precipitation were collected and analysed.

In principle, any pollutant could be studied in this system. The OECD project was, however, limited to sulphur dioxide and sulphate on particles in air, and the content of sulphate ions and strong acid in precipitation, as the main components responsible for the acidification of the precipitation.

Simple sampling methods were used, and the samples analysed at a central laboratory in each of the participating countries, according to recommended procedures. In order to make sure that the methods would work satisfactorily, the procedures were not distributed until they had been thoroughly tested with satisfactory result at two independent institutes.

As the project proceeded, various voluntary studies showed that other chemical components in the air had an appreciable influence on the situation. Nitrogen oxides from various combustion processes could give rise to considerable amounts of nitric acid in precipitation and ammonia from natural decay processes and agricultural activity is important in the transformation of sulphur dioxide to sulphates. Therefore in 1973 a study of these and other compounds was made during a

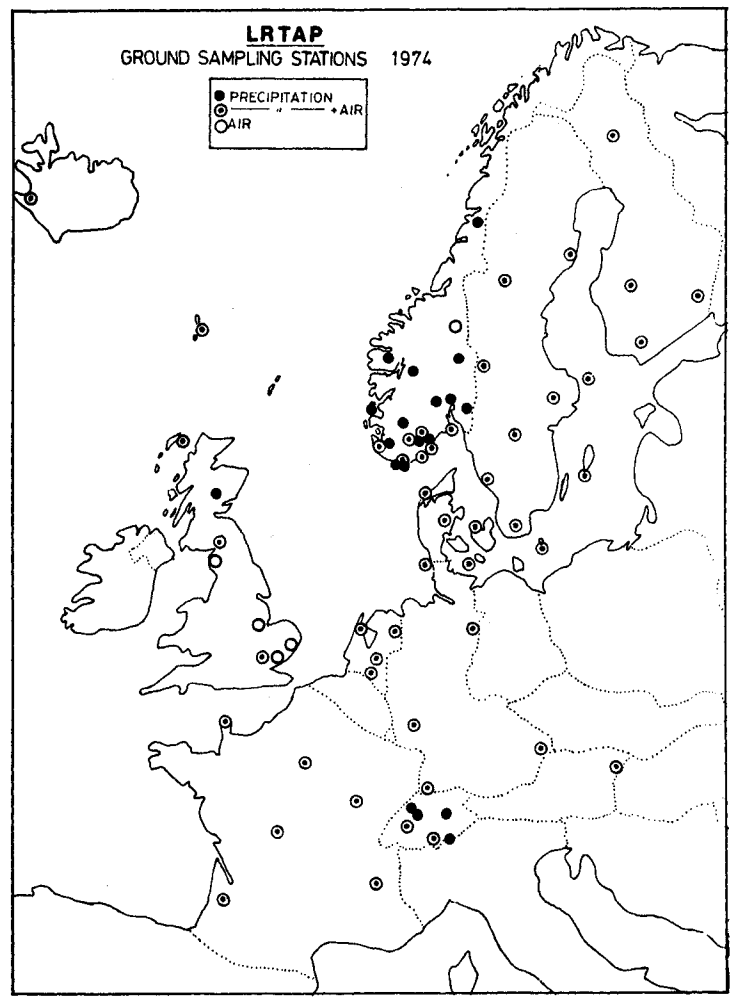

Fig 7-3
Figure 3. LRTAP Ground Sampling Stations.

100-day programme within NORDFORSK. These analyses have since been repeated in the OECD project during two periods of 45 days each (A. Semb ibid).

Another extension of the measurement programme is the sampling of sulphur dioxide and sulphate from aircraft. The sampling flights have been carried out during alerts with forecasted high concentrations and specific transport situations. An example, which illustrates the importance of measurements at higher levels, is given in figure 4.

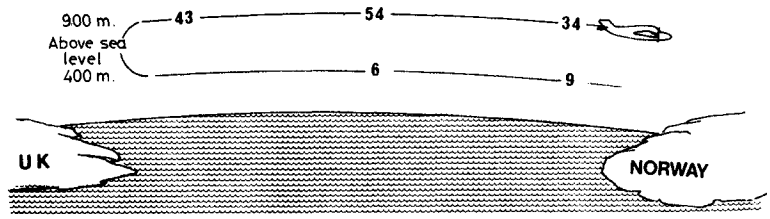

Figure 4. Aircraft sampling May 9th 1974, sulphur dioxide concentration in $\mu g/m^3$ at 400 and 900 meter above sea level.

RESULTS

The long range transport of air pollutants in Europe is primarily due to the emissions from the large industrialized areas. The emission survey in figure 5 shows that these areas are situated in a belt across Europe from England (5 million tonnes SO_2/year) past the Ruhr area and adjointed part of the Netherlands, Belgium and France (5 million tonnes SO_2/year), into Eastern Germany with Polen and Czechoslovakia (10 million tonnes SO_2/year). Downwind of these source areas, there will nearly always be an appreciable concentration of air pollutants. Aircraft measurements have shown that usually the main part of the pollutants are found below a height of 1 - 2 km above sea level. At a distance of 100 - 200 km downwind, the pollutants are more or less evenly distributed within this height. While near the sources relatively rapid dilution takes place due to turbulent diffusion, the dilution further downwind is generally much lower and governed by deposition (particularly precipitation), chemical transformations and dispersion on a synoptic scale (larger than 500 km).

Near the source areas, the precipitation is nearly always highly acid, thus in the Netherlands, the yearly average pH value of the precipitation is close to 4. Further away from the sources, the occurence of acid precipitation evidently depends on the wind direction and the meteorological conditions. The importance of orographic precipitation is illustrated in figure 6, which shows the deposition of sulphate by precipitation in Southern Norway. The deposition of acid is related to the amount of precipitation, but the maximum is situated east of the maximum for the precipitation. The reason for this is that the western part more often receives precipitation with clean air from the Atlantic.

When orographic precipitation is considered in relation to the long range transport of air pollutants it becomes evident that a major part of the pollution will be deposited on the slopes of the hills and mountain ranges facing the larger emission areas. Thus, large amounts

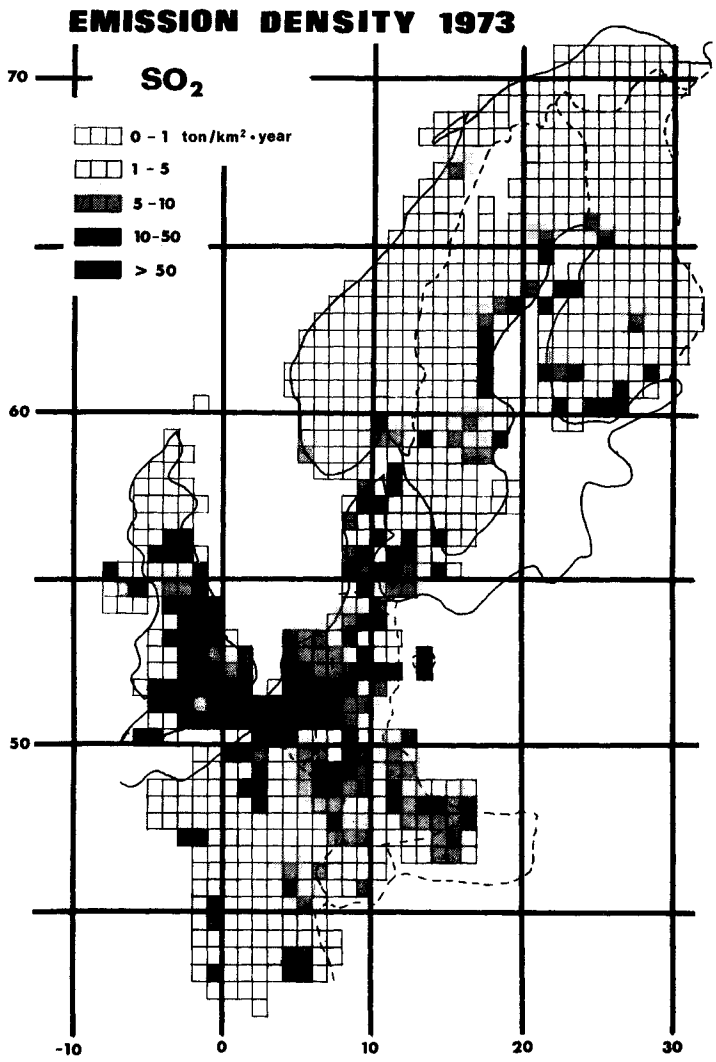

Figure 5. Emission density 1973.

of acid precipitation are deposited in the foot hills of the Alpes as well as in Scandinavia. For model studies, the Scandinavian situation is ideal, because the North Sea with no sources of importance, separates the Scandinavian area from the main source areas in Europe.

Conversely, mountain ranges and orographic precipitation may be considered as barriers, limiting the very long range transport of air pollutants, this leaves only a limited number of possibilities open. One is transport east of the Scandinavian mountains and up along the Baltic Sea. A situation of this type was observed on the 5th March 1972.

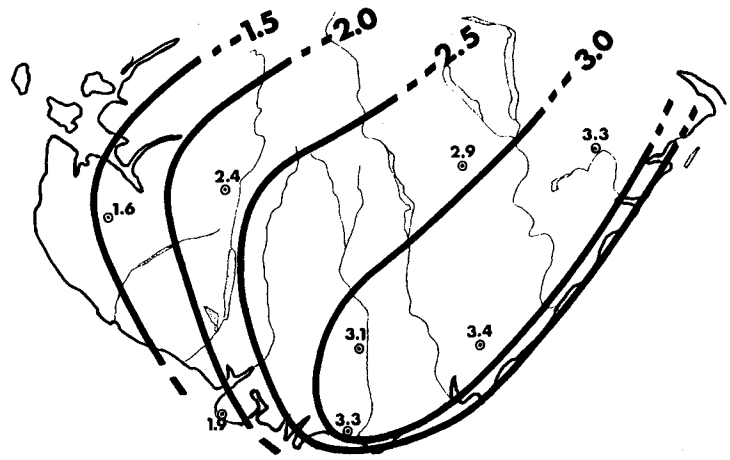

Figure 6. Precipitated sulphate in southern Norway January 1st to June 30th 1972 in g/m^2, ≃ 80% acid.

In this case, amounts up to 0.4 g/m^2 of sulphate ions (≃ 80% acid) were deposited in Southern Norway, see figure 7 and later an unusual high

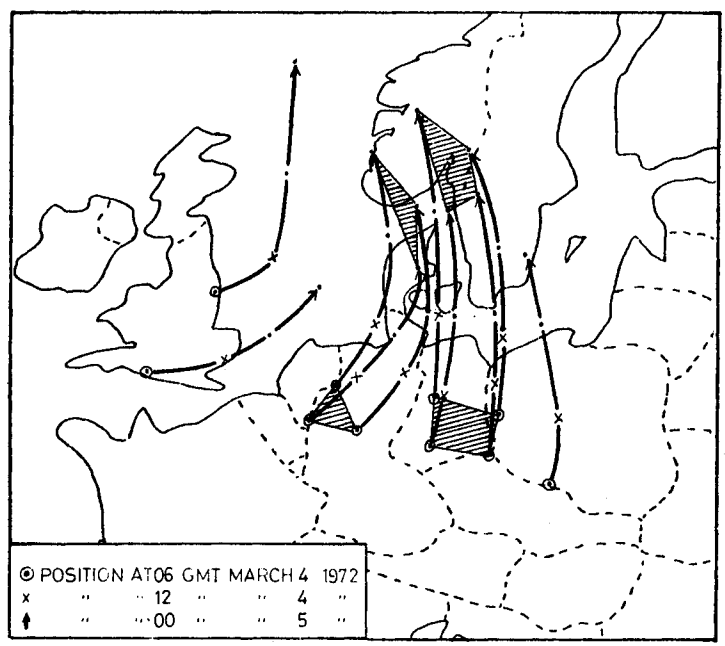

Figure 7. Transport of polluted air to Scandinavia March 4th - 5th 1972.

concentration of particles was observed with polluted air in Northern Norway, see figure 8 (Rahn, 1973). In other cases, the polluted air

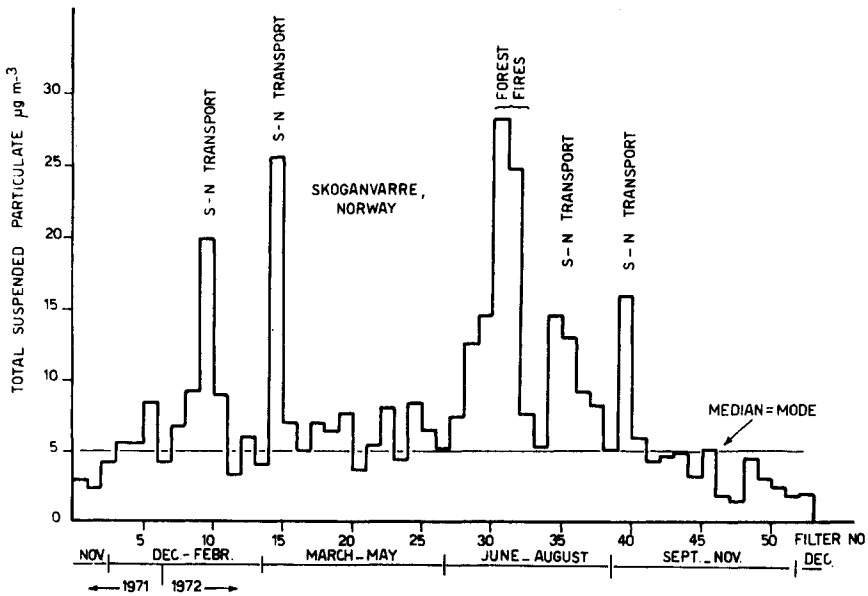

Figure 8. Concentration of suspended particles in the air at Skoganvarre, North Norway.

masses are brought out over the North Sea, between Scandinavia and England. If the air masses pass over England, new amounts of pollutants are added to the air masses. On occasions, the polluted air masses may pass out into the Atlantic Ocean, south of Ireland. In all these situations, cases have been found when the polluted air masses later turn eastward and give rise to acid precipitation in Scotland and along the western and northern coast of Norway. On a few occasions, acid precipitation originating from similar situations has also been observed at the Faroe Islands and at Iceland. The concentration of sulphate aerosol at the Faroes has been shown to increase sharply with transport of air from Great Britain and continental Europe (Prahm et al., 1974), from a value of less than 0.5 $\mu g/m^3$ sulphate for Atlantic air, to a value of 8-10 $\mu g/m^3$.

Generally, the occurence of acid precipitation is less probable further away from the major source areas because of the special weather conditions required. However, the amount of acidity deposited may be the same, or even larger than in the central areas if orographic precipitation comes into the picture.

The various atmospheric dispersion models developed are used for different purposes. Calculated concentration fields are suitable for studies of air pollution episodes when measured data are available for a larger area. Generally, the models give a satisfactory description of the situations.

By calculating the pollution concentration along air trajectories leading up to a given point, the fractions of the pollution originating from nearby and distant sources may be evaluated.

In order to be able to evaluate possible effects, the geographical distribution of the deposition is required, and in addition some statistical information on the occurance of episodes with highly acid precipitation. So far, only some preliminary evaluations, merely to test the various computer programmes, have been made. It may be concluded from this material that the contribution from the long range transport of air pollutants in many places constitute a considerable part of the total deposition.

A well established atmospheric dispersion model also has more sophisticated applications. By changing the emission field and repeating the statistical calculations, they can be used to estimate the effect of various abatement policies.

Using special sets of weather data, worst cases may be estimated. By comparing trajectories and observed concentrations at a given point for different geographical sectors, the reliability of the emission field may be controlled. Least square analysis may be used to determine best values of various parameters entering the dispersion model.

The OECD project was limited to a study of sulphur compounds, but various measurements have shown that there are a number of other components which are of importance in connection with Long Range Transport of Air Pollutants (LRTAP), such as nitrogen oxides and particulate matter. Also micropollutants as chlorinated hydrocarbons and trace metals are despersed by the same processes. Although they are present in the atmosphere in minor amounts, over the decades they will accumulate in the environment and after long periods of time, their toxic properties may become apparent. Thus, the highest content of lead in mosses in Scandinavia (Tyler, 1972) is found in the southeastern part of Norway, the same area where orographic precipitation brings down the largest amounts of acid precipitation.

The OECD project is terminated by the end of 1975. But, the results show that it is highly desirable to establish a long range monitoring of air pollutants in Europe on a more permanent basis, and that it will be essential to obtain participation from both Eastern and Western European countries. Such a system is at present planned under the auspices of the United Nation's Economic Commission for Europe, in cooperation with other international organizations such as the World Meteorological Organization and the GEMS programme of United Nations

Environmental Programme (UNEP). This system aims at observing the emission, dispersion and deposition of pollutants in the region and later on it is envisaged that the system will be supplied with coordinated observations concerning the long range effects of the pollutants. Such observations will form a necessary part of the basis needed in order to deal effectively with the long range air pollution problems in Europe.

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MEASUREMENT OF ACID PRECIPITATION IN NORWAY

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ABSTRACT

Since January 1972, chemical analysis of daily precipitation samples from about 20 background stations in Norway has been carried out on a routine basis. Air monitoring is carried out at six stations.

The chemical analysis programme is: sulphate, pH and acidity in precipitation, sulphates and sulphur dioxide in air. In addition, more detailed chemical analysis of aerosol and precipitation has been carried out at selected stations. Some results for the measurement period 1972-1974 are presented. Comparison of air and precipitation concentrations of sulphur compounds show that the precipitation scavenging efficiency is very high under the conditions in Southern Norway.

INTRODUCTION

In connection with the OECD Programme "Long Range Transport of Air Pollutants", a monitoring programme based on daily air and precipitation samples was started in October 1971.

This monitoring network was designed to give quantitative data for the deposition of air pollutants in the exposed parts of Norway where extensive damage to freshwater fish was known to occur. In addition to providing data from representative sites to check and control atmospheric models for transport of air pollutants in the OECD Programme, the network was also designed to measure the actual deposition of the deposition of air pollutants in the part of Southern Norway where extensive damage to freshwater fish was known to occur. Because of the orographic precipitation effects (Nordø, 1972), precipitation sampling was considered most important. Air monitoring was included at some of the sampling sites (Figure 1).

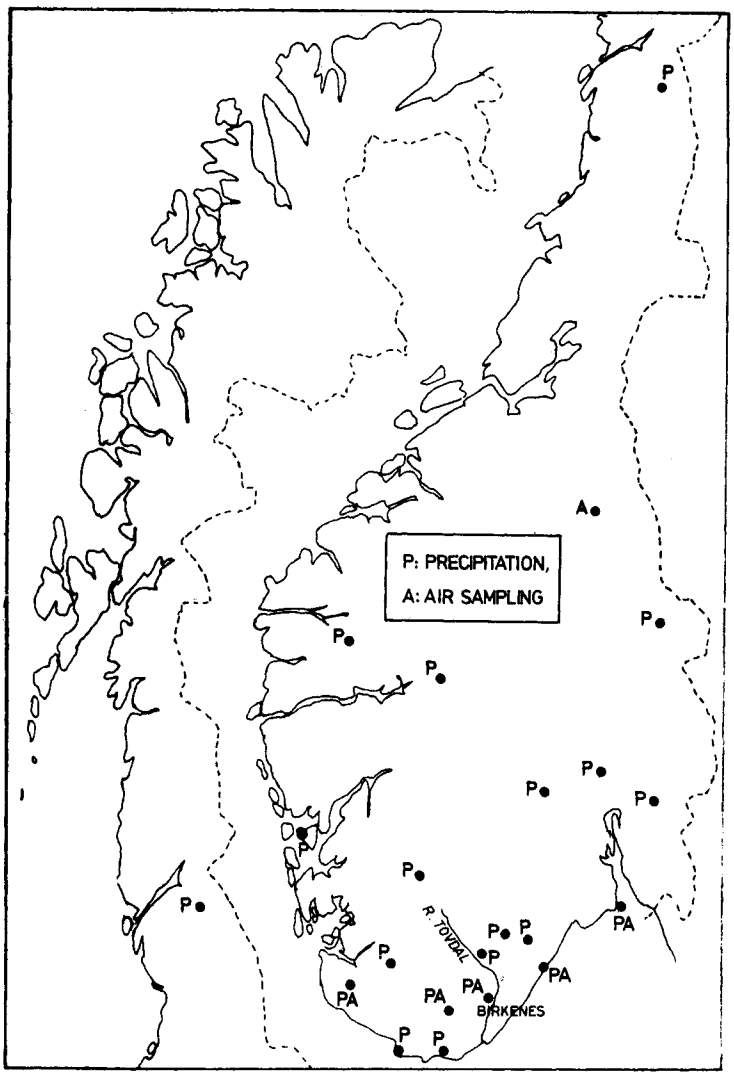

Figure 1. LRTAP Ground Sampling Stations in Norway.

SAMPLING AND ANALYSIS METHODS

The programme included determination of sulphur dioxide as sulphate by the barium-perchlorate-thorin method (Persson, 1966) after absorption in an acid hydrogen peroxide solution, determination of airborne particulate sulphate by X-ray fluorescence (Grennfelt et al., 1971), sulphate in precipitation by the barium-perchlorate-thorin method after ion exchange, and the excess acidity due to strong acids by Gran's plot titration (Liberti et al., 1972).

In addition to this programme, chemical parameters were determined at one of the stations since April 1974. The additional components include nitrate, ammonium, calcium, potassium and sodium in precipitation and aerosol samples, and strong acid in the aerosol samples (Brosset, 1973). Ammonium is determined by the indophenol blue reaction, nitrate by a method based on reduction to nitrite and diazotation (Selmer-Olsen and Henriksen, 1970), while the additional components are determined by standard laboratory methods.

Air monitoring was carried out with simple air pollution sampling equipment (OECD, 1964). Precipitation gauges from polyethylene were used for precipitation sampling. The gauges were made to WMO specifications. Open, dustfall-type polyethylene jars are used for snow collection. The gauges are rinsed with distilled water every day at the time of sample collection.

In the selection of sampling sites WMO criteria for regional background stations were followed (WMO, 1971). Special care was taken to avoid influence of local sources, and the stations were generally placed sites in elevated, or hilly country. Stations in the meteorological precipitation network were generally preferred.

Because of the orographic effects, the amount of precipitation is very variable from one place to another, as illustrated in Figure 2. Also the amount of precipitation varies from one year to another. Compilation of the precipitation chemistry data has shown, however, that the mean weighted concentration of sulphate is a more conservative parameter (Figures 3-5). It is seen that there is a marked gradient from the coast to the inland, and that the pattern of the mean weighted concentrations is consistent from one measurement period to another. Some additional precipitation data from the SNSF-project is included in Figure 5.

From the precipitation data and the data in Figures 3-5, the yearly precipitation amount of sulphate may be calculated. In the maximum zone the deposition of sulphate by precipitation is up to about 5 g SO_4/m^2 year. The emission of sulphur dioxide from sources in the Oslofjord area are about half of the total emission in Norway. The contribution from the local sources in this area is estimated to be 10-30%, and is probably reflected in the precipitation data for 1972 (Figure 3).

Most of the wet deposition due to long range transport takes place in a few events with heavy precipitation. Table I gives a listing of individual days accounting for 50% of a yearly deposition of sulphate. Such events may be critical for small water systems.

The air concentrations of sulphur dioxide and sulphate are generally low and the frequency distributions of sulphur dioxide and sulphate are approximately lognormal (Figure 6).

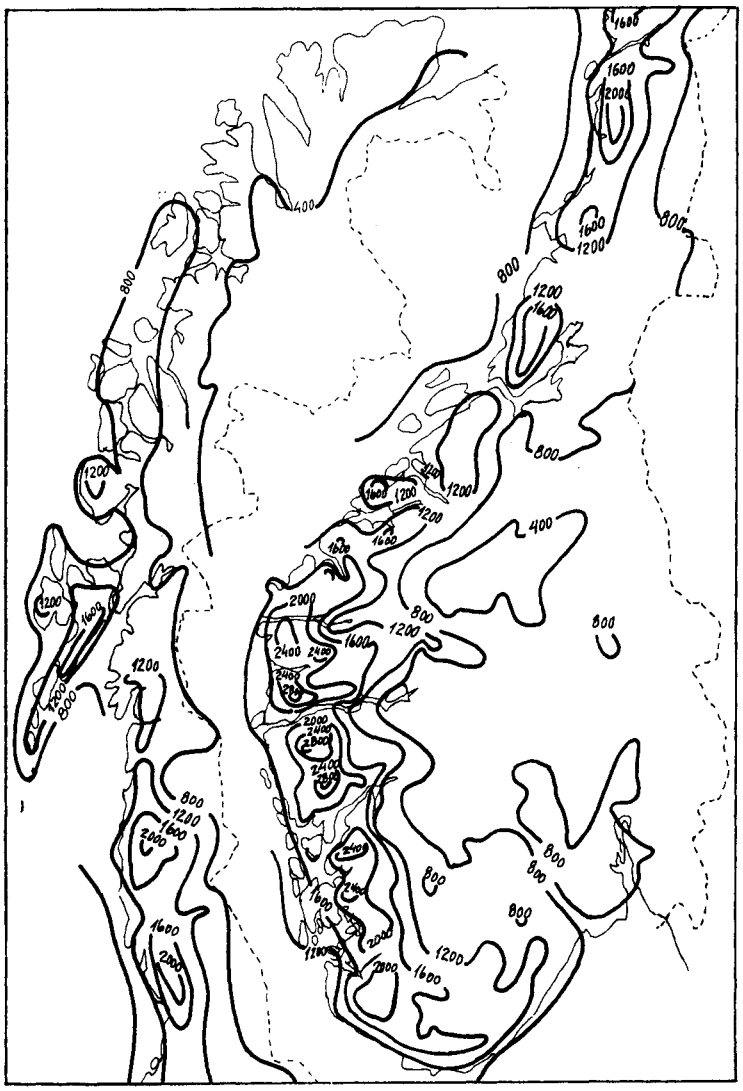

Figure 2. Mean yearly precipitation (mm) in Norway 1901-1930. After I Bruun (1949).

The detection limit for the sulphur dioxide method is about 3 $\mu g/m^3$, and a more sensitive method is desirable for the measurement of sulphur dioxide on a day-to-day basis.

The measured air concentrations are, however, consistent with trajectory calculations based on standard values for the rate of SO_2 removal by dry deposition and transformation from SO_2 to sulphates (Eliassen and Saltbones, 1975). Applying standard values for the dry deposition velocity of SO_2, this deposition may be roughly estimated from the ambient air concentrations to around 50% of the sulphate

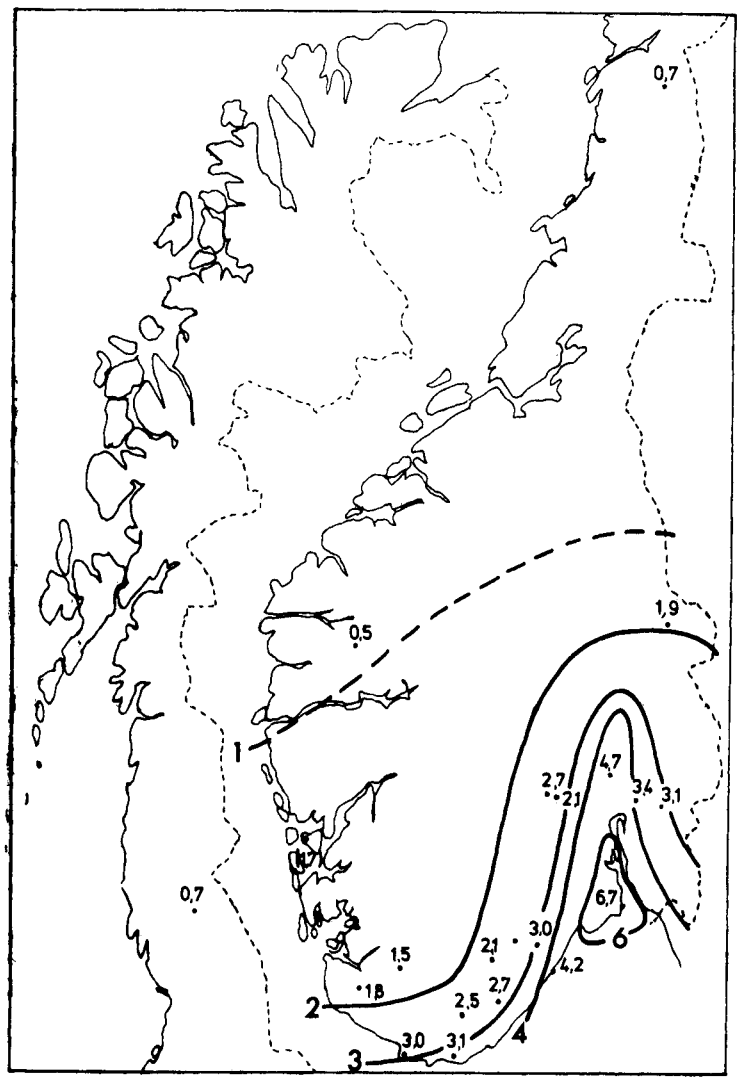

Figure 3. Mean weighted concentrations of sulphate in precipitation. July - December 1972. Unit: mg SO_4/ℓ.

deposition by precipitation.

Aerosol sulphate is generally associated with ammonium, but there is sometimes a considerable proportion of ammonium hydrogen sulphate or sulphuric acid aerosol. Ammonium and sulphate usually makes up 30-50% of the aerosol mass. In precipitation nitrate is also an important constituent, and the acidity is generally well described by the sum of nitrate and sulphate equivalents minus ammonium. Weighted mean concentrations in precipitation for one year is given in Table I, and mean concentrations of watersoluble precipitation and aerosol

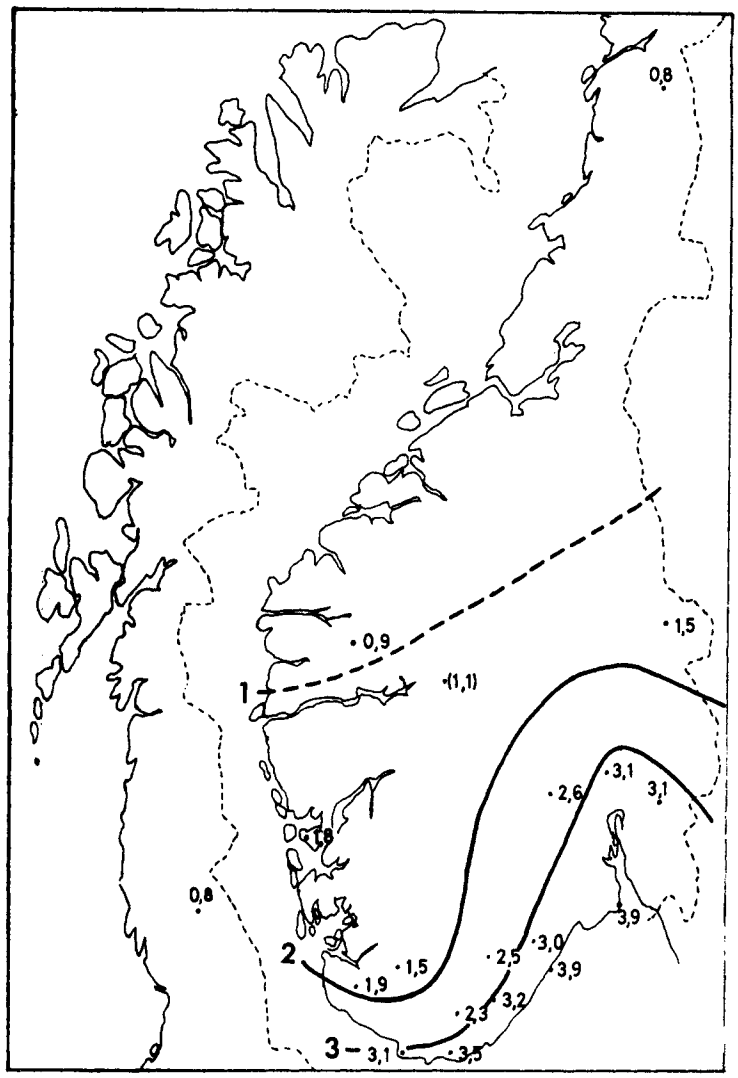

Figure 4. Mean weighted concentrations of sulphate in precipitation. January - December 1973. Unit: mg SO_4/ℓ.

constituents for a three-month period in 1973 are given in Figure 7. An episode with highly acid aerosol was observed in the period 23rd to 31st May 1973, concurrently with similar observations in Sweden (Brosset et al., 1975).

One of the objectives of the precipitation network is to provide input data for effect studies. An example of the impact of precipitation on freshwater chemistry is given in Table II, which summarizes calculated deposition and runoff in one of the rivers in Southern

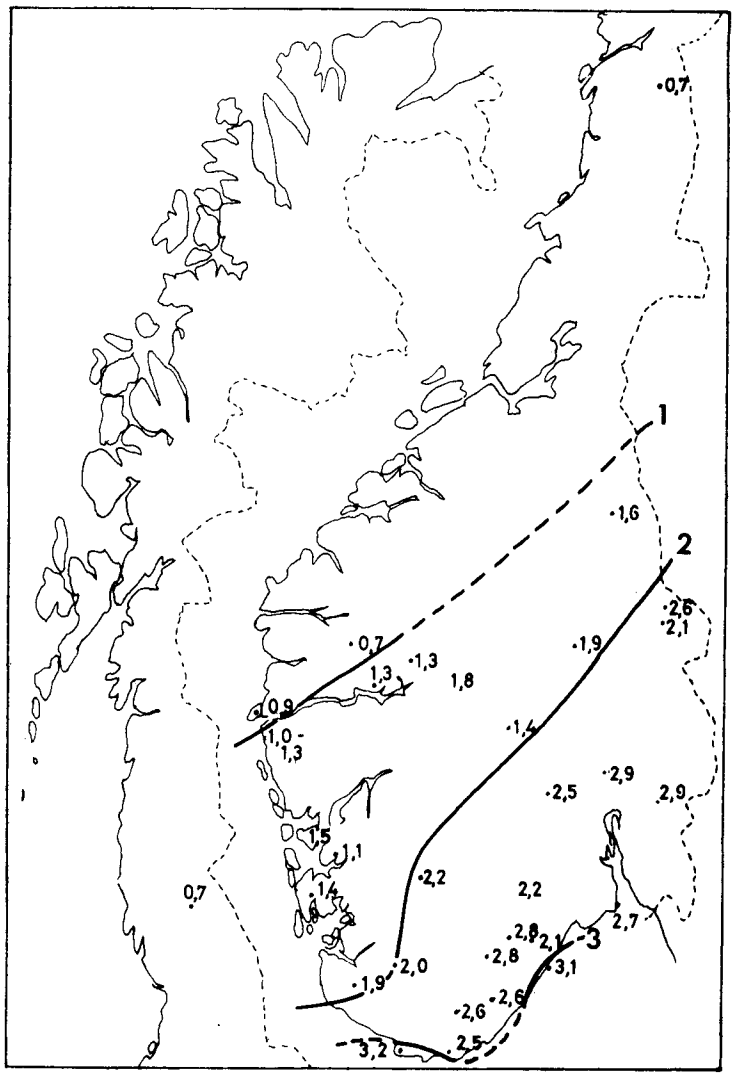

Figure 5. Mean weighted concentrations of sulphate in precipitation. July - September 1974. Unit: mg SO_4/ℓ.

Norway for 3 hydrological years. Both nitrate and ammonium concentrations in the river water are much lower than in precipitation, presumably because of biological fixation. Sulphate is therefore the main anion species in the river water and the runoff can be estimated by the runoff of hydrogen ions and total hardness. It is seen from the table that this runoff corresponds well with the sulphate precipitation. The 20% excess runoff can readily be explained as due to dry deposition and precipitation collection efficiency.

Table I.

Major precipitation events and weighted mean concentrations in precipitation at Birkenes in 1974.

Date	Precip. mm	H^+ µeq/l	NH_4-N mg/l	Ca mg/l	NO_3-N mg/l	SO_4 mg/l	SO_4 mg/m^2	% of total
741019	68,1	113	0,95	0,17	0,91	5,0	339	6,53
741018	36,6	42	0,21	0,09	0,20	4,6	169	8,55
741124	34,7	105	0,92	0,21	0,89	4,8	167	11,77
740107	29,8	91	1,61	0,40	1,30	5,6	166	14,99
741119	15,3	239	0,20	0,06	0,38	10,8	164	18,15
740902	37,4	50	0,63	0,43	0,41	3,9	147	20,98
740916	21,5	107	1,00	0,43	0,88	6,8	146	23,79
740108	29,0	96	0,86	0,08	0,58	4,7	136	26,41
740303	13,1	109	2,35	0,88	1,80	9,2	120	28,72
740205	30,9	74	0,60	0,14	0,74	3,4	106	30,76
741108	15,3	123	1,55	0,21	1,30	6,5	100	32,69
740113	35,3	55	0,49	0,14	0,47	2,8	100	34,62
740826	6,6	152	-	1,27	-	15,3	98	36,51
740109	13,4	84	2,10	0,45	1,19	7,2	96	38,36
740110	22,0	29	1,00	1,06	1,15	4,1	91	40,11
740302	8,3	110	2,50	1,98	2,30	11,0	91	41,86
741114	39,6	47	0,46	0,17	0,35	2,2	88	43,56
740907	46,2	31	0,25	0,17	0,23	1,9	87	45,24
740111	30,2	14	0,71	0,09	0,35	2,8	85	46,88
740216	8,1	248	1,00	0,22	1,45	10,2	83	48,48

Mean weighted concentrations

	H^+	NH_4-N	Ca	NO_3-N	SO_4
mg/l	-	0,52	0,21	0,50	3,24
µeq/l	59	37	11	35	69

Total precipitation (1974): 1562,7 mm

The sulphate concentrations in the 155 lakes sampled in connection with the SNSF regional lake survey also reflect the main structure of the precipitation sulphate concentrations in Figures 3-5

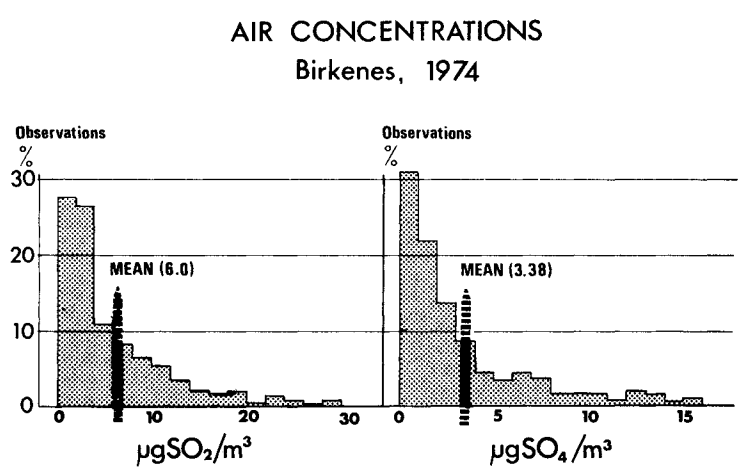

Figure 6. Frequency distribution of daily mean concentrations of sulphur dioxide and sulphate in air. Birkenes 1974.

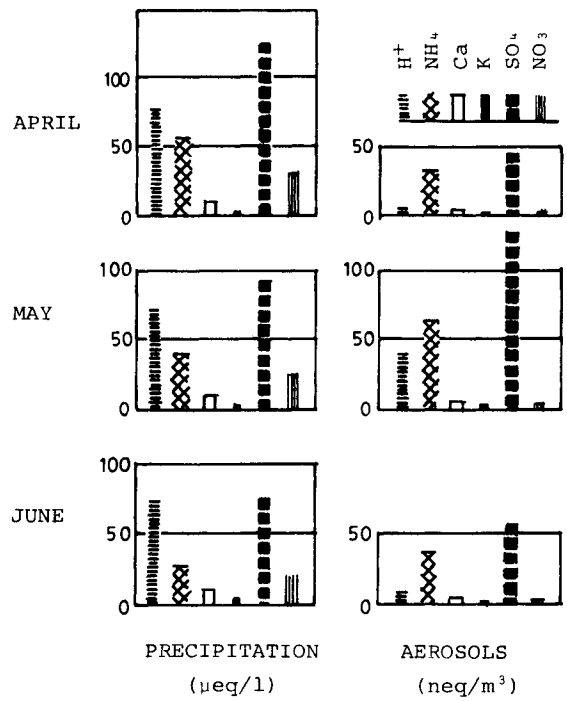

Figure 7. Mean concentrations of watersoluble constituents in air and precipitation at Birkenes in southern Norway. May - June 1973.

Table II.

Precipitation and deposition of sulphate with precipitation in the River Tovdal watershed, compared with river runoff for 3 hydrological years, September 1971 - August 1974.

PRECIPITATION		RUNOFF			
Water ($m^3 \times 10^{-6}$)	SO_4^{--} (equivalents $\times 10^{-6}$)	Water ($m^3 \times 10^{-6}$)	H^+ ($eq.10^{-6}$)	ΣMe^+ ($eq.10^{-6}$)	Total ($eq.10^{-6}$)
2083	150	1731	24	174	198
1864	115	1260	17	120	137
1620	112	1221	18	135	153

(Wright et al., 1975). Slightly higher concentrations are found in southeastern parts where evaporation is more important in relation to the annual precipitation. Also the contribution by dry deposition may be more important in this region.

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THE USE OF ARL TRAJECTORIES FOR THE EVALUATION OF PRECIPITATION CHEMISTRY DATA

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JAMES N. GALLOWAY, Section of Ecology and Systematics, Cornell University, Ithaca, New York 14853.
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ABSTRACT

One of the major problems in interpreting precipitation chemistry data is determining the possible source areas of the materials found in the precipitation. To investigate this problem, the trajectory program developed at Air Resources Laboratories (NOAA) was used to compute five-day backward air trajectories from Ithaca, New York (1).

Two types of precipitation collections were made at Ithaca, New York, during the period of study (August 1974 to January 1975). These were weekly composite samples and samples taken on an individual event basis. In the first case, we conclude that trajectories are not useful to investigate source areas for materials in composite precipitation chemistry samples because of the many trajectories that represent the air movements over a given week. This result suggests that a monitoring network would require some sampling of individual events to evaluate source areas of acid precipitation.

The trajectory program also was used to investigate individual event cases during the period. Unfortunately, there was not enough data to make a definitive conclusion. As more chemical data on individual events become available, it is hoped that a pattern of sources can be established for Ithaca.

We feel that the trajectory technique has great potential in evaluating the source areas for chemical components in precipitation.

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SULFUR BALANCE IN POWER PLANT PLUMES: A CRITICAL REVIEW

WILLIAM E. WILSON, United States Environmental Protection Agency.

ABSTRACT

Numerous attempts have been made to measure the rate of loss of SO_2 in power plant plumes. If SO_2 decreases more rapidly than an inert pollutant, the control measures necessary to meet SO_2 standards would be eased. More recently, Swedish studies of acid rain, thought to be due to long range transport of sulfuric acid, and U.S. correlations of sulfate loading with health effects, have led to efforts to determine sulfate formation and transport. However, most of the efforts to date indicate very little SO_2 conversion and do not support a significant role for power plant SO_2 in the production of acid precipitation. Careful analysis of these studies, in light of present day knowledge, indicates that they all have serious flaws which render their results useless. An "ideal" plume experiment will be described and the scientific tools, both experimental and theoretical, which are required for the job will be defined. EPA programs to provide these tools will be discussed. The tools include: improved analytical techniques for SO_2, particulate sulfate and particulate mass, aerosol size distribution from which aerosol volume can be calculated, light scattering, microscopic techniques for analysis of airborne particles, dry deposition measurements for SO_2, and development of models to be used in data analysis including meteorological models, homogeneous chemical kinetic models, and heterogeneous chemical kinetic models. A new EPA study of sulfur balance in power plant plumes, project MISTT, Midwest Interstate Sulfur Transport and Transformation, performed by an interdisciplinary group of contractors and university grantees will be described. Preliminary results from this program will be discussed. These results will be interpreted in an explanation of how tall stacks, by increasing the time available for SO_2 to be converted to sulfate before SO_2 is removed by dry deposition, increase sulfate formation, long range transport and acid precipitation.

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THE EFFECT OF PRECIPITATION COLLECTOR DESIGN ON THE MEASURED ACID CONTENT OF PRECIPITATION

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ABSTRACT

In order to evaluate the effect of different types of collectors on the measured chemical constituents of monthly precipitation collections, an array of fourteen precipitation samplers of five different designs has been in operation at Woodbridge, Ontario since March 1974. The collectors are located in an open field near the city of Toronto in an area of approximately 325 square meters, and it is anticipated that the chemical constituents of the precipitation would be uniform across the array for monthly sample collections.

Of the five different collector designs, three have automatic covers which are only open during precipitation events, whereas the other two are open to the atmosphere for the entire precipitation collection period. As expected, dry deposition markedly effects the concentration of the chemical constituents in precipitation. Significant errors can also arise from evaporation losses as has been shown in separate evaporation tests.

The measured acid content of precipitation collected at the six Canadian WMO regional collection stations are discussed in view of the sampler evaluation program. Further analyses of the acidity of Canadian precipitation, collected during field studies in urban and industrial regions, are also presented.

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CALIBRATION OF COLLECTION PROCEDURES FOR THE DETERMINATION OF PRECIPITATION CHEMISTRY[1]

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ABSTRACT

Precipitation is currently collected by several methods, including several different designs of collection apparatus. We are investigating these differing methods and designs to determine which gives the most representative sample of precipitation for the analysis of some 25 chemical parameters. The experimental site, located in Ithaca, New York, has 22 collectors of 10 different designs. The designs include bulk (wet and dry deposition collected together), wet only (only rain and snow) and wet/dry (collects wet and dry deposition separately). In every sampling period, which varies from one day to one month, depending on the time variable being tested, the following chemical parameters are determined: conductivity, pH, Ca, Mg, Na, K, NH_4, NO_3, N_{total}, SiO_4, PO_4, P_{total}, Cl, SO_4, DOC, Zn, Cu, Mn, Fe, Al, Ni, Cd, Pb, Ag, DDT, DDE, Dieldrin and PCB's.

The results of the investigation lead us to conclude that:

1. Precipitation samples must exclude dry deposition if accurate information on the chemical content of precipitation is required.
2. Substantial contamination results when glass and plastic collectors are used to sample precipitation for inorganic and organic components, respectively.
3. The inorganic components of precipitation samples of low pH (3.5-4.5), with the exception of PO_4 and Cl, exhibited no significant change in concentration when stored at 4 C for a period of eight months. We believe this is due to the stabilizing influence of a large concentration of hydrogen ions.
4. If quantitative information on the chemical composition is required, precipitation samples should be collected at no longer than weekly intervals if immediate collection is not possible.

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[1]This study was funded by the National Oceanic and Atmospheric Administration.

I. INTRODUCTION

The current studies of precipitation chemistry underway in the United States include precipitation networks operated by the U.S. Geological Survey and the Environmental Protection Agency. Unfortunately, a wide variety of collection procedures, sampling devices and analytical procedures are utilized in these studies. This problem of diversity of techiques also applies to historical investigations of precipitation chemistry (MacIntire and Young 1923, Wilson 1926, Collison and Mensching 1932, Leland 1952, Carroll 1962, Gambell and Fisher 1966, Lodge et al. 1968, Pearson and Fisher 1971, Likens 1972, Likens and Bormann 1974). Because of the importance of establishing reliable benchmark data and evaluating trends in the composition of precipitation, some calibration of current data-collection procedures is urgently needed. This paper describes an investigation of the calibration of collection procedures for the determination of precipitation chemistry.

The major problems in attempting to characterize the chemical composition of precipitation are related to the collection and storage of samples, rather than analytical difficulties. These problems include (1) the effect of the design of the collector in obtaining a representative sample of precipitation and its chemical content; (2) geochemical or biological changes occurring within the container once the sample has been collected, as related to the presence of foreign particles in the samples or on a filtering apparatus through which the precipitation passes; (3) effect of storage, including *in situ* collection time, on chemical composition; (4) leaching or absorption of substances from or to collector surfaces; and (5) effects of sampling interval, both during intra- and inter-storm periods.

II. PROCEDURES

A. COLLECTOR LOCATION

Twenty-two precipitation collectors (ten different designs) were used in the calibration investigations. A listing of the collectors is presented in Table I. The collectors were positioned randomly in an enclosure near the Department of Commerce (NOAA) Climatological Data Network Station at the Cornell University Game Farm in Ithaca, New York. Climatological data from the weather station was used to determine the amount of precipitation and the wind direction at the intercalibration site. In addition, a long history of precipitation chemistry for the area, dating to 1918, was available.

The intercalibration site became operational on 1 August 1974. This report covers the period from 1 August 1974 to 1 May 1975.

TABLE I

Collector	N	Type	Manufacturer	Container Material
Hubbard Brook Rain (HB)	6	Bulk*	Hubbard Brook Project	plastic
Hubbard Brook Snow (SN)	3	Bulk	Hubbard Brook Project	plastic
Bulk Glass (BG)	3	Bulk	this laboratory	glass
Misco (MS)	3	Wet**	Misco Scientific	plastic
Wong (WOG)	2	Wet	Wong Scientific	plastic
Swiss (ERN)	1	Wet	ERNI and Company	stainless steel
Finnish (FIN)	1	Wet/Dry†	Parelco Oy, Finland	plastic
USAEC (AEC)	1	Wet/Dry	U.S. Atomic Energy Commission	plastic
ISWS (GEM)	1	Wet/Dry	Illinois State Water Survey	plastic
Swedish (ING)	1	Wet/Dry	Lennart Granat, Sweden	glass

* A BULK collector is open to the atmosphere at all times and collects both wet and dry deposition.

** A WET collector is a powered collector open to the atmosphere only when it rains or snows.

† A WET/DRY collector is a powered collector that samples precipitation and dry deposition in separate containers.

Each precipitation sample was analyzed for Ca, Mg, K, Na, NH_4, H, SO_4, NO_3, Cl, PO_4, SiO_4, conductivity and DOC, while in selected samples PCB, DDT, DDE, Dieldrin, Aldrin, Zn, Cu, Cd, Ni, Ag, Fe, Mn and Al were determined. In this report only the first group of chemical compounds will be discussed.

B. ANALYTICAL

The analyses for Ca, Mg, K and Na were performed on a Perkin-Elmer Model 403 atomic absorption spectrophotometer. Appropriate amounts of lanthanum and HCl were added to subsamples to avoid interferences with the Ca and Mg determinations. Hydrogen ion concentration was determined with a pH meter. Standard procedures adapted and automated for use with a Technicon Autoanalyzer were used for analysis of NH_4, NO_3, SO_4, PO_4, Cl, and SiO_4. NH_4 was determined by an alkaline phenolhypochlorite method (Solorzano 1969), NO_3 by hydrazine reduction (Kamphake et al. 1967), SO_4 by colormetric measurement of barium-thymol blue complex (Lazrus et al. 1968), Cl by the liberation of thiocyanate ion from mercuric thiocyanate in the presence of ferric iron (O'Brien 1962) and dissolved SiO_4 by reduction of silicomolybdate to heteropoly blue with aminonaphtholsulfonic acid (American Public Health Association 1965). Soluble reactive phosphate was determined from a molybdenum blue complex after reduction with ascorbic acid in the presence of a small amount of antimony (Murphy and Riley 1962).

All collection containers were acid washed after each sampling. The plastic containers were washed with 6N HCl and rinsed with deionized water. The glass containers were washed with chromic acid and rinsed with double distilled water. Samples were stored at 4 C until time of analysis.

III. RESULTS AND DISCUSSION

A. COLLECTOR RELIABILITY

The effect of collector design on the collection efficiency of precipitation is presented below together with the mechanical and structural problems associated with each collector type.

1. Bulk Collectors

Hubbard Brook Rain Collector (HB) - Bulk

This collector is composed of a plastic funnel attached to a plastic bottle by a length of plastic tubing. An additional bottle, which acts as a vapor trap, and a loop in the plastic tubing prevent evaporative losses from occurring. The only source of difficulty experienced with this design was that the clamps holding the components to the supporting stand had a tendency to become loose, thus affecting the collection efficiency when the funnel tilted.

Hubbard Brook Snow Collector (SN) - Bulk

This collector is a large plastic garbage can that is secured to a wooden post such that the collector opening is five feet from the ground. This is an excellent collector for snow samples as it collects large amounts of precipitation due to the large opening of the collector.

Glass Collector (BG) - Bulk

Aside from the contamination problem resulting from the glass (Section III-B), there are no obvious design problems except that the sample in this open collector is subject to evaporation. However, the glass contamination makes this collector unsuitable for most all chemical parameters except pesticides, PCB's and other organics and a few inorganic species.

2. Automated Collectors

The potential problems associated with automated collectors are much greater than those associated with bulk collectors. For proper sampling the collector motor, sensor and thermostat must all be operating perfectly. It is clear that if a collector is not mechanically reliable for extended periods in the field, then it is of little use in the collection of precipitation. The following description of the automated collectors tested in this investigation relies heavily on mechanical integrity.

Misco Collector (MS) - Wet

The Misco collectors have a sliding lid that uncovers the collection vessel during precipitation. Of the three Misco collectors, only one operated satisfactorily, while the other two worked about fifty percent of the time in both rain and snow collection (Tables IIA and IIB). The primary problem with this collector was that the motors

TABLE IIA

RELIABILITY OF AUTOMATIC COLLECTOR IN SUMMER AND FALL 1974*

Collector	MS1	MS2	MS3	FIN	AEC	GEM	ERN	WOG	ING
1 Aug- 8 Aug	o	o	-	o	o	-	x	-	-
9 Aug-15 Aug	o	o	-	o	o	-	x	-	-
16 Aug-22 Aug	o	o	-	o	o	-	x	-	-
23 Aug-29 Aug	o	x	-	o	o	-	x	-	-
30 Aug- 5 Sep	o	x	-	x	o	-	x	-	-
6 Sep-12 Sep	o	x	-	x	o	-	x	-	x
13 Sep-19 Sep	o	x	-	x	o	-	x	-	x
20 Sep-26 Sep	o	x	-	x	o	-	x	-	x
27 Sep- 3 Oct	o	x	o	x	o	-	o	-	x
4 Oct-10 Oct	o	o	x	o	o	-	x	-	x
11 Oct-17 Oct	o	o	x	o	o	-	x	-	x
18 Oct-24 Oct	o	o	x	o	o	o	x	o	x
25 Oct-31 Oct	o	x	o	o	o	o	x	x	x
1 Nov- 7 Nov	o	x	o	o	o	o	x	x	x
8 Nov-14 Nov	o	x	o	o	o	o	x	o	o

* o = collector functioning at beginning of week

x = collector not functioning at beginning of week

\- = collector not available

failed. Counting the three original motors, a total of six motors have been used to keep these collectors operating. For the field operator, this is a very expensive situation, in both money and time.

In addition, on the rare occasion when all three collectors were operating simultaneously and when all three sensing adjustments were set at their most sensitive position, the three collectors collected different amounts of precipitation. In winter substantial amounts of time were spent on maintaining the thermostats and heating elements in the sensing units. Undoubtedly, part of the variation in collection efficiency (Table IV) between the different Misco collectors was a result of thermostat malfunction

This collector has a very bad splash problem, i.e., the collection vessel sits below the metal rim of the collector and the sliding cover is adjacent and above the collection vessel. In addition, the area of the opening is too small (0.0143 m^2) to collect ample precipitation for complete chemical analysis unless the storm is large (>2 cm of rain).

TABLE IIB

RELIABILITY OF AUTOMATIC COLLECTOR IN WINTER AND SPRING 1974-1975*

Collector	MS1	MS2	MS3	FIN	AEC	GEM	ERN	WOG	ING
6 Dec-12 Dec	o	x	o	o	o	o	x	x	o
13 Dec-19 Dec	o	x	o	o	o	o	x	x	o
20 Dec-26 Dec	o	x	o	o	o	x	x	x	o
27 Dec- 2 Jan	o	x	o	o	o	x	x	x	o
3 Jan- 9 Jan	o	x	x	o	o	x	x	x	o
10 Jan-16 Jan	o	x	x	o	o	x	x	x	o
17 Jan-23 Jan	o	o	o	x	o	x	x	x	o
24 Jan-30 Jan	o	o	o	x	o	x	x	x	o
31 Jan- 6 Feb	o	x	o	x	o	x	x	x	o
7 Feb-13 Feb	o	x	o	o	x	o	x	o	x
14 Feb-20 Feb	o	x	o	o	x	o	x	o	x
21 Feb-27 Feb	o	x	o	o	x	o	x	o	x
28 Feb- 6 Mar	o	o	x	x	x	o	x	x	x
7 Mar-13 Mar	o	o	x	x	x	o	x	x	x
14 Mar-20 Mar	o	o	x	x	x	o	x	x	x
21 Mar-27 Mar	o	o	x	x	x	o	x	x	x
28 Mar- 3 Apr	o	o	x	x	x	o	x	x	x
4 Apr-10 Apr	o	o	x	x	x	o	x	x	x
11 Apr-17 Apr	o	o	x	x	o	x	x	x	x
18 Apr-24 Apr	o	o	x	x	o	x	x	x	x
25 Apr- 1 May	o	o	x	o	o	x	x	o	x

* o = collector functioning at beginning of week

x = collector not functioning at beginning of week

TABLE III

THE EFFECT OF A GLASS COLLECTOR ON PRECIPITATION CHEMISTRY *

Sample period	H	Ca	Mg	Na	K	NH_4	NO_3	PO_4	Cl	SO_4
9 Aug-17 Aug 74	0.85	0.48	0.49	3.0	2.3	1.3	1.2	1.5	1.3	0.98
18 Aug-24 Aug 74	0.76	1.2	1.2	1.8	2.4	1.1	1.0	1.5	-	0.93
4 Aug-28 Oct 74	-	1.2	1.5	4.6	3.0	-	2.0	-	-	-
29 Aug- 5 Nov 74	-	0.74	0.90	2.2	1.1	-	1.0	1.4	-	-
5 Nov-13 Nov 74	-	1.3	1.0	2.0	1.9	-	1.1	1.2	-	-
29 Oct-13 Nov 74	0.79	0.69	0.73	1.0	1.0	-	-	-	-	-
13 Nov-25 Nov 74	1.0	0.60	0.69	1.5	2.3	-	-	-	1.6	1.0
Mean ± Std. Error	0.85±.05	0.88±.13	0.93±.13	2.3±.4	2.0±.3	-	1.3±.2	1.4±.1	-	0.97±.02

* The table values represent the following ratio:

$$R = \frac{\text{Mean of concentration in bulk glass collector (N=1)}}{\text{Mean of concentration in bulk plastic collector (N=6)}}$$

At R=1, glass and plastic collectors have no or identical effect on sample chmistry

At R>1, glass collector contaminated sample or plastic collector adsorbed element from sample

At R<1, plastic collector either contaminated sample or glass collector adsorbed element from sample

TABLE IV

MEAN COLLECTION EFFICIENCY (percent) AS
A FUNCTION OF COLLECTOR TYPE & PRECIPITATION TYPE

	Rain	Snow
HB	90	--
SN	--	74
MS1	88	69
MS2	85	52
FIN	81	85
AEC	84	86
ING	--	73
WOG	82	--
GEM	--	76

Wong Collector (WOG)

Mechanically this collector worked relatively well; it suffered from an initial handicap in that it was not a new instrument as were the other collectors that we tested. The major maintenance problem we had with the collector was with the sensing unit; it corroded very quickly and thus the sensitivity to precipitation varied with time.

This collector has a large amount of metal area that precipitation can splash off of into the collector. This is especially true in the winter when a sloping roof is placed on the sliding cover to prevent snow accumulation. In addition, there is a gap between the sliding lid and the collection vessel, allowing dry deposition to contaminate the rain or snow sample.

ERNI Collector

A wet only collector, the ERNI has the best designed covering system of any of the automatic collectors. When the collector is open, the lid is entirely removed from the sampling orifice. There is little possibility of splash occurring. However, since the original collector we received has not functioned consistently because of electronic problems, further comparisons with other designs are not possible.

Finnish Collector (FIN)

Despite the poor record of performance for the FIN collector (Tables IIA and IIB), this has been one of the most mechanically reliable collectors. The primary problem is that the manfacturer is in Finland, and therefore replacement parts may take a long time to arrive. This collector is rugged, well suited for field work and, as will be

illustrated in the following section, collects reliable samples of precipitation for most chemical parameters.

U.S. Atomic Energy Commission Collector (AEC)

This collector has been the most reliable of all the automatic collectors. Both the design and the construction of the collector are well suited for collection of wet and dry deposition in the field. The construction is rugged, which is of importance in the winter when ice and snow can accumulate on the collector. The sample containers have large openings (.0683 m^2), enabling one to collect 0.175 ℓ of precipitation with 0.25 cm of rainfall. This is four times the volume that our smallest collector (Misco) would collect with an equivalent amount of precipitation. There exists the possibility of contamination from splash due to the large lid that covers the collection vessels.

Illinois State Water Survey Collector (GEM)

This collector is built from the blueprints of the AEC collector with the exception that it is poorly constructed, which results in severe and rapid deterioration of the gears in the drive unit. We have used three sets of gears in six months. This illustrates very well the importance of constructing a strong collector for use in the field.

Granat Collector, Sweden (ING)

This collector was lent to us by Dr. Lennart Granat, University of Stockholm, Sweden. This is the most intricate collector that we have, and is a finely tooled and machined instrument. Unfortunately, its tolerances for routine field collection of precipitation are too fine. It does not withstand abuse, and is awkward to transport. At its best it collects samples just as well as the other collectors, but it is subject to too many small aberrations that compromise the integrity of the precipitation sample. However, of all the wet/dry collectors, this one has the best design to prevent splash problems; the two collection vessels are far apart without any large expanse of metal between them. There may be some problem from the brass lid, but this has not been evaluated.

B. MATERIALS

The materials primarily used in the construction of the collection vessels are plastic (polyethylene) and glass (pyrex). The project has sixteen plastic collectors and five glass collectors. The comparison between samples collected in the bulk plastic (N = 6) and the bulk glass (N = 1) is given in Table III. The values are ratios of the mean of concentration for the bulk glass divided by the mean of the

concentration for the bulk plastic. The ratios indicate the following:

ratio = 1, no, or similar, contamination or adsorption from either collector

ratio > 1, contamination from the glass collector or adsorption by the plastic collector

ratio < 1, contamination from the plastic collector or adsorption by the glass collector

It is obvious that the glass collector seriously contaminates a precipitation sample with respect to Na, K and PO_4. It also appears that a sample collected in glass may be contaminated with Cl, although there are only two sampling events. Glass has a much more active surface than plastic; therefore, ratios that are less than one may be explained by adsorption of the chemical species on the glass surface. This is certainly possible for hydrogen.

C. EFFICIENCY OF PRECIPITATION COLLECTION

The mean efficiency of collection of rain and snow is presented in Table IV. This is defined as the volume collected, multiplied by 100, divided by the volume expected as determined by the weather station. As is evident the bulk collectors and the Misco collectors have lower sampling efficiencies in the winter. For the Misco collectors the malfunctioning of the thermostat causes the poor efficiency. The lower collection efficiency of the Hubbard Brook snow collector (SN) is due to the effect of blown snow and wind turbulence. The FIN and AEC have about identical collection efficiencies for rain and snow.

D. PRECIPITATION CHEMISTRY REPLICABILITY AS A FUNCTION OF COLLECTOR TYPE

Operationally the collectors are divided into the following functional groups.

Bulk plastic: collects bulk precipitation with plastic containers (HB, SN).

Wet plastic: collects wet precipitation with plastic containers (AEC, MS, FIN and GEM).

Dry plastic: collects dry precipitation with plastic containers (AEC, FIN and GEM).

The chemical replicability data for the above classes of collectors are presented in Table V. The values in the table represent the stand-

TABLE V

MEAN PERCENT ERROR+ IN CHEMICAL ANALYSIS OF PRECIPITATION AS A FUNCTION OF COLLECTOR TYPE AND PRECIPITATION TYPE

Collector Type	N	Volume	H	Ca	Mg	Na	K	NH_4	NO_3	PO_4	Cl	SO_4
Bulk Plastic* (rain)	6	3.2	5.2	4.8	7.0	7.1	12	4.4	2.6	25	19	3.8
Bulk Plastic** (snow)	3	1.9	4.7	2.8	3.0	4.7	6.8	1.5	2.1	17	13	2.4
Wet Plastic* (rain)	6	-	8.4	17	34	16	20	21	5.8	32	20	6.4
Wet Plastic** (snow)	6	-	8.6	25	28	28	12	12	10	20	28	11
Wet Plastic** (snow) (except Misco)	3	-	5.9	22	14	19	9.3	4.8	5.2	15	27	5.8

* average of 8 sampling events

** average of 7 sampling events

+ For each sampling event, an elemental mean and standard error was determined for all collectors of the same type (bulk or wet plastic). The standard error, divided by the mean and multiplied by 100 was defined as PERCENT ERROR. The MEAN PERCENT ERROR tabulated here is the mean of the PERCENT ERRORS for all sampling events.

ard error, multiplied by 100 and divided by the mean for each chemical species per storm. Then all the storm events were summed and a "mean" percent error was determined. These values give an indication of the percent error in determining a chemical species when N samplers of the same design are used.

For the bulk plastic collectors it is evident that except for PO_4, Cl and K the error is less than ten percent in both the rain and snow collectors. This implies that the bulk plastic samplers collect identical samples, and that the sample does not vary in chemical composition while in the collector. The percent error is generally lower in the bulk snow collectors, presumably because of the lower amount of biological activity in the winter.

The percent errors are larger in the wet plastic collectors than the bulk plastic. The wet plastic collectors are all of different designs and construction materials, unlike the bulk plastic which were of identical design and construction. In addition, the bulk plastic collectors were completely cleaned after every sampling event, while in the wet plastic collectors only the actual collection vessel was cleaned and the metal superstructure of the sampler was not. Thus a burden of dust and impacted aerosols could accumulate on the metal superstructure and possibly contaminate future samples by splash. In addition, it appears that the Misco collectors contribute significantly to

the large error values. Comparing the wet plastic (snow) numbers, which represent all of the wet plastic collectors, with the wet plastic (snow, except Misco) numbers, which represent all the percent errors decrease in the latter instance, often by a factor of two. It appears that the most conservative chemical parameters are H, NO_3 and SO_4 in both the rain and snow samples.

E. EFFECT OF SAMPLING INTERVAL ON PRECIPITATION CHEMISTRY

At the beginning of the sampling period two bulk collectors (SN) were placed at the site; one was sampled and replaced after every storm and the other was sampled after three storms. The amounts of each element in the three samples from the first collector were totalled and compared to the composite sample of the three storms in the second collector. The results are presented in Table VI as ratios (total in

TABLE VI

EFFECT OF SAMPLING TIME ON PRECIPITATION CHEMISTRY*

Sampling Period	Volume	H	Ca	Mg	Na	K	NH_4	NO_3	PO_4	Cl	SO_4
31 Dec 74-17 Jan 75	1.8	1.4	1.2	.98	.95	1.1	1.6	1.2	-	1.3	1.2
17 Jan- 7 Feb 75	.99	.80	1.0	.68	1.2	1.0	2.8	1.0	1.2	1.1	.76
7 Feb-27 Feb 75	.99	.86	.93	1.5	2.7	.98	1.0	.93	.82	1.5	.92
27 Feb-21 Mar 75	1.1	.94	.87	.85	.87	1.0	.93	1.1	.64	1.0	.70
21 Mar- 4 Apr 75	1.2	1.4	.95	.90	1.4	.98	1.1	1.1	1.0	1.3	.98

*The table values represent the following ratio:

$$R = \frac{\text{Sum of element amount in individually collected storms over a set period.}}{\text{Amount of element in a composite sample collected over same period.}}$$

At R=1, a three week sampling period had no adverse effect on the chemical composition.

At R>1, the three week sampling period resulted in a lower estimate of chemical composition then did the sampling by event for that period.

At R<1, the three week sampling period resulted in a larger estimate of chemical composition then did the sampling by event for that period.

individual storms/composite of sampling period).

Considering that the composite samples were in the field for a period of two to four weeks, the agreement between the sum of the individual events and the composite samples is good. A large degree of the agreement is undoubtedly caused by the low pH of the precipitation and the fact that the experiment was performed in the winter, when biological activity is at a minimum.

F. COLLECTION OF DRY DEPOSITION, BULK VS. WET/DRY COLLECTORS

It is of importance to know if the composition of a precipitation sample collected in a bulk sampler is identical to the sum of the compositions collected in a wet sampler and a dry sampler. Table VII

TABLE VII

A COMPARISON BETWEEN THE COMPOSITION OF PRECIPITATION AS DETERMINED BY A BULK COLLECTOR AND BY THE SUM OF A WET AND DRY COLLECTOR*

Event	Ca	Mg	Na	K	NH_4	NO_3	PO_4	Cl	SO_4
15 Sep 74-27 Sep 74	0.98	1.03	1.22	1.16	0.87	1.00	--	0.66	1.49
27 Sep 74- 4 Oct 74	1.09	1.19	0.81	1.16	0.68	0.84	0.65	0.84	1.48
4 Oct 74-28 Oct 74	1.01	1.09	1.25	1.20	0.95	1.10	--	0.95	1.42
13 Nov 74-25 Nov 74	0.92	0.86	1.01	1.44	1.00	0.99	1.43	0.96	1.14
6 Dec 74-18 Dec 74	0.99	0.84	1.15	1.29	1.13	0.97	0.94	1.56	1.04
18 Dec 74-31 Dec 74	0.79	0.67	0.99	1.24	1.54	1.10	0.74	1.09	1.05
31 Dec 74-17 Jan 75	1.03	1.40	1.09	1.21	--	--	--	1.29	1.71
7 Feb 75-27 Feb 75	1.41	1.19	1.14	1.10	0.95	0.91	0.54	0.73	1.08
Mean ± Std. Error	1.02±.06	1.04±.03	1.08±.05	1.22±.04	1.02±.10	0.99±.04	0.86±.16	1.01±.11	1.30±.09

*The table values represent the following ratio:

$$R = \frac{\text{AMOUNT IN WET COLLECTOR + AMOUNT IN DRY COLLECTOR}}{\text{AMOUNT IN BULK COLLECTOR}}$$

presents results of eight comparisons between wet/dry collectors and bulk collectors that sampled the same event. These data are presented as ratios, amount of element deposited per unit area by wet precipitation plus amount of element deposited per unit area by dry deposition, divided by the amount of element deposited per unit area by bulk precipitation. If the ratio equals one, it indicates that the bulk and the wet/dry collector sample dry deposition with equal efficiency. If the ratios are greater than one, it means that either the wet/dry collector is contaminating the sample or that the bulk collector is losing the sample. Conversely, if the ratio is less than one, the reverse is true; the bulk sampler is contaminating the sample or the wet/dry collector is losing the sample.

The comparisons are better than one would expect (Table VII). In fact, for NO_3 and to a lesser extent Mg and Ca (and in the winter, SO_4), the results are very close, indicating that the dry/wet totals are certainly comparable to the bulk samples (Table VII).

G. INFLUENCE OF DRY DEPOSITION ON PRECIPITATION CHEMISTRY

The previous section has discussed the reliability and efficiency of collecting dry deposition; this section discusses the influence of dry deposition on the chemical composition of rain and snow.

Dry deposition is defined as the material that is added to ecosystems through the atmosphere when it is not raining or snowing. The term is somewhat nebulous with several components, such as direct particle fallout, aerosol impaction onto foliage and gaseous adsorption by the ground or foliage. Our collection devices measure particle deposition by gravity and almost no impaction or gaseous inputs. They, therefore, are underestimates of the material added to ecosystems during periods of no rain or snow.

We use two methods to assess the importance of dry deposition on the chemistry of rain and snow collected in a bulk precipitation collector. The first is to compare, for the same period, the composition of the bulk sample (wet and dry deposition) to the composition of the wet only sample; this is of course dependent on the amount of rain that fell and the length of time the bulk sampler collected dry deposition. This technique of comparison of bulk vs. wet collection arrives at a value for dry deposition by difference. The second method is to make the actual measurements of wet and dry deposition separately.

Measurement of the Influence of Dry Deposition on Wet Precipitation by Difference

The ratio of the mean of the species concentration collected in a bulk sampler vs. the mean of the species concentration collected in a wet sampler is presented as a function of season (Table VIII). The August-November bulk samples were collected in the Hubbard Brook rain collectors. The December-March bulk samples were collected in the Hubbard Brook snow collector. The wet only collectors for both time periods were identical. The ratios indicate the following:

ratio > 1, species in question is a component in both wet and dry deposition.

ratio = 1, species in question is a component in wet only precipitation.

ratio < 1, species in question is affected in some way by the mixture of wet and dry deposition.

The results of the August-November collection period indicate that there is a substantial dry deposition influence on the chemistry of the bulk precipitation samples for Ca, Mg and PO_4. For K, NH_4, NO_3, SO_4 and perhaps Cl, there appears to be a negligible contribution from dry

TABLE VIII

A COMPARISON OF THE CHEMICAL COMPOSITION OF BULK VERSUS WET PRECIPITATION*

Event	H	Ca	Mg	Na	K	NH_4	NO_3	PO_4	Cl	SO_4
9 Aug 74-17 Aug 74	1.06	2.6	2.3	.62	.93	.53	.80	1.2	1.0	1.1
17 Aug 74-24 Aug 74	.95	.93	.95	.82	.82	.98	.98	1.3	-	1.1
1 Sep 74-13 Sep 74	.83	-	2.2	.74	1.2	.79	1.0	1.4	-	1.0
15 Sep 74-27 Sep 74	.88	2.0	1.7	1.1	1.5	1.2	.98	3.7	-	.86
27 Sep 74- 4 Oct 74	1.00	1.6	1.5	1.1	.93	1.4	1.1	2.0	.87	.95
4 Oct 74-28 Oct 74	.77	2.3	1.4	1.5	1.5	1.4	1.1	.80	1.4	.93
29 Oct 74-13 Nov 74	-	1.8	1.6	.9	.71	1.0	1.0	1.5	1.1	.92
13 Nov 74-25 Nov 74	.91	2.8	.90	2.7	1.4	1.4	1.3	1.3	2.6	1.1
6 Dec 74-18 Dec 74	.93	1.6	.88	1.7	1.0	1.4	1.2	1.1	1.5	1.1
Mean ± Std. Error	.92±.03	2.0±.2	1.5±.2	1.2±.2	1.1±.1	1.1±.1	1.1±.1	1.6±.3	1.4±.3	1.0±.0
18 Dec 74-31 Dec 74	1.3	7.6	2.8	5.3	2.6	3.9	2.3	2.6	2.5	2.3
31 Dec 74-17 Jan 75	1.2	4.4	4.8	5.7	2.8	2.3	2.3	2.5	3.6	1.5
17 Jan 75- 7 Feb 75	.66	4.7	3.5	4.7	2.9	1.7	2.1	1.6	2.8	1.8
7 Feb 75-27 Feb 75	1.3	2.8	1.8	2.3	1.4	1.8	1.5	2.2	2.0	1.4
27 Feb 75-21 Mar 75	.94	2.9	2.4	2.1	1.7	1.7	1.7	1.0	1.6	1.3
21 Mar 75- 4 Apr 75	1.1	-	4.1	4.7	2.0	1.9	1.8	1.4	4.9	1.6
Mean ± Std. Error	1.1±.1	4.5±.9	3.1±.5	4.1±.6	2.2±.3	2.2±.3	2.0±.1	1.9±.3	2.9±.5	1.6±.1

*The table values represent the following ratio:

$$R = \frac{\text{MEAN OF CONCENTRATION IN BULK PLASTIC COLLECTOR}}{\text{MEAN OF CONCENTRATION IN WET PLASTIC COLLECTOR}}$$

deposition. It is especially interesting that the ratio for hydrogen is less than one. This indicates that some of the acidity in the rain is being neutralized by the dry deposition component. In the December-March samples it is evident that all species, with the exception of H, have a large dry deposition component, which for some elements (Ca, Mg, and Na) completely dominates the chemistry of bulk precipitation samples.

Therefore, the influence of dry deposition on the composition of samples is much larger in the winter and affects all parameters measured, while in the summer and autumn it is only the terrestrial components (Ca, Mg and PO_4) that are affected.

Measurement of the Influence of Dry Deposition on Wet Precipitation by Actual Analysis

The second method of determination of the dry deposition influence on bulk precipitation samples is to measure it actually with a separate collection vessel. A summary of the second method and a comparison to a summary of the first method is presented in Table IX. It is evident

TABLE IX

THE INFLUENCE OF DRY DEPOSITION ON PRECIPITATION SAMPLES

	Ca	Mg	Na	K	NH_4	NO_3	PO_4	Cl	SO_4
				Rain Samples					
Bulk Rain/Wet	2.0± .2	1.5± .2	1.2±.2	1.1±.1	1.1± .1	1.1±.1	1.6±.3	1.4±.3	1.0±.1
Wet & Dry/Wet	3.2±1.7	3.5±1.8	2.4±.7	2.1±.5	1.7± .2	1.2±.1	1.5±.2	1.9±.7	1.4±.1
				Snow Samples					
Bulk Snow/Wet	4.5± .9	3.1± .5	4.1±.6	2.2±.3	2.2± .3	2.0±.1	1.9±.3	2.9±.5	1.6±.1
Wet & Dry/Wet	4.4±1.8	3.1± .4	4.0±.7	2.3±.5	3.0±1.6	1.6±.1	1.6±.1	1.6±.2	2.0±.6

that in December-March (snow samples) the agreement between the two methods is quite good; they both show that the dry deposition component contributes significantly to the composition of the bulk sample. For the August-November period (rain) the agreement is poor, especially for Ca, Mg and Na, which have large dry deposition components. The reason for the poor agreement in the August-November period as opposed to the good agreement in December-March is due to the design of the dry deposition collector. In the rain period, the bulk collector is a funnel/bottle apparatus arrangement and the individual dry deposition collector is an open-mouthed cylinder, two very different designs, while in the snow period, both the bulk and the wet/dry collectors are open-mouthed cylinders. It appears that the open-mouthed barrel collects dry deposition more efficiently than the shallow funnel, but it is not clear which of these collects the most representative sample of dry deposition. Two opposing arguments can be made for each type of collector. On one hand the funnel, because of its shallow nature, will lose dry deposition due to the scouring action of the wind. However, it also can be argued that the open-mouthed cylinders can act like a snow fence, and therefore collect more dry deposition than is representative. This problem will be investigated further in the second year of the project.

It is apparent that regardless of the type of bulk collector used, the collection of dry deposition with wet precipitation can severely affect the apparent chemical composition of the rain and snow, sometimes by factors of two to three. Therefore it is recommended that wet only collectors be used in any determination of precipitation chemistry.

H. EFFECTS OF STORAGE ON PRECIPITATION CHEMISTRY

The effect of storage on the chemical integrity of the precipitation sample has been studied in the following manner. Twelve liters of precipitation were well mixed and then divided into three equal fractions. The first fraction was put on a shelf in the laboratory at 21 C. The second aliquot was put in the refrigerator at 4 C. The third aliquot was subaliquoted into one hundred 30-cc bottles and frozen at -4 C. Aliquots of the three fractions have been analyzed for the different chemical species over the course of seven months (Table X).

TABLE X

EFFECTS OF STORAGE ON CHEMICAL COMPOSITION OF PRECIPITATION SAMPLES

	pH	Ca	Mg	Na	K	NH_4	NO_3	PO_4	Cl	SO_4
				A. Sample Stored at 21°C.						
Nov 1974	3.91	.40	.061	.063	.042	.37	2.15	.004	.43	4.2
Dec	-	.43	.061	-	-	.43	-	-	.91	3.9
Jan 1975	-	.38	.043	.065	.039	.42	2.20	.026	.92	4.0
Feb	4.03	-	-	-	-	-	-	-	-	-
Mar	-	.45	.061	.064	.043	.42	2.05	.030	.86	4.2
Apr	-	.42	.063	.064	.035	.38	-	-	1.28	3.9
				B. Sample Stored at 4°C.						
Nov 1974	4.03	.42	.063	.065	.039	.38	2.20	.004	.44	4.5
Dec	-	.42	.064	-	-	.43	-	-	.94	4.0
Jan 1975	-	.38	.042	.065	.039	.43	2.20	.018	.97	3.8
Feb	4.06	-	-	-	-	-	-	-	-	-
Mar	-	.44	.061	.064	.040	.38	2.15	.019	.92	4.0
Apr	-	.42	.064	.064	.037	.38	-	-	.98	4.0
				C. Sample Stored at -4°C.						
Nov 1974	4.03	.42	.061	-	.045	.40	2.15	.025	.57	4.0
Dec	-	.45	.084	-	-	.46	-	-	1.42	3.9
Jan 1975	-	.38	.043	-	.038	.42	2.10	.046	1.15	3.7
Feb	4.03	-	-	-	-	-	-	-	-	-
Mar	-	.42	.063	.064	.043	.40	2.30	.0065	.97	4.2
Apr	-	.42	.061	.062	.036	.41	-	-	1.33	3.9

There are two questions to answer:

1. Is there a change in the chemical composition, as a function of time, at a constant temperature?

2. Is there an optimum temperature at which to store samples until the time of chemical analysis?

We have found that with the exception of PO_4 and Cl, all chemical parameters showed negligible change when stored for seven months at 21, 4 and -4 C. We believe that this is due to the low pH of the solution inhibiting biological growth and losses to the walls by adsorption. In the case of phosphorus the diversity of concentrations is an excellent example of the pitfalls in the analytical chemistry of phosphorus at low concentrations. There are two primary reasons for the diversity of concentration encountered. First, when plastic containers are used, as they were in this case, there can be substantial losses to the walls by adsorption (Annet and D'Itri 1973). Secondly, only molybdate-reactive phosphorus was analyzed, and due to the lability of phosphorus the amount in the molybdate-reactive reservoir changes with time.

The variability of chloride is not as readily explained. There was an increase in the chloride concentration by about a factor of two from the first analysis to the second at all temperatures and the concentrations have remained high. This is indicative of a laboratory error and further work is being done with this element to clarify the situation.

IV. SUMMARY

The following conclusions have been reached about the collection of precipitation for chemical analysis:

1. It is important to use a collector that excludes dry deposition due to its impact on the chemistry of rain and snow.

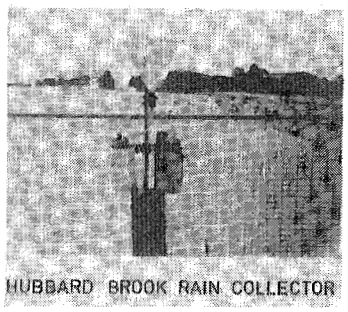
2. If using an automatic collection device, it is necessary that the collector be of rugged design, capable of withstanding long periods in the field. It is recommended that a collector of the type built by the U.S. Atomic Energy Commission be used.

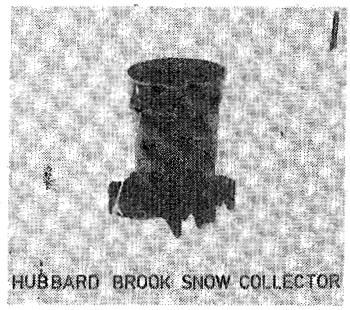
3. For the collection of precipitation for inorganic chemical analysis, it is recommended that plastic be utilized. For the collection of precipitation for organic chemical analysis, it is recommended that glass, stainless steel or aluminum be utilized.

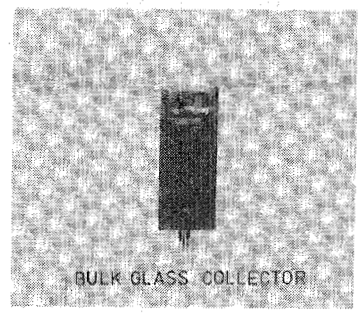
4. For those investigations that require a high degree of accuracy in the determination of precipitation chemistry, it is recommended that samples be collected on an "event" basis, that is, after every storm. In areas where the pH of the precipitation is low (< 4.5) weekly collections are adequate depending on the chemical parameters being analyzed.

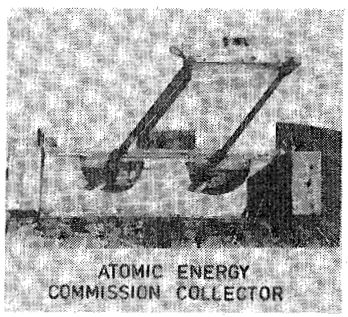
5. As a general rule the samples should be analyzed immediately. However, if this is not feasible, our investigations have shown that when the pH of the precipitation is less than 4.5 the storage of samples at 4 C is adequate.

The following figure is a pictorial array of nine of the precipitation collectors used in this investigation.

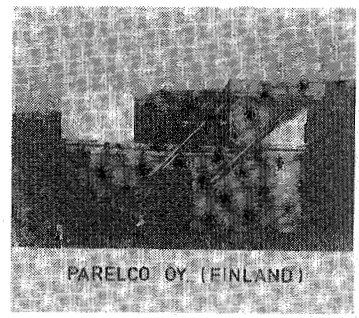

HUBBARD BROOK RAIN COLLECTOR


HUBBARD BROOK SNOW COLLECTOR


BULK GLASS COLLECTOR


ATOMIC ENERGY COMMISSION COLLECTOR

ILLINOIS STATE WATER SURVEY COLLECTOR


PARELCO OY (FINLAND)

ERNI & CO. COLLECTOR

WONG COLLECTOR

MISCO COLLECTOR

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A CONTRIBUTION TO THE PROBLEM OF STRONG ACID DETERMINATION IN AIR

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ABSTRACT

The main indicator for acidic substances in the atmosphere is, now as before, the pH of rainwater. Factors influencing the acidity of precipitation are discussed, using results of air monitoring stations in Germany.[6]

These results seem to confirm the general assumption, that mainly sulphuric acid is responsible for the increase in atmospheric acidity. Only little information exists, however, on the concentration of sulphuric acid and other strong acids (HCl, HNO_3) in air. A few attempts have been made to solve this analytical problem, and the present situation in this field is briefly reviewed.[1-3,5,7]

Finally a simple radiochemical thermodiffusion-procedure for the selective determination of strong acids is described. The basis of this technique is the reaction between a strong acid and sodium chloride, labelled with ^{36}Cl:

$$H^+B^- + Na^{36}Cl \rightarrow H^{36}Cl\uparrow + Na^+B^-$$

The reaction is carried out in an aqueous or partially aqueous medium at temperatures, at which the labelled hydrochloric acid is easily volatilized. The acitivity of the volatilized acid is proportional to the amount of protons of strong acids present in the sample.

Experimental details of this new method are presented as well as results of interference studies. The thermodiffusion technique can be applied to the analysis of precipitation and air-borne particulate matter. Its combination with a selective extraction[2] and a new sensitive sulphate-specific method[4] makes possible the analysis of air samples for strong acids in total and for sulphuric acid separately.

ACKNOWLEDGEMENT

This work was supported by a research grant of the German Research Society.

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A METHOD OF MEASURING AIRBORNE ACIDITY: ITS APPLICATION FOR THE DETERMINATION OF ACID CONTENT ON LONG-DISTANCE TRANSPORTED PARTICLES AND IN DRAINAGE WATER FROM SPRUCES

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ABSTRACT

The acid properties of particles have been investigated by means of measuring the content of mainly strong acid in leaching solutions of particle samples and in drain water from trees. The measurements are based on Gran's plot and on a study of its curvature.

INTRODUCTION

Great attention is now focused on the acidification of lakes and land which seems to be the immediate result of i.a. increasing emissions of SO_2. The lack of quantitative data on the supply of air-borne acid to receptors of different kinds makes it difficult to handle these problems. Below a method is described that provides such data. Some results of its application in the research of the acid properties of air-borne particles are reported.

DEFINITION

To be able to develop a method of measuring a quantity it is necessary to have a definition of the quantity in question. In the present case the relevant quantity is acid for which, as is well known, there is a number of more or less general definitions. If the problem is limited to water-soluble systems only, which seems to be possible in this case, the respective definition will be simple, namely:

An acid is an electrically neutral or charged group which is able to donate protons to a water system. If the donation is made quantitatively even at high concentrations, the acid is referred to as strong, otherwise as weak.

SCOPE OF THE INVESTIGATION

The problem of measuring air-borne acidity can of course be limited to the determination of the amount of protons being transferred to a receptor with defined properties by a certain deposition e.g. as particles or precipitation. In many cases it is, however, interesting to determine the acid properties of a potential deposition without taking the nature of the receptor into account. The latter case actually implies the determination of the nature and concentration of all acids present in the relevant sample. This in turn is a very exacting task which, however, can be limited in many cases. As a guidance for such a limitation a compilation of the most important anthropogenic acids (and their respective pk_a values) occuring in air-borne systems have been made in Table I. Organic acids have not been

Table I

Antropogenic Acids and their approximate Strength

Acid	Strength (pk_a)	Acid	Strength (pk_a)	Acid	Strength (pk_a)
HCl	strong	HF	3.2	$B(OH)_3$	9.0
HNO_3	strong	$Fe(H_2O)_6^{3+}$	∿3	NH_4^+	9.3
H_2SO_4	strong	$Fe(H_2O)_5OH^{2+}$	∿3	HCN	9.4
H_2SO_3	1.9	$Al(H_2O)_6^{3+}$	∿5		
HSO_4^-	2.0	H_2S	6.9		
H_3PO_4	2.1	HSO_3^-	7.2		
		$H_2PO_4^-$	7.2		

considered here, since information about their occurrence in precipitation and particles so far has been very sparse. However, at "The First International Symposium on Acid Precipitation and the Forest Ecosystem" in Columbus, Ohio in May 1975, a paper was presented, dealing with i.a. identification of organic acids in precipitation. The only acid that has been identified until now is the triprotonic isocitric acid (Galloway et al. 1975). If aluminium ions and the isocitric acid with

$$pk_{a_1} = 3.4, \quad pk_{a_2} = 4.75 \quad \text{and} \quad pk_{a_3} = 5.4$$

(Galloway, 1975) are disregarded, the acids in Table I can be divided in two groups: A stronger group which includes acids with $pk_a < \sim 3$ and a weak group including acids with $pk_a > \sim 7$.

The following comments can be made regarding the stronger group of acids in Table I. H_2SO_3 has a limited life in air-borne systems. It oxidizes to H_2SO_4. The acid H_3PO_4 has never been observed in measurable concentrations in the samples (some hundred) which up to now have been analysed in Sweden under the direction of the author. Occurrence of high concentrations of the acid HF is generally connected to certain premises. Trivalent iron ions do occur in almost all samples but as a rule in very low concentrations compared to other acids.

This means that if it is possible to determine free hydrogen ions and hydrogen ions bound in acids belonging to the stronger group ($pk_a < 3$), the sum of the concentration of strong acids and the acid HSO_4^- will be obtained with usually sufficiently good accuracy. As this concentration sum often is of major interest a procedure has been developed which makes it possible to decide to what extent also other weak acids have been titrated when merely determining strong acid and the acid HSO_4^-. This procedure has been used for determining i.a. the acid properties of air-borne particles.

METHODOLOGY

On a proposal from Christer Askne (Askne and Brosset, 1972) investigations were made to establish whether it was possible to determine the concentration of strong acid in particles and precipitation by means of Gran's titration method (Gran, 1952). This has resulted in the development of the following routine method.

The titration is as usual carried out potentiometrically, however, in such a way that the volume of the sample will remain unchanged. As a rule this is achieved by inserting microlitre quantities of a 0.01 N solution of NaOH to 5 ml of the sample which has been released from CO_2 by means of conditioning with N_2 (if necessary a known amount of $HClO_4$ is added to the sample). Now, the remaining amount of hydrogen ions (H^+) calculated from the measured potential is plotted against the

amount of added hydroxyl ions (OH^-). If the acid being titrated is strong, a straight line with a slope of -1 will, as is well known, be obtained. The intersection by the line of the x-axis ($H^+ = 0$) will give the point of equivalence. If weak acids are present in the sample the slope will be >-1 and the curve can bend markedly. The slope of the curve thus gives a certain information about the occurrence of acids of different strengths in the sample. For this reason it seemed to be of interest to deduce the slope of Gran's plot.

Assume that an acid solution is being titrated with sodium hydroxide in steps, and that the remaining amount of hydrogen ions (H^+) is determined after each addition. Then

$$\begin{aligned}\Delta OH^- = {} & H_1^+ - H_2^+ + [(HA')_1 - (HA')_2] + [(HA")_1 - (HA")_2] + \ldots \\ & + 2[(H_2A')_1 - (H_2A')_2] + 2[(H_2A")_1 - (H_2A")_2] + \ldots \\ & + 3[(H_3A')_1 - (H_3A')_2] + 3[(H_3A")_1 - (H_3A")_2] + \ldots \\ & \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\end{aligned} \qquad (1)$$

and so on will be obtained where H_1^+ is the amount of free hydrogen ions before addition of ΔOH and H_2^+ the amount of free hydrogen ions after this addition. The terms in brackets express the decrease of hydrogen ions bound to the different groups originating from the n-protonic acids H_nA', $H_nA"$, and so on.

From the total concentration C_t of the respective acids and their equilibrium equations, the concentrations of the different groups can be expressed in terms of the total concentration (C_t), the hydrogen ion concentration c_H^+ and the equilibrium constants ($k_1 \ldots k_n$). If these terms are inserted in equation (1) and if $H_2^+ \to H_1^+$ the following formula will be obtained

$$\frac{dH^+}{dOH^-} = - \frac{1}{1 + (C_t)_1\alpha_1 + (C_t)_2\alpha_2 + (C_t)_3\alpha_3 + \ldots}$$

where, as already mentioned, C_t is the total concentration of the weak acid and α a function of the hydrogen ion concentration and the dissociation constants of the acid according to the following

$$\alpha = \frac{\beta_1 + \beta_2 + \beta_3 + \ldots + \beta_n}{\left[1 + \frac{c_H^+}{k_n} + \frac{c_H^{+2}}{k_{n-1} \cdot k_n} + \ldots + \frac{c_H^{+n}}{k_1 \cdot k_2 \cdots k_n}\right]^2}$$

The quantity β stands for the following expression

$$\beta_1 = \frac{1}{k_n}$$

$$\beta_2 = \frac{4c_{H^+}}{k_{n-1} \cdot k_n} + \frac{c_{H^+2}}{k_{n-1} \cdot k_n^2}$$

$$\beta_3 = \frac{9c_{H^+}{}^2}{k_{n-2} \cdot k_{n-1} \cdot k_n} + \frac{4c_{H^+}{}^3}{k_{n-2} \cdot k_{n-1} \cdot k_n^2} + \frac{c_{H^+}{}^4}{k_{n-2} \cdot k_{n-1}^2 \cdot k_n^2}$$

and so on. In the expression for α the numerator for monoprotonic acid is β_1, for diprotonic acid $\beta_1 + \beta_2$ and so on.

As can be seen every weak acid affects the slope of the curve by the term $C_t \cdot \alpha$ in the denominator, where α is varying with c_H^+. The implication of this can easily be explained if the expression for the slope of a monoprotonic acid is regarded. In this case the following formula is valid

$$\frac{dH^+}{dOH^-} = - \frac{1}{1 + C_t \cdot \frac{1/k}{[1 + \frac{c_{H^+}}{k}]^2}}$$

As can be seen dH^+/dOH^- is constant for low as well as high values of c_H^+ in relation to k.

In the first mentioned case

$$\frac{dH^+}{dOH^-} \rightarrow - \frac{1}{1 + \frac{C_t}{k}} \qquad (c_{H^+} << k)$$

is obtained. In the second case the following is valid

$$\frac{dH^+}{dOH^-} \rightarrow - 1 \qquad (c_{H^+} >> k)$$

Table II is a compilation of α-values for monoprotonic acids with acid constants and c_{H^+} values in the relevant ranges. α-values for phosphoric and isocitric acids are given in Table III. Table IV and V contain dH^+/dOH^- calculated from the respective values.

Table II

Calculated α-values

Monoprotonic Acids

k_a	c_{H^+} mole/l					
	10^{-3}	$3\ 10^{-4}$	10^{-4}	$3\ 10^{-5}$	10^{-5}	10^{-6}
10^{-2}	83	94	98	99	100	100
10^{-3}	250	592	826	943	980	1000
10^{-4}	83	625	2500	5920	8260	9800
10^{-5}	10	104	826	6250	25000	82600
10^{-6}	1	11	98	1040	8260	250000

Table III

Calculated α-values

	c_{H^+} mole/l					
	10^{-3}	$3\cdot10^{-4}$	10^{-4}	$3\cdot10^{-5}$	10^{-5}	10^{-6}
Phosphoric Acid $k_{a_1} = 10^{-2.15}$ $k_{a_2} = 10^{-7.21}$ $k_{a_3} = 10^{-12.36}$	111	140	194	865	6350	846000
Isocitric Acid *) $k_{a_1} = 10^{-3.4}$ $k_{a_2} = 10^{-4.75}$ $k_{a_3} = 10^{-5.4}$	220	800	3180	10200	50400	196000

*) Acidity constants according to Galloway (private communication)

Table IV

Monoprotonic Acids

Values of $-\frac{dH^+}{dOH^-}$

k_a	c_t	c_{H^+} mole/l					
		10^{-3}	$3\cdot10^{-4}$	10^{-4}	$3\cdot10^{-5}$	10^{-5}	10^{-6}
10^{-2}	mole/l						
	10^{-6}	1.00	1.00	1.00	1.00	1.00	1.00
	10^{-5}	1.00	1.00	1.00	1.00	1.00	1.00
	10^{-4}	0.99	0.99	0.99	0.99	0.99	0.99
	10^{-3}	0.92	0.91	0.91	0.91	0.91	0.91
	10^{-2}	+0.55	0.52	0.51	0.50	0.50	0.50
10^{-3}							
	10^{-6}	1.00	1.00	1.00	1.00	1.00	1.00
	10^{-5}	1.00	0.99	0.99	0.99	0.99	0.99
	10^{-4}	0.98	0.94	0.92	0.91	0.91	0.91
	10^{-3}	0.80	0.63	0.55	0.51	0.51	0.50
10^{-4}							
	10^{-6}	1.00	1.00	1.00	0.99	0.99	0.99
	10^{-5}	1.00	0.99	0.98	0.94	0.92	0.91
	10^{-4}	0.99	0.94	0.80	0.63	0.55	0.51
10^{-5}							
	10^{-6}	1.00	1.00	1.00	0.99	0.98	0.92
	10^{-5}	1.00	1.00	0.99	0.94	0.80	0.55
	10^{-4}	1.00	0.99	0.92	0.62	0.29	0.11
10^{-6}							
	10^{-6}	1.00	1.00	1.00	1.00	0.99	0.80
	10^{-5}	1.00	1.00	1.00	0.99	0.92	0.29
	10^{-4}	1.00	1.00	0.99	0.91	0.55	0.04

Table V

Phosphoric and Isocitric Acids

Values of $-\frac{dH^+}{dOH}$

		c_H^+ mole/l					
	c_t	10^{-3}	$3 \cdot 10^{-4}$	10^{-4}	$3 \cdot 10^{-5}$	10^{-5}	10^{-6}
Phosphoric Acid	mole/l						
	10^{-6}	1.00	1.00	1.00	1.00	0.99	0.54
	10^{-5}	1.00	1.00	1.00	0.99	0.94	0.11
	10^{-4}	0.99	0.99	0.98	0.92	0.61	0.01
Isocitric Acid							
	10^{-6}	1.00	1.00	1.00	0.99	0.95	0.84
	10^{-5}	1.00	0.99	0.97	0.91	0.66	0.34
	10^{-4}	0.98	0.93	0.76	0.50	0.17	0.05

Now, assume that Gran's plot during titration is linear within the c_H^+ range $3 \cdot 10^{-4}$ - $3 \cdot 10^{-5}$ mole/l. This is generally the case when titrating leaching solutions of particle samples. The tables IV and V will now give the following information about the possible content in the solution part from strong acid.

1) Sulphate can be present in concentrations up to above 10^{-3} mole/l. If the slope of the curve is markedly above -1 the sulphate concentration is probably above 10^{-4}.

2) The concentration of monoprotonic acid with $pk_a \sim 3$ is below 10^{-4} and with $pk_a \sim 4$-6 below $\sim 10^{-5}$.

3) The concentration of phosphoric acid is below $\sim 10^{-4}$ and of isocitric acid below $\sim 10^{-5}$.

4) Most of the acids with $pk_a <\sim 3$ have been titrated in the actual c_H^+ range, whereas the major part of those with $pk_a > 6$ have not. Higher concentrations of acids with $pk_a \sim 4$-5 would here give non-linearity which would preclude a meaningful evaluation of the titration.

In this connection, finally, something ought to be mentioned regarding the ions $Al(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ which show a somewhat

specific picture. The dissociation of the aquo-aluminium ion is complicated and not completely understood. The acidity constant for the first step

$$Al(H_2O)_6^{3+} \rightarrow Al(H_2O)_5OH^{2+} + H^+$$

is $\sim 10^{-5}$ and this reaction is slow (Brosset, 1952). If only the first step is being considered an aluminium ion concentration of 10^{-5} mole/l will give a linear titration curve down to $c_{H^+} \sim 10^{-4}$ (Table IV). The fact that the reaction is slow will manifest itself by slowly reaching the equilibrium concentrations and the corresponding EMF-value. A creeping of the EMF is thus usually a good indication of the presence of aluminium ions of interfering concentrations. In Figure 1 a

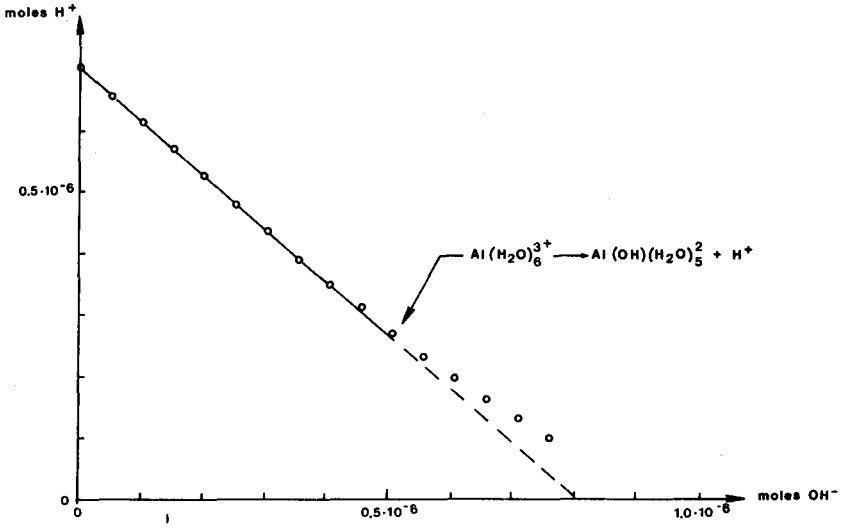

Figure 1. 5 ml sample solution containing 3.75×10^{-7} moles H_2SO_4 ($= 0.7 \times 10^{-6}$ moles H^+) and 1.5×10^{-7} moles Al^{3+}. The titration gives 0.8×10^{-6} moles H^+.

titration diagram is given which was obtained when titrating a 5 ml sample containing $7 \cdot 10^{-5}$ mole/l of H_2SO_4 and $3 \cdot 10^{-5}$ mole/l Al^{3+}. As can be seen from this diagram the linear extrapolation made has resulted in somewhat high a value.

The acid dissociation constants of trivalent iron ions have been determined by many authors (Sillén, 1971). The results differ to a great extent. However, in general it can be said that the first constant is around 10^{-3} and the second just below this value. The subsequent dissociation results in precipitation of iron hydroxide (solubility product at 20° around $3.2 \cdot 10^{-36}$) (Evans and Pryor, 1949).

Figure 2 illustrates the result of titration in the presence of rather

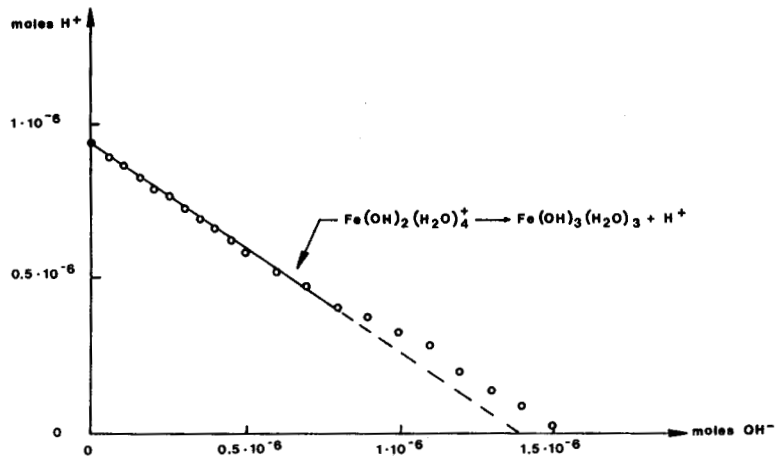

Figure 2. 5 ml sample solution containing 5×10^{-7} moles H_2SO_4 (= 1.0×10^{-6} moles H^+) and 2×10^{-7} moles Fe^{3+}. The titration give 1.39×10^{-6} moles H^+ corresponding to sulphuric acid and trivalent iron as diprotonic acid ($1.0 \times 10^{-6} + 2.2 \times 10^{-7} = 1.4 \times 10^{-6}$ moles).

high a concentration of iron. The sample contained $1.0 \cdot 10^{-4}$ mole/l of H_2SO_4 and $4 \cdot 10^{-5}$ mole/l of an iron salt. Thus the 5 ml being titrated contained $1.0 \cdot 10^{-6}$ moles of H^+ and $2 \cdot 10^{-7}$ moles of Fe^{3+}. Titration and extrapolation of the linear part of the curve (c_{H^+} range $2 \cdot 10^{-4} - 1 \cdot 10^{-4}$ mole/l) give $1.39 \cdot 10^{-6}$ moles corresponding to two H^+ per H_2SO_4 and two H^+ per Fe^{3+}. The trivalent iron has thus been titrated as a diprotonic acid. The third dissociation step and the subsequent precipitation manifest themselves by the parallel displacement of the curve at H^+ $\sim 0.3 \cdot 10^{-6}$ moles (c_{H^+} $\sim 6 \cdot 10^{-5}$ mole/l).

This titration procedure has been used at our laboratory for more than two years. We have found that it is always possible to titrate precipitation samples in this way, which as a rule is pertinent to leaching solutions of particles also. High concentrations of aluminium, which prevent the exact titration, have been observed a few times.

RESULTS OF DETERMINATION OF THE ACID PROPERTIES OF PARTICLES

Since the autumn 1972 air-borne particles have been studied by our institute mainly at a remote station on the Swedish west coast, 40 km south of Gothenburg. In this connection 24 hour samples have been taken partly of total suspended matter and partly of particle fractions with a diameter of $<\sim$ 15 µm. The particles have been leached with water and the concentrations of SO_4^{2-}, NH_4^+ and H^+ in the leaching solution have been determined. In the last mentioned case the above methodology was used. The material obtained this way, part of which has been reported (Brosset et al. 1975) (Brosset, 1975), indicates to some extent what role particles may play in acidification. These indications are reported below.

BLACK AND WHITE EPISODES

A vast material shows that during the winter half of the year and under special meteorological conditions high concentrations of black particles can be built up in Scandinavia as a result of long-distance transport (Brosset and Åkerström, 1972) (Rodhe et al. 1972). Around 50% of the mass of these particles can be water-soluble and consist of mainly $(NH_4)_2SO_4$, sometimes combined with some acid (Brosset, 1973). There are strong reasons to believe that ammonium sulphates have been formed by oxidation of SO_2 to H_2SO_4 under the influence of catalysing substances present in the particles in combination with high humidity and a subsequent neutralization by NH_3 of the sulphuric acid formed (Brosset, 1975). Lack of NH_3 results in somewhat acid particles. However, it should be noted that a high concentration of acid cannot occur here as the solubility of the sulphur dioxide decreases with increasing acidity in the liquid phase covering the particles (Junge, 1958). It is uncertain whether these rather neutral particles play a part in acidification. However, this would certainly be the case if NH_4^+ ions were oxidized resulting in the formation of acid.

During the summer half of the year there is a higher concentration of acid in the particles than during the winter. Our measurements have shown that small white particles ($\varnothing < 0.3\mu m$) consisting of the phase $(NH_4)_3H(SO_4)_2$ or even NH_4HSO_4 can be transported to the Swedish west coast chiefly from south-west. It seems likely that these acid ammonium sulphates have been formed by photochemical oxidation of SO_2 to SO_3 (several types of reactions are possible here) and that the latter is hydrated and partly neutralized by NH_3. If the last mentioned processes occur in a NH_3-poor atmosphere, e.g. over the North Sea the neutralization will, as observed, be very incomplete (Brosset, 1975).

The contribution to the acidification of land and lakes by these

white particles is probably limited due to the fact that the white episodes occur rather seldom. However, when these episodes are present a human being can breathe around 100 µg of sulphuric acid for 24 hours (Brosset, 1975).

During the last week in May, 1973, an episode occured during which it was possible to make studies of the water-soluble phase of the particles analytically as well as by means of X-ray diffraction. The results are given in Table VI. As can be seen all three of the above-mentioned

Table VI

Comparison between Results of Chemical Analysis and Phase Identification by Means of X-ray Diffraction.

Sampling Date	$NH_4^+/_{H^+}$ by Analysis	Phases Identified	Phases not Identified
23 May 12.25-14.00 hours	15.1	$(NH_4)_2SO_4$	traces
24 May 09.15- 25 May 14.00 hours	3.0	$(NH_4)_3H(SO_4)_2$	traces
29 May 06.00-12.00 hours	1.0	NH_4HSO_4	traces

ammonium sulphate phases have been identified. The analytical result is further in good agreement with the stoichiometrical compositions of the phases identified by means of X-ray diffraction.

THE NEUTRALIZATION OF ACID PARTICLES

During August 1974, 24 hour samples of suspended matter were taken at the remote station Råö, mentioned previously, as well as at four sampling sites located as indicated on the map in Figure 3. The samples were analysed in the usual manner for H^+, NH_4^+ and SO_4^{2-}. The intention was to get an idea how the composition of the water-soluble part of the particles varied with different places in South Sweden. The measuring results obtained from an episode which occured during

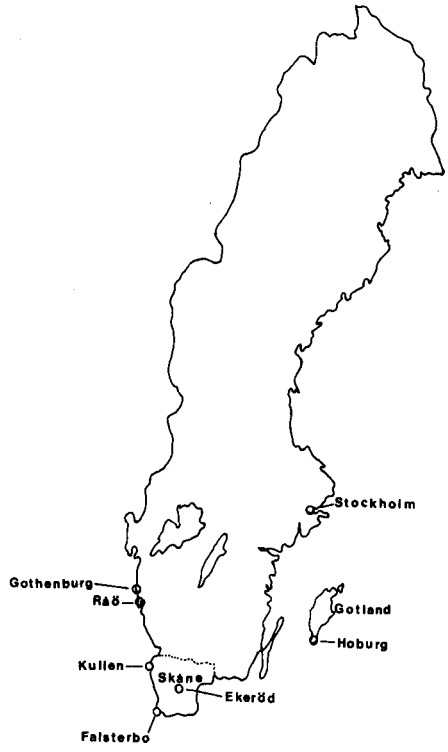

Figure 3. Sampling stations.

7-14 August are illustrated in Figure 4. As can be seen the equivalent concentration of sulphate on this occasion has almost been equal to the sum of the equivalent concentrations of H^+ and NH_4^+. This means that the water-soluble part of the particle fraction sampled, for the most part consisted of more or less acid ammonium sulphates. On this occasion the wind direction was south-west, through which Råö will be subjected to the air masses that had drifted over the North Sea and Skagerack and which evidently contained rather acid particles.

At the above-mentioned wind direction the station at Kullen about 300 km south of Råö is situated to the leeward of Denmark. This is even more the case as regards the station at Falsterbo. As can be seen from Figure 4 there is a decrease in acidity of the particles sampled at these stations as compared to Råö. This may indicate that the particle-borne acid has been neutralized by NH_3 during transportation of the particles over Denmark. It is further very interesting to note that all acid has become neutralized as the particles reach the station at Ekeröd situated in the middle of the province of Skåne, which is a large agricultural district.

The station at Hoburg lighthouse on the south point on the island of Gotland shows a very moderate maximum of acid on 11 August. By this it seems that the acid particles have proceeded this far two days after

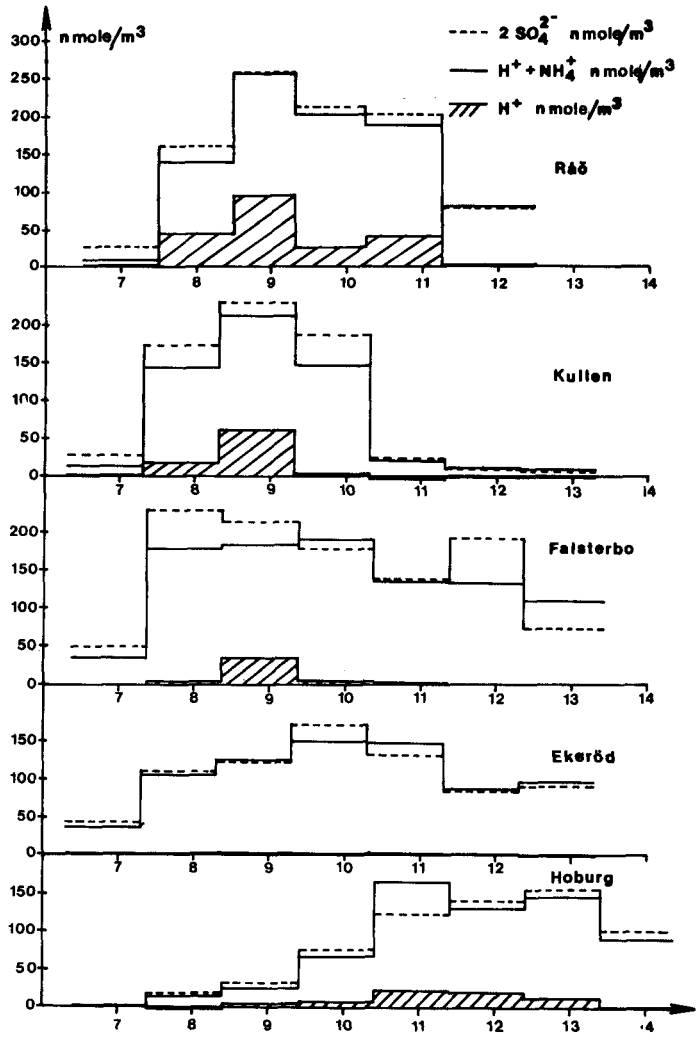

Figure 4. Episode 7-14/8 1974. Concentrations at stations on the Swedish west coast, in Skåne and on Gotlan.

passing the western coast-line. During transport they drifted over land to rather a great extent and somewhat over the sea.

The above observations indicate that certain districts of land may act as ammonia sources and that acid particles passing these districts may be more or less neutralized. It is likely that the neutralization may alter the properties of the particles from the viewpoint of effects. However, the possible oxidation of NH_4^+ resulting in acid has to be taken into account in some cases.

PRELIMINARY MEASUREMENTS OF THE PARTICLE DEPOSITION ON SPRUCES

It has earlier been pointed out that particles containing neutral or acid ammonium sulphate due to their small size (Ø < 1 µm) can cause undesirable effects by deposition in e.g. the respiratory tracts. For the same reason it is, however, likely that they would play a secondary part in the acidification of land and lakes caused by wet deposition since such small particles, unless they would increase in size will be washed out to a small extent only by precipitation during transport. On the other hand marked effects can be expected due to dry deposition if the receptor has a large surface as for example a forest.

Many measurements have previously been carried out with the objective of determining the extent of the dry deposition on trees by analysis of the precipitation filtered by the needles and the respective leaves of trees (Nihlgård, 1970). However, a quantitative determination of acid has not yet been made in this connection. Therefore it seemed of interest to investigate whether the application of the titration procedure described above could give any further information.

In two forest areas north and south of Gothenburg (see map Figure 5) a number of spruces were chosen as subjects of the experiment.

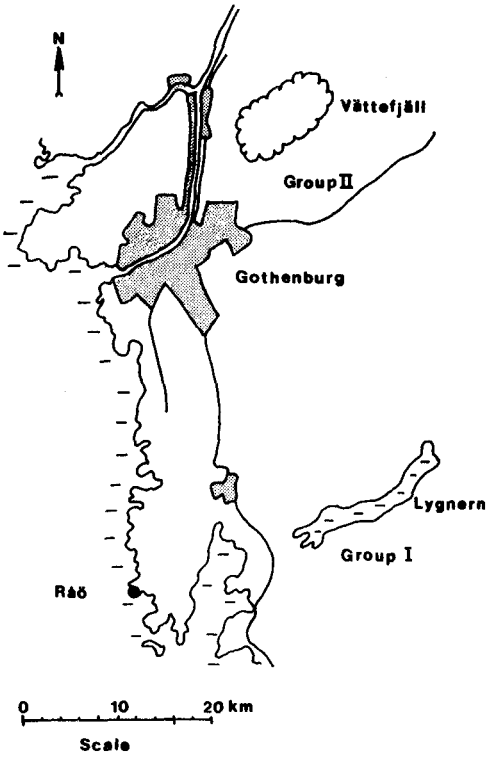

Figure 5. Map showing the location of the different groups of trees.

8 vessels (Ø 0.3 m) were placed beneath the spruces to collect the drain water from the respective tree. The vessels were numbered and placed in numerical order in the respective point of the compass according to Figure 6. The test series included three spruces in group I (the

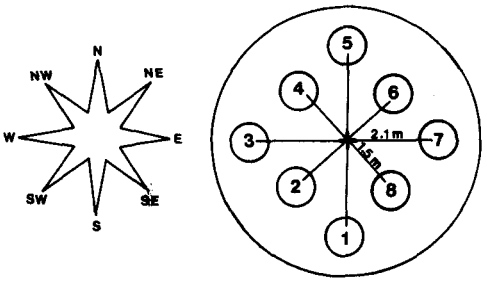

Figure 6. Location of the sample collectors beneath the respective tree.

southern sampling site) and three spruces in group II (the northern sampling site). In this very case the vessels were placed after a rainfall on 28 August, 1974, and brought back on 9 September, 1974. During this period it had been raining mainly for the last few days. It was most likely that the rainwater collected in the vessels had washed out at least part of the particles deposited on the respective spruces during the period 28 August - 9 September. Further a similar vessel was placed outside each tree group to collect rainwater which had not been in contact with the trees. The results given in Figure 7 indicate the amounts of H^+, NH_4^+, and SO_4^{2-} in the respective precipitation samples.

Table VII is a compilation of the amounts of H^+, $NH_4^+ + H^+$ and $2SO_4^{2-}$ contained in the drain water from every tree in the southern (I) as well as northern (II) group, expressed in m moles. This table also includes the sum of the amounts of the respective groups. Correction has been made for the amounts observed in pure rain water. If the values obtained are representative for the deposition on trees at those from each other rather remotely situated test areas the conclusion must be drawn that for trees of the type chosen (spruces as symmetrical as possible about 8-10 m high with a ground level Ø of ∿ 5-6 m) the deposition of the different kinds of ions investigated was almost the same for trees within the respective group as for trees belonging to different groups. This concerns above all the trees numbered 1, 2, 4, and 5. The material is obviously too small for drawing any certain positive conclusions. However, if the observations made should prove not to be occasional it means that the dry deposition in the two areas must be associated with long-distance transport of pollutants and that the city

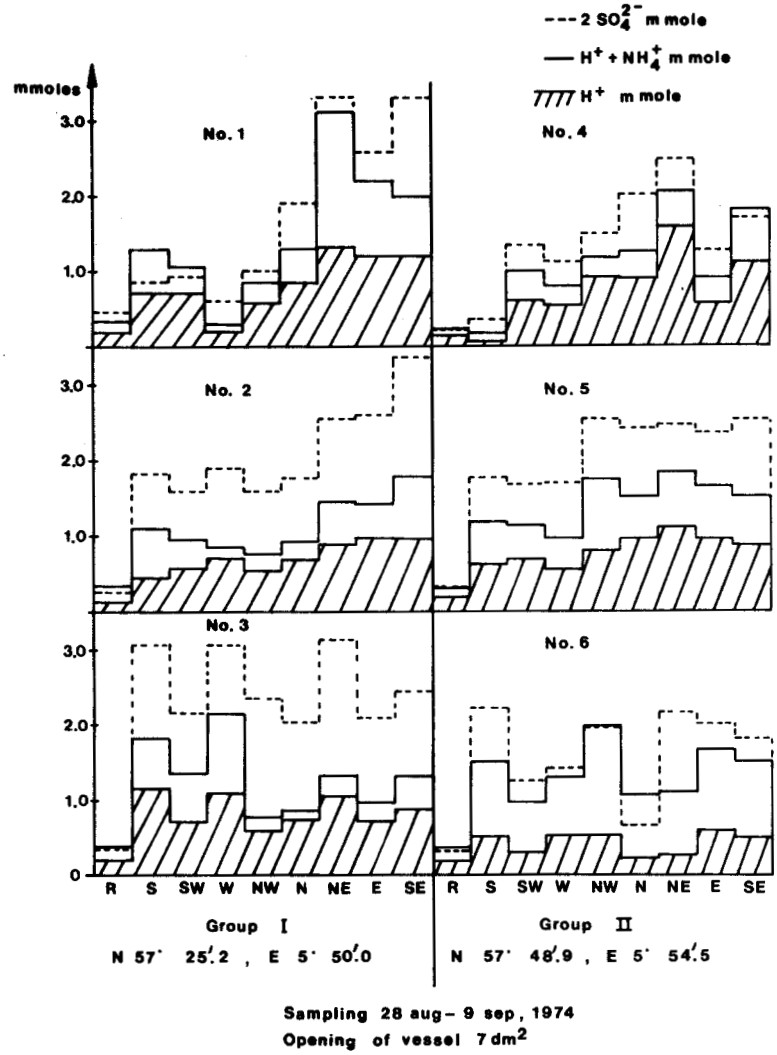

Figure 7. H^+, $NH_4 + H^+$ and SO_4^{2-} in precipitation samples (R) and samples of drain water (S-SE).

Table VII

Content of Some Ions in Drain Water from Trees.

Tree No	mmole			
	H^+	$NH_4^+ + H^+$	$2SO_4^{2-}$	
1	5.5	9.8	11.4	
2	5.0	7.0	14.6	Group I
3	6.4	9.5	19.3	
Σ	16.9	26.3	45.3	
4	5.2	7.4	9.9	
5	5.7	10.0	16.1	Group II
6	2.7	9.6	12.2	
Σ	13.6	27.0	38.2	

of Gothenburg (500,000 inhabitants) is a source of secondary importance in this respect.

Another interesting observation is the high acid to ammonium ratio in the drain water compared to that observed on particles simultaneously sampled at Råö which is situated close to the sampling site of the southern group (see map Figure 5). Data concerning the particles are illustrated in Table VIII. In Table IX comparison is made between the ratio of $H^+ : (NH_4^+ + H^+) : 2SO_4^{2-}$ contained in drain water from the trees and in leaching solutions of the particles.

As appears from Table IX the ratio of $H^+ : (NH_4^+ + H^+)$ in the drain water is ten times higher than the corresponding ratio for the particles. On the other hand the ratio $2SO_4^{2-} : (NH_4 + H^+)$ is on an average 16% higher. This indicates that in spite of the fact that the sulphate concentrations observed are sufficient for explaining the H^+ amounts found as deposited sulphuric acid, other mechanisms may be the reason for the observations made. To get a clear picture of these problems, which seem to be important from the viewpoint of acidification, a much more

Table VIII

H^+, $NH_4^+ + H^+$ and $2SO_4^{2-}$ in Particle Samples from Råö.

(n mole/m^3)

Date	H^+	NH_4^+	$NH_4^+ + H^+$	$2SO_4^{2-}$
Aug 28	1	16	17	26
Aug 29	- 2	9	7	10
Aug 30	11	68	79	98
Sep 3	3	57	60	90
Sep 4	0	66	66	88
Sep 6-9	1	24	25	58

Table IX

The Ratio of $H^+ : (NH_4^+ + H^+) : 2SO_4^{2-}$ in Drain Water from Trees and Particles.

	H^+	:	$NH_4^+ + H^+$	:	$2SO_4^{2-}$
Group I	0.64	:	1	:	1.72
Group II	0.50	:	1	:	1.42
Particles	0.05	:	1	:	1.35

extensive sampling must be carried out and the samples be subjected to a more detailed programme of analysis. Such investigations are now in progress.

SUMMARY

A titration procedure based on Gran's plot has been developed. The method which enables the determination of stronger acids (pk_a <∿ 3) has been applied for investigations of different depositions. The water-soluble part of particles (Ø <∿ 1 μ) has been found mainly to consist of more or less acid ammonium sulphates. The phases $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$ and NH_4HSO_4 have been identified. It also appears that acid particles are successively becoming neutralized during transport over land by uptake of ammonia. Finally one preliminary experiment has been carried out regarding the concentrations of H^+, NH_4^+ and SO_4^{2-} in drain water from spruces. The equivalent ratios have been compared with those observed in the leaching solution of particles sampled during the same time interval. The results indicate the following possible effects.

It is likely that particles containing more or less acid ammonium sulphate can cause undesirable effects e.g. when being inhaled. They may be of secondary importance as regards the acidification of land and lakes caused by wet deposition. On the other hand it seems as if dry deposition of particles on coniferous trees with subsequent secondary reactions and wash out can result in large depositions of acid on the ground level beneath the trees.

ACKNOWLEDGEMENT

I would like to express my thanks to Bo Nilsson, Department of Inorganic Chemistry, Chalmers University of Technology, for valuable assistance in sampling and analysis of drain water from spruces.

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A MECHANISM FOR HYDROCHLORIC ACID PRODUCTION IN CLOUD

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ABSTRACT

A theoretical model describing the general interaction between atmospheric trace gases, such as SO_2, NH_3, CO_2 and O_2, chemical reactant gaseous product H_2SO_4 and hydrometeors containing NaCl is proposed to study a possible mechanism for hydrochloric acid production in non-precipitating cloud and the determination of the pH value of cloud droplets.

Four different cloud droplet distributions have been used to estimate the upper limit of the amount of gaseous HCl released into the atmosphere resulting from the evaporation of cloud droplets. It is shown that the acid production and the amount of HCl released depend on the following factors: (a) the temperature of the cloud; (b) the oxidation rates; (c) the ambient concentration of SO_2, NH_3, and H_2SO_4; (d) the life cycle of the cloud; and (e) the liquid water content of the cloud.

This proposed chemical model also predicts a pH value spectrum depending on the cloud droplet distribution. Field measurements for the dependence of pH value on particle size and spatial distribution of gaseous HCl are recommended.

I. INTRODUCTION

Recently there is a growing awareness of the acidity of precipitation produced by cloud in a polluted environment. Not only because acid rain has detrimental effects on local fishing industry, agricultural crops and forest ecosystem, but also it has no country boundary.

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*The National Center for Atmospheric Research is sponsored by the National Science Foundation.

One country's industrial activity may produce acid rain in another country. Although in the field of air pollution scientists focus almost exclusively on the emission of SO_2 from burning of fossil fuel and the subsequently low pH value of the rain drop in the polluted atmosphere, sulfuric acid is by no means the unique acid in the rain drop. As a matter of fact, more recently there is an increasing urgency to better understand the role of free hydrochloric acid in the atmosphere due to the following reasons:

(a) HCl plays an important role in the air chemistry. Previous interest in the HCl problem resulted mainly from the research to explain the changing sodium to chlorine ratio from the ocean. (1,2) Indeed, the general tendency of the increase of that ratio with distance from the coast can easily be explained by assuming the release of free hydrochloric acid from cloud nuclei during their courses toward continent. Currently attention has been given to the air chemistry of stratosphere in which HCl will compete if present in the natural stratosphere with NO, OH, etc., in the catalytic destruction chain of ozone ($HCl + OH \rightarrow H_2O + Cl$, $Cl + O_3 \rightarrow CLO + O_2$, $ClO + O \rightarrow Cl + O_2$) (3).

(b) Positive small ions at tropospheric and lower stratospheric levels consist of clusters of the type: $NH_4^+ \cdot (NH_3)_n \cdot (H_2O)_m$ with $n \sim 1\text{-}3$ and $m \sim 1\text{-}10$ depending on temperature and ambient (NH_3) and (H_2O) concentration. The presence of these ions in the atmosphere may induce reactions leading to the formation of aerosols, or at least to the existence of free NH_4Cl molecules whenever traces of ammonia and hydrochloric acid are in collisional contact with ions. Calculation shows that by assuming an ion density of 10^3 cm^{-3} would result in an average lifetime for HCl in the order of 10 days ($HCl \rightarrow NH_4Cl$). If NH_4Cl is absorbed by cloud droplets, the possibility of subsequent HCl formation and release cannot be excluded, i.e., some HCl could be continuously recycled. On the other hand, if aerosol NH_4Cl is formed, that may be a significant sink for atmospheric HCl.

(c) It is believed that most of the gaseous HCl molecules in the atmosphere are the end product of interactions between trace gases and hydrometeors. According to Duce, (4) the annual production rate of HCl in a global scale through this mechanism is 6×10^8 metric tons. Because HCl is highly dissolvable, the subsequent absorption of HCl into the rain drops will further lower the pH value and increase the acidity of acid rain during the rain-out process. Since HCl is vitally linked with other trace gases in the atmosphere and the acidity of rain, a full understanding of HCl will be helpful in understanding the fate of other atmospheric trace gases and the sources of acid rain.

It is the purpose of this paper to suggest a model to estimate the upper limit of the amount of gaseous HCl released into the atmosphere resulting from the interactions between the trace gases and hydrometeors and the evaporation of cloud droplets. The proposed model includes both the liquid phase oxidation mechanism and gas phase oxidation mechanism.

In addition to the interactions between the trace gases such as SO_2, NH_3, CO_2 and O_2 and the hydrometeors containing NaCl, the model also introduces the interaction between chemical reactant gaseous product H_2SO_4 and the hydrometeors containing NaCl. However, it is important to point out here that the accuracy of this model is severely limited by insufficient parameters for most precursor reactions leading to the formation of HCl and governing its fate in the intricate atmospheric system. Though quantitatively our estimations are highly speculative, qualitatively we have identified some of the important parameters that govern the amount of HCl liberated from the evaporation of the cloud droplets, thus providing a framework for further studies in this interesting subject.

This proposed model is also utilized to determine the pH value of cloud droplets. Because of the introduction of the kinetic effect into the model, a pH value spectrum depending on the cloud droplet distribution is found.

In section II, we briefly review various mechanisms proposed to study the production of HCl in the atmosphere. The pH value of the cloud droplets estimated by our model including both the liquid and gas phase oxidation of trace gases is presented in section III. In section IV we utilize our proposed model to estimate the amount of HCl released from cloud droplets. Finally, we discuss the important factors for the production of HCl and recommend future field experiments on this subject.

II. OVERVIEW

In this section, we briefly review various mechanisms proposed to study the production of HCl in the atmosphere.

Cauer (5) suggested that the oxidation of chloride by ozone is responsible for the low pH values of precipitation. In his studies of atmospheric condensation nuclei, he assumes that the sodium and chloride added to the atmosphere by bursting bubbles or breaking waves go through entirely different cycles. In the presence of small amounts of ozone in the lowest strata of the atmosphere (0-100 μgm^{-3}), those chlorine ions contained in sea spray droplets may be oxidized to free chlorine gas, which in turn, under the influence of sunlight and water vapor, can be hydrolyzed to form hydrochloric acid. The proposed reaction scheme to form HCl can be summarized as follows:

$$O_3(g) + Cl^-(aq) \rightarrow O_2(g) + ClO^-(aq)$$

$$ClO^-(aq) + 2H^+(aq) + Cl^-(aq) \rightarrow Cl_2(g) + H_2O\ (liq)$$

$$2Cl_2 + 2H_2O\ (liq) \rightarrow 4HCl\ (liq) + O_2(g)$$

However, these reactions are unlikely to happen in the atmosphere, because experimentally Kohler and Bath (6) have carried out a simulating experiment and found that the reaction is insufficient to account for the observed geographical variation of sodium to chloride ratio.

Later on the following route has been suggested for converting particulate chloride to hydrogen chloride or chlorine in the atmosphere (7):

$$NaCl + 2NO_2 \xrightarrow{H_2O} NaNO + MOCl$$

$$NOCl + H_2O \rightarrow HCl + HNO_2$$

$$NOCl \xrightarrow{hV} NO + Cl$$

However, Robbins et al. (8) did not observe the formation of nitrosyl chloride, thus the free HCl in the atmosphere cannot come from direct reaction between sea-salt particles and nitrogen dioxide.

Based on experimental results, Robbins et al. suggested the reaction route via hydrolysis of nitrogen dioxide (NO_2) to form nitric acid (HNO_3) vapor followed by either adsorption of HNO_3 vapor by dry sodium chloride particle at low relative humidities, or by solution droplets containing sodium chloride when relative humidities are high. The final step is the chemical reaction of nitric acid with sodium chloride leading to the desorption of hydrogen chloride, either immediately following the reaction or during subsequent evaporation of the droplets. Since the existence of gaseous HNO_3 in urban areas is well recognized today, we do believe that this HCl-formation mechanism in the presence of HNO_3 produced by gas phase oxidation process is one of the important mechanisms to form HCl and lower the pH value of the cloud droplets containing sodium chloride. However, among all the possibilities, the process most often quoted is summarized by the following chemical reaction sequence:

$$(H_2SO_4 + NaCl)_{aq} \rightarrow (Na_2SO_4)_{aq} + (2HCl)_{gas}$$

This leads us to the still controversial problem in atmospheric chemistry dealing with the production of SO_4^{--} in liquid droplet through the oxidation of SO_2. There are two possible pathways to produce SO_4^{--} in aquaeous solution droplet in the atmosphere. The most recognized pathway is the oxidation of dissolved SO_2 in liquid phase. However, the process involving the oxidation of SO_2 to form gaseous H_2SO_4 and followed by vapor transfer to the liquid droplet should also be considered

For gas phase oxidation, in the presence of third body, gaseous SO_2 can be oxidized in the atmosphere through the following schemes:

$$\text{(R1a)} \quad SO_2 + OH + M \rightarrow HSO_3 + M \quad \text{(Davis, 1974) (9)}$$

(R1b) $HSO_3 \rightarrow H_2SO_4$

(R1b) steps have not been established yet, however the (R1a) is assumed to be rate determining for the formation of H_2SO_4 molecules.

(R2a) $(H_2SO_4)_n + (H_2O)_m \xrightarrow[\text{nucleation}]{\text{heteromolecular}}$ sulfuric acid droplets

(R2b) sulfuric acid vapor transfer to particles or cloud droplets.

On the other hand, organic radicals can also be used to oxidize SO_2:

(R3) $ROO + SO_2 \rightarrow RO + SO_3$ (Cadle 1972) (10)

(R4) $SO_3 + H_2O \rightarrow H_2SO_4$ followed by reaction (R3).

Most authors believe that in the lower troposphere, the most likely source of sulfate is through the oxidation of dissolved SO_2 in cloud droplets:

(R5) $SO_2 \rightarrow$ dissolved in cloud droplets $\xrightarrow{\text{catalysts}} SO_4^{--}$

In the lower troposphere, ammonia is probably one of the best candidates of catalyst for that reaction. In fact, the SO_2-NH_3-CO_2 water system has been treated by Scott and Hobbs (11) and recently by Easter and Hobbs (12) who also critically reviewed the published rate constants entering the reaction scheme.

In this paper, we estimate the amount of HCl production by considering $(H_2SO_4 + NaCl)_{aq} \rightarrow (Na_2SO_4)_{aq} + (2H_2O)_{gas}$ chemical reaction mechanism. Both liquid phase and gas phase oxidation of SO_2 to form SO_4^{--} in liquid droplet will be considered.

III. ESTIMATION OF THE pH VALUE OF THE CLOUD DROPLETS

1. Liquid phase oxidation (see Figure 1a)

As noted earlier, the ammonia catalyzed SO_2 oxidation in the liquid phase is currently considered as the most likely route to produce sulfate compounds. However, if sodium chloride is present in the droplets, free hydrogen and chloride ions will combine and finally be released into the atmosphere in the form of free hydrochloric acid during the evaporation process of cloud droplets in a non-precipitating cloud. We therefore, incorporate this process in our model calculation and determine the pH value of the cloud droplet and the amount of HCl that

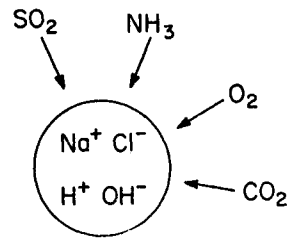

Figure 1a. A diagram to show the interaction between trace gases (SO_2, NH_3, CO_2), O_2 and hydrometeors containing NaCl

could be liberated from the cloud droplets.

Scott and Hobbs (11) have summed up the chemical reaction equations involved and the corresponding equilibrium constants. (See Table 1.)

Table 1

Liquid-Phase Reactions in the SO_2 - NH_3 - CO_2 - Water System

Eq.	Chemical Equilibrium Equation	Equilibrium Constant
(1)	$H_2O \rightleftharpoons H^+ + OH^-$	$K_w = [H^+][OH^-]$
(2)	$(SO_2)g + H_2O \rightleftharpoons SO_2 \cdot H_2O$	$K_{hs} = [SO_2 \cdot H_2O] / P_{SO_2}$
(3)	$SO_2 \cdot H_2O \rightleftharpoons H^+ HSO_3^-$	$K_{1s} = [H^+][HSO_3^-]/[SO_2 \cdot H_2O]$
(4)	$HSO_3^- \rightleftharpoons H^+ + SO_3^{--}$	$K_{2s} = [H^+][SO_3^{--}]/[HSO_3^-]$
(5)	$(NH_3)g + H_2O \rightleftharpoons NH_3 \cdot H_2O$	$K_{ha} = [NH_3 \cdot H_2O]/P_{NH_3}$
(6)	$NH_3 \cdot H_2O \rightleftharpoons NH_4^+ + OH^-$	$K_{1a} = [NH_4^+][OH^-]/[NH_3 \cdot H_2O]$
(7)	$(CO_2)g + H_2O \rightleftharpoons CO_2 \cdot H_2O$	$K_{hc} = [CO_2 \cdot H_2O]/P_{CO_2}$
(8)	$CO_2 \cdot H_2O \rightleftharpoons H^+ + HCO_3^-$	$K_{1c} = [H^+][HCO_3^-]/[CO_2 \cdot H_2O]$

As pointed out by McKay (13), those equilibrium constants are highly dependent upon the temperature. McKay has listed these equilibrium constants at 25 C and 15 C. By assuming constant enthalpy for each set of constants, those constants can be extrapolated to values at other temperatures.

In our model we assume that chemical equilibria between SO_2 and NH_3 and their various dissolved forms in liquid are established at all

time. It is also assumed that, in the aqueous phase, the diffusion of SO_2 is so fast that the oxidation rate rather than diffusion is a controlling factor. We also assume that the cloud is at the 600 mb level and its temperature is 0°C.

The concentration of H^+ ions and SO_4^{--} ions can be estimated by solving the following equations:

$$\frac{d[SO_4^{=}]}{dt} = K[SO_3^{=}] \tag{1}$$

$$[SO_3^{--}] = K_{2s} K_{1s} K_{hs} \frac{P_{SO_2}}{[H^+]^2} \tag{2}$$

$$\{1 + \frac{K_{ha} K_{1a}}{Kw} PNH_3\}[H^+]^3 - 2[SO_4^{--}][H^+]^2$$

$$- \{Kw + K_{hc} K_{1c} Pco_2 + K_{hs} K_{1s} Pso_2\}[H^+]$$

$$- 2K_{hs} K_{1s} K_{2s} P_{so2} = 0 \tag{3}$$

The oxidation rate constant k in Eq. (1) is still a controversial subject. Up to now three different expressions have been suggested. Their differences are so large that further experimentation to clarify this problem is urgently needed.

The first expression was suggested by Scott and Hobbs (11) in 1967. Based upon the experimental results of Van den Heuval and Mason (14) they evaluated the value of k at 25°C was 0.0017 sec^{-1}.

Using the experimental results of Fuller and Crist, (15) McKay (13) in 1971 suggested a rate value depending upon the hydrogen ion concentration. This rate value k at 25°C can be expressed as following:

$$k = 0.013 + 59[H^+]^{1/2} \ sec^{-1}$$

$$= 0.032 \ sec^{-1} \text{ at neutrality}$$

In 1972, Miller and de Pena (16) used a different value of k, 0.003 sec^{-1}, to do their calculations.

All these oxidation rate constants depend on the temperature. As suggested by McKay, (13) and Easter and Hobbs, (12) an activation energy of 18.3 k cal $mole^{-1}$ should be used to obtain the rate constant at varying temperatures. Rate constants of k suggested by different authors and calculated at different temperatures are shown in Table 2.

Table 2

Rate Constant k (sec^{-1})

Suggested by Different Authors and at Different Temperatures

Author	25°C	15°C	10°C	0°C	-3°C
Scott & Hobbs	0.0017	0.00058	0.00033	0.0001	0.000069
McKay	0.013+	0.0048	0.0026+	0.00078+	0.00054+
	$59[H^+]^{\frac{1}{2}}$	$20[H^+]^{\frac{1}{2}}$	$11.57[H^+]^{\frac{1}{2}}$	$3.43[H^+]^{\frac{1}{2}}$	$2.44[H^+]^{\frac{1}{2}}$
(at neutrality)	0.032	0.011	0.00628	0.00192	0.00133
Miller & dePena	0.003	0.001	0.0059	0.00018	0.000124

2. Gas phase oxidation (see Fig 1b)

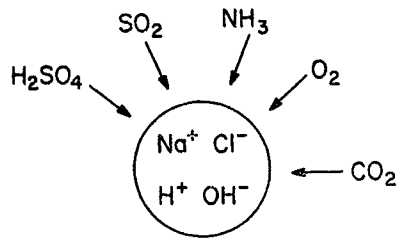

Figure 1b. A diagram to show the interaction between trace gases (SO_2, NH_3, CO_2), O_2 and hydrometeors containing NaCl with the impinging of chemical reactant gaseous production H_2SO_4 molecules.

In order to have a more realistic model, the gas phase oxidation of trace gases to produce acid molecules should not be neglected. As noted earlier, the gas phase oxidation of SO_2 leading to the formation of H_2SO_4 in the atmosphere is through the following scheme:

$$\text{(R1a)} \quad SO_2 + OH + M \rightarrow HSO_3 + M$$

where M is the third body responsible to take away the excess energy produced in the reaction. On the basis of micro-observations (17) the steps following the reaction to produce H_2SO_4 are so fast, we can assume that the rate-limiting process leading to the formation of H_2SO_4 is (R1a). The rate constant of reaction (R1a) can be approximated to be 3×10^{-31} cm^6 sec^{-1}. (9) The OH concentration is taken to be 5×10^6 cm^{-3}. By assuming the cloud is at 2 km, the value of the third body concentration M can be taken as 2.09×10^{19} cm^{-3}. (18) The conversion rate of SO_2 to H_2SO_4 is then expressed as a function of the

environment concentration of SO_2. If we set SO_2 = m ppbv, then the production rate of H_2SO_4 is:

$$P_1 = \frac{d[H_2SO_4]}{dt} = k[OH][M][SO_2]$$

$$= 6.6 \times 10^4 \text{ m molecules cm}^{-3}\text{sec}^{-1}$$

It is obvious that the relative importance of the gas phase oxidation rate is dependent on the ambient concentration.

In order to determine the actual number of acid molecules sticking on the cloud droplets, we assume an accomodation factor of 1 and the impinging rate (i.e., the number of molecules that arrive at the surface of the droplet per unit area per unit time) is estimated by the formula:

$$\beta = \frac{P}{\sqrt{2\pi mkt}} = \left(\frac{kT}{2\pi m}\right)^{1/2} N_B = bN_B, \qquad (4)$$

$$b = \left(\frac{kT}{2\pi m}\right)^{1/2}$$

where P is the pressure of H_2SO_4, k is the Boltzmann constant, m is the mass of one acid molecule, and N_B is the number concentration of the gaseous acid which we can assume equal to the production rate of that species times a certain factor.

The concentration of H_2SO_4 in the cloud droplet due to impinging can be expressed as:

$$C = \frac{bs}{AV} \cdot N_B \cdot t \cdot 10^3 \text{ (moles liter}^{-1}\text{)}$$

$$= \frac{3bt}{Ar} \cdot N_B \cdot t \cdot 10^3 \text{ (moles liter}^{-1}\text{)} \qquad (5)$$

where r = radius (cm)

S = area (cm^2)

V = volume (cm^3)

$b = \left(\frac{KT}{2\pi m}\right)^{1/2}$ (cm sec^{-1})

A = Avogadro Number

t = time (sec)

N_B = concentration (cm^{-3})

It is obvious from Eq. (5) that the smaller the droplet size and the longer the time of reaction, the greater the importance of the gas phase reaction followed by impinging to produce H^+ ions in the droplet.

Indeed, the gas phase reaction must be incorporated with the liquid phase reaction since those two processes are acting simultaneously. Consequently, Eq. (3) should be modified to include the gas phase reaction term as following:

$$\{1 + \frac{K_{ha}K_{1a}}{K_w} PNH_3\}[H^+]_t^3 - \{2[SO_4^{--}]_t + \Sigma\Sigma a_j n_i \frac{3b_j t}{Ar_i} N_j \cdot 10^3\}[H^+]_t^2$$

$$- \{K_w + K_{hc}K_{1c}P_{co2} + K_{hs}K_{1s}P_{so2}\}[H^+]_t - K_{hs}K_{1s}K_{2s}P_{so2} = 0 \qquad (6)$$

where i refers to size index

j refers to species index

n_i is the number of droplets with radius r_i

a_j is the covalence of species j

Eqs. (1), (2), and (6) form a closed set from which concentrations of different species in the droplet can be evaluated as a function of time for a given set of initial concentrations of ambient SO_2 and NH_3. The initial concentration of H^+ is a solution to Eq. (6) with an initial condition where $[SO_4^{--}]$ equals zero. The substitution of the value of $[H^+]$ to Eq. (2) will yield the value of $[SO_3^{--}]$. The $[SO_4^{--}]$ at a later time will then be determined from Eq. (1). The whole calculation scheme may then be repeated and the pH value of the droplet at any instant can then be evaluated.

Fig. (2) is a graph indicating the variation of pH value with the droplet size distribution. Curves A and B correspond to an ordinary cloud at 0° C with ambient SO_2 and NH_3 gas concentrations 1 ppbv and 3 ppbv, respectively. Curves C and D correspond to a polluted cloud with ambient SO_2 and NH_3 gas concentrations 10 ppbv and 3 ppbv, respectively. Curves A and C have included the production of sulfuric acid through gas phase oxidation. In an unpolluted environment, concentrations of gaseous H_2SO_4 molecules have been estimated as 1×10^7.

Here, we estimate the concentration of H_2SO_4 molecules by:

$$N_B = \frac{C_B}{Sb}, \quad b = \sqrt{\frac{kT}{2\pi m}} \qquad (7)$$

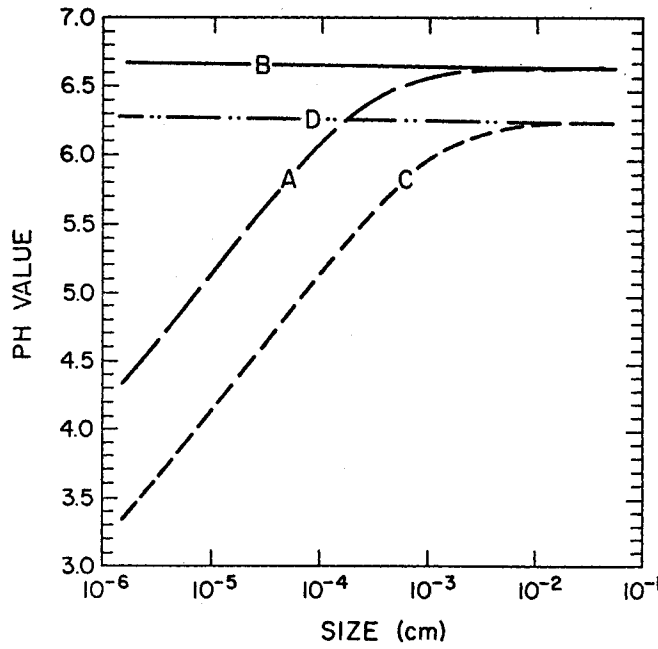

Figure 2. pH value of the cloud droplet as a function of its size. Curves A and B correspond to an environmental SO_2 and NH_3 concentrations 1 ppbv and 3 ppbv respectively. Curves C and D correspond to an environmental SO_2 and NH_3 concentration 10 ppbv and 3 ppbv respectively. Curves A and C are obtained by considering both the gases phase and liquid phase oxidation, but Curves B and D are obtained by considering the liquid phase oxidation alone. All values are obtained by using the oxidation rate suggested by McKay, and by assuming the cloud is at a level of 600 mb and the temperature is 0°C. The time of reaction is 10 minutes.

where C_B is the rate of production of H_2SO_4 and can be obtained by $C_B = k[OH][SO_2][M] = 6.6 \times 10^4$ molecules/(cm sec) for 1 ppb SO_2, and S is the total surface area of aerosol per cubic centimeter ($\simeq 10^2$ $\mu m^2/cm^3$ in rural area and $\simeq 10^3$ $\mu m^2/cm^3$ in urban area (19)). Equation (7) gives a steady state concentration of H_2SO_4. N_BSb is the total rate of the loss of H_2SO_4 to aerosol surface and in a steady state the total rate of the loss is assumed to be equal to the total rate of production (C_B). Thus, in the rural area the steady state concentration of H_2SO_4 is in the order of 10^7 molecules/cm^3. In a polluted environment, their

concentrations are accordingly increased by ten fold. Curves B and D correspond to the result obtained without considering the gas phase oxidation. Results shown in Figure (2) are obtained by assuming a cloud of liquid water content 0.2 gm/m^3 of air and exposed to the trace gases for 10 minutes. Here we used McKay's oxidation rate constant.

A comparison of curves A, C with B, D indicates that the additional consideration of gas phase oxidation will produce a pH value spectrum depending on the droplet size distribution, while the ignoring of gas phase oxidation will produce a pH value which is independent of the droplet size distribution. It is obvious that the consideration of gas phase oxidation in addition to the liquid phase oxidation will produce a lower pH value of cloud droplets.

Curve C indicates that a droplet with radius 0.01μ will have a pH value as low as 3.0. This is true as long as the droplet remains small, because in this case the hydrogen ions in the droplet are mainly due to the impinging of gaseous acid molecules. The concentration of hydrogen ions in the droplet due to impinging is inversely proportional to its radius. In the real atmosphere the droplet will grow. The lower the pH value of the droplet, the smaller is its partial water vapor pressure, and the greater is the number of water vapor molecules impinging on its surface. Consequently, the pH value will increase due to the growth of droplet.

In order to see the effect of temperature on the pH value of the cloud droplets, Figure (3) has been plotted by assuming a temperature of 10°C. A comparison of these two figures indicates that the lower the temperature, the higher the pH value. Figure (4) is obtained with the same environmental conditions as that of Figure (2) except here we use Scott and Hobbs' oxidation rate constant.

Finally, in order to see the effect of time duration on the average pH value of the cloud, a plot of average pH value versus time at 0°C with McKay's rate constant is shown in Figure (5). At the beginning, the difference between the two models, considering both the gas and liquid phase oxidations, and only the liquid phase oxidation is small. However, as the reactions continue, their differences increase. This is because the gas phase oxidation is proportional to time, the longer the time of reaction, the more important is the gas phase oxidation. On the other hand, the liquid phase oxidation is slowed down due to the increasing amount of free hydrogen ions in the droplet as reaction proceeds.

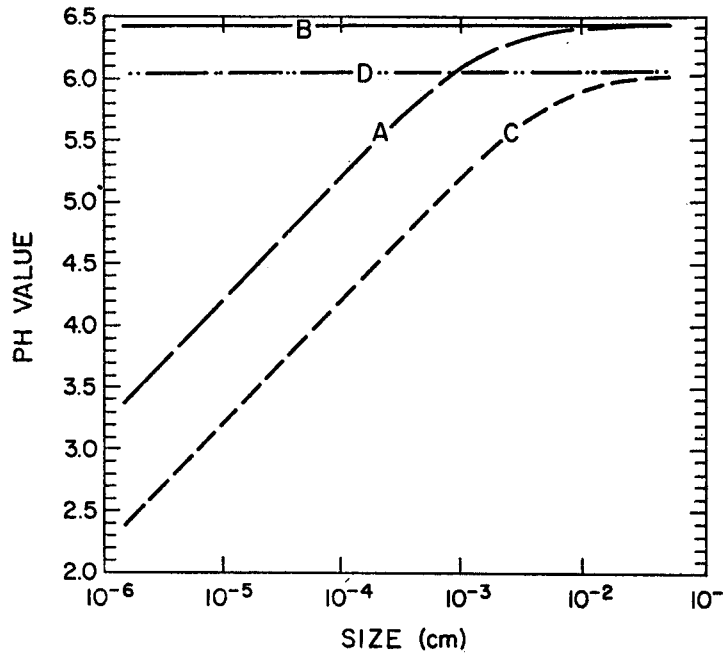

Figure 3. The same as Figure 1, except the temperature of the cloud is 10 C.

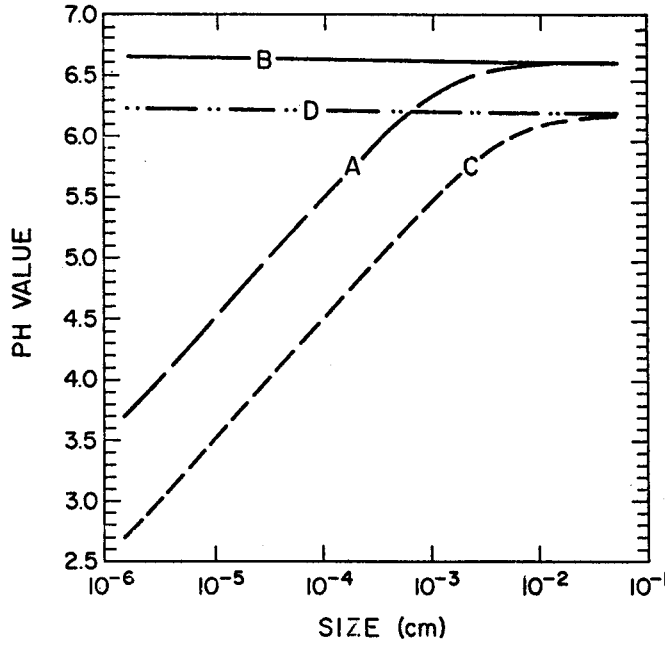

Figure 4. The same as Figure 2, except the oxidation rate is the one suggested by Scott and Hobbs and the H_2SO_4 concentration has been decreased by a factor of 2.

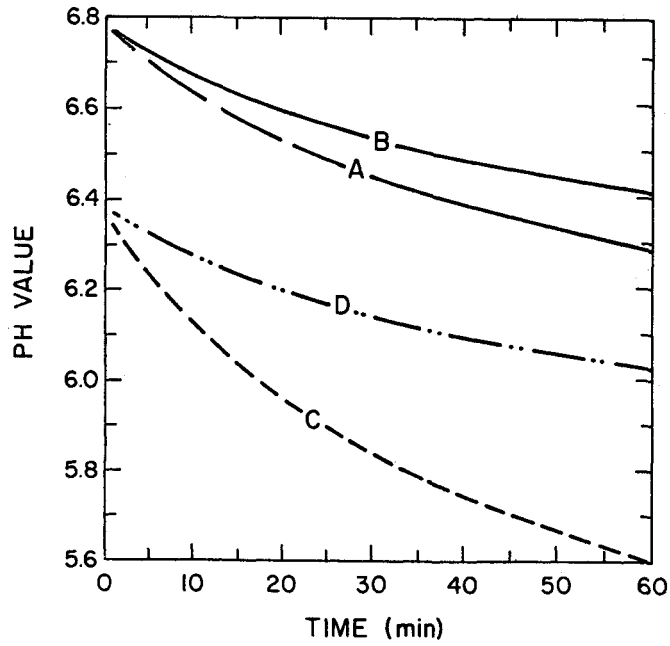

Figure 5. The average pH value of the cloud as a function of time Curves A and B correspond to an environmental SO_2 and NH_3 concentrations 1 ppbv and 3 ppbv, respectively. Curves C and D correspond to an environmental SO_2 and NH_3 concentrations 10 ppbv and 3 ppbv respectively. Curves A and C are obtained by considering both the gas phase oxidation and the liquid phase oxidation, but curves B and D are obtained by considering the liquid phase oxidation alone. All values are obtained by using the oxidation rate suggested by McKay and by assuming the cloud is at a level of 600 mb and the temperature is 0 C.

IV. ESTIMATION OF THE AMOUNT OF HCl RELEASED FROM THE CLOUD DROPLETS (See Figure 6)

In order to estimate the amount of HCl released into the atmosphere we must know the distribution of cloud droplets containing NaCl. Though different forms of sea-salt nuclei distributions have been suggested, four types are widely used. (Arnason and Greenfield). (20)

Based on nuclei distributions in the trade wind region (Woodcock)

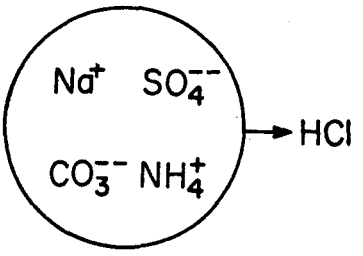

Figure 6. A diagram to show the release of HCl into the atmosphere from the hydrometeors during the evaporation process.

(21) Eriksson (22) suggested the following analytical form:

$$\frac{dn}{dr} = n(r) = a_1 \mathrm{Exp}(-br^{1/2})$$

where n is the number of sea-salt particles per cubic centimeter of radii smaller than r, and a_1 and b are constants having the values 6.31×10^2 and 6.9 respectively, when r is measured in microns. Another distribution, given by Mordy (23) in his numerical simulation of condensation, represents maritime conditions also based on observation by Woodcock. The third distribution, also maritime, is used by Warner (24) in a computation of droplet growth by condensation.

In contrast to the above three maritime distributions, the fourth one is more or less typical of continental conditions (25):

$$\frac{dn}{dr} = n(r) = \frac{c}{2,30} r^{-4} \qquad (9)$$

where c is a constant in the order of 10^{-7} to 10^{-8} if r is given in microns.

The equilibrium radii in response to a change in supersaturation S can be computed by means of the following equilibrium equation (26):

$$S - \frac{a}{r} + \frac{b}{r^3} = 0 \qquad (10)$$

where a $\frac{3.3 \times 10}{T}$, (T is absolute temperature), and b $\approx$ 4.3i m/M.

The amount of hydrogen chloride released into the atmosphere from a cloud at a supersaturation S after it moves to an unsaturated environment can be estimated by the following formula:

$$M_j = 36.5 \times 10^{-3} \sum_{K=1}^{n} \frac{4}{3} \Pi \left(\frac{r_s^k + r_s^{k+1}}{2}\right)^3 \cdot \Delta N_j^k \cdot [H^+]_k \qquad (11)$$

where M_j is the amount of HCl released into the atmosphere in units of $\mu g/m^3$ of air

r_s^k is the equilibrium radius at supersaturation S with group index k

ΔN_j^k is a particular distribution (j) of nuclei per cubic centimeter for a range r with group index k to k+1

$[H^+]$ is the concentration of H^+ ions for a particular cloud at the end of its life cycle and its unit is in moles/liter.

The amount of HCl released into the atmosphere as a function of life cycles of the cloud at 0°C for different types of nuclei distribution at an environment of zero percent supersaturation is shown in Figures (7) and (8). Curves A, B, C and D in Figures (7) and (8) correspond to the results obtained by using the above mentioned four types of nuclei distributions respectively. Here we use McKay's oxidation rate and assume the ambient concentration of SO_2 and NH_3 are 1 ppbv and 3 ppbv respectively. Graphs in Figure (7) are results obtained by considering both the gas and liquid phase oxidation of SO_2. Graphs in Figure (8) are results obtained by considering only the liquid phase oxidation of SO_2. A non-precipitating cloud may go through more than one cycle and more HCl will be released from an "older" cloud (recycled cloud condensation nuclei). Here the life cycle is assumed to be one hour.

Figures (9) and (10) are obtained by assuming the cloud is at a polluted environment; i.e., the ambient concentration of SO_2 and NH_3 are 10 ppbv and 3 ppbv respectively. Results in Figure (9) are obtained by considering both the gas and liquid phase oxidation of SO_2. Results in Figure (10) are obtained by considering only the liquid phase oxidation of SO_2.

As the supersaturation of the environment changes the liquid water content of the cloud will change accordingly. Consequently, the amount of HCl released from such cloud will change. In order to see the effect of liquid water content of the cloud on the amount of HCl released into the atmosphere, plots of the amounts of HCl released as a function of the liquid water content of the cloud for different environmental conditions at the end of the first life cycle of the cloud are shown in Figure (11). Results are obtained by considering both the liquid and gas phase oxidation of SO_2. Here we assume that the concentration of ambient SO_2 is 1 ppbv, and curves A, B, and C correspond to concentration of NH_3 1 ppbv, 2 ppbv and 3 ppbv respectively. The increases of environmental NH_3 concentration will decrease the production of HCl from a non-precipitating cloud.

In order to evaluate the significance of the production of HCl through the mechanism discussed in this paper, here we present a rough

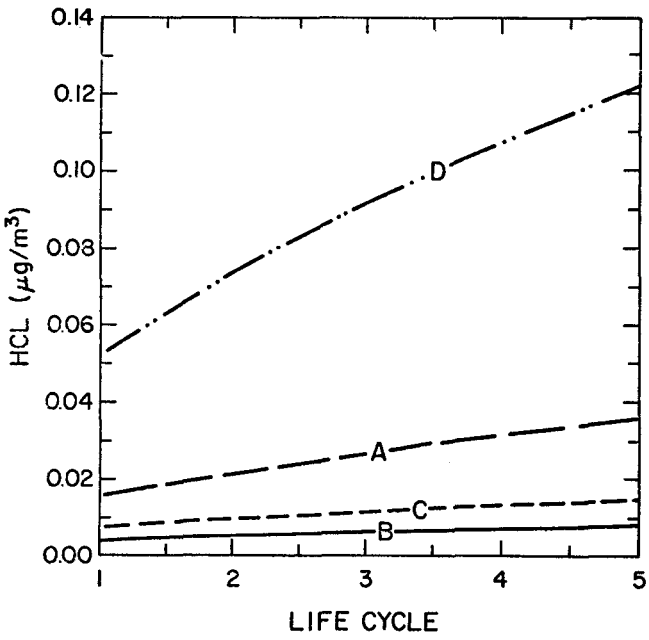

Figure 7. Amount of HCl released into the atmosphere from the cloud as a function of its life cycle. The cloud is at 600 mb and its temperature is 0 C. The environmental SO_2 and NH_3 concentrations are 1 ppbv and 3 ppbv respectively. The life cycle is assumed to be one hour. The results are obtained by using McKay's oxidation rate and considering both the liquid and gas phase oxidation of SO_2. Curves A, B, C and D correspond to nuclei distributions suggested by Erikson, Mordy, Warner and Junge respectively.

estimation of the global production of HCl through the interaction between trace gases and hydrometeors. We assume an average cloud thickness of 2000 meters and the mean global cloud cover as 0.54 (27). We further assume that the life cycle of a cloud is one hour and a cloud can go through five cycles which takes ten hours. If the SO_2 and HN_3 concentrations are both 1 ppbv and we only consider liquid phase oxidation, the global production of HCl is 1.73×10^8 tons/year. However if additionally we consider the gas phase oxidation, the global production of HCl changes to 2.2×10^8 tons/year. If we assume the SO_2 concentration is 10 ppbv and the NH_3 concentration is 1 ppbv and consider both the gas and liquid phase oxidation, the global production of HCl is 9.32×10^8 tons/year. Our estimation is of the same order of magnitude as the annual production rate of 6×10^8 tons calculated by Duce (4).

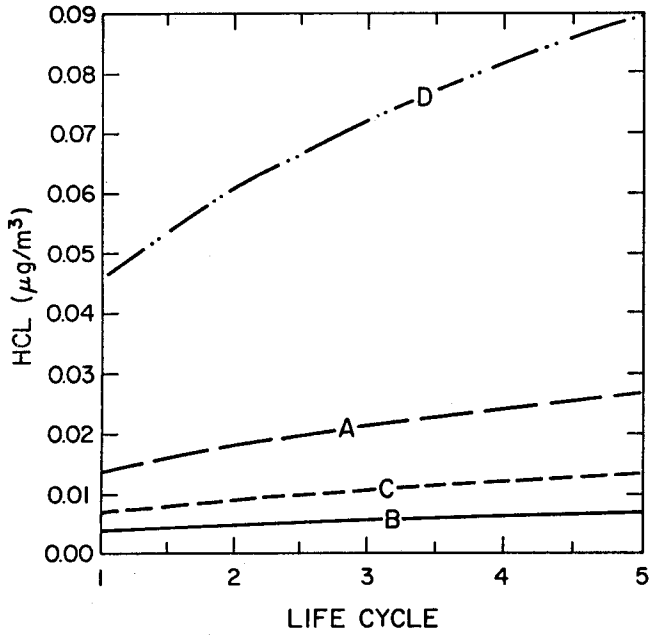

Figure 8. The same as Figure 7, except only the liquid phase oxidation of SO_2 has been considered.

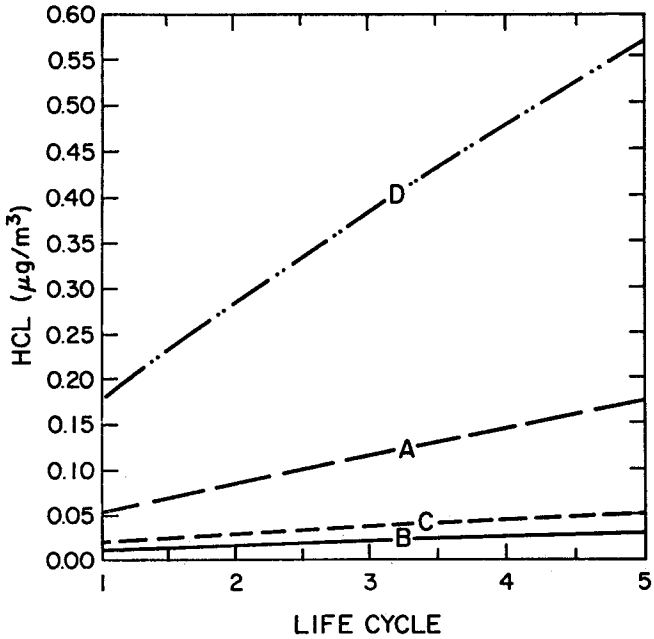

Figure 9. The same as Figure 7, except the cloud is at a polluted environment in which the concentrations of SO_2 and NH_3 are 10 ppbv and 3 ppbv respectively.

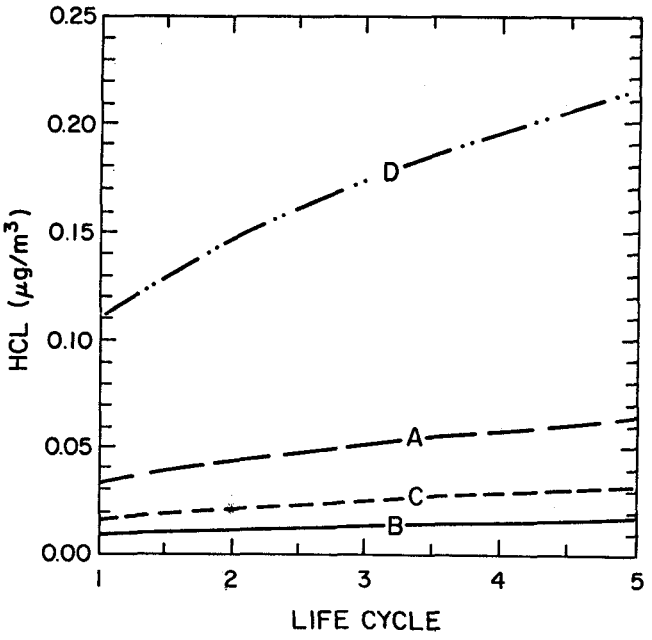

Figure 10. The same as Figure 9, except only the liquid phase oxidation of SO_2 has been considered.

It is important to point out here that the above calculations for the amount of HCl production due to the interactions between the trace gases and hydrometeors is based on the assumptions that the HCl gaseous molecules are released from the cloud droplets only when the cloud droplet is undergoing evaporation process. For a non-evaporating cloud droplet the amount of HCl released from the cloud droplet is depending on the concentration of HCl in the air around the cloud droplet and the partial pressure of HCl in the cloud droplet. If the partial pressure of HCl in the air is much less than the partial pressure of HCl in the cloud droplet, our calculation would be essentially correct. Therefore, the calculation presented in this paper represent an upper limit for HCl production. A more accurate calculation for the production of HCl by the proposed mechanism should consider the difference of the partial pressures of HCl in the cloud droplet and its surrounded air.

V. CONCLUSIONS AND DISCUSSIONS

We have discussed the differences between the chemical models considering only the liquid phase oxidation of trace gases and the more realistic model considering both the gas and liquid phase oxidations. The additional consideration of gas phase oxidation of trace gases will further lower the pH value of the cloud droplets and will produce a pH

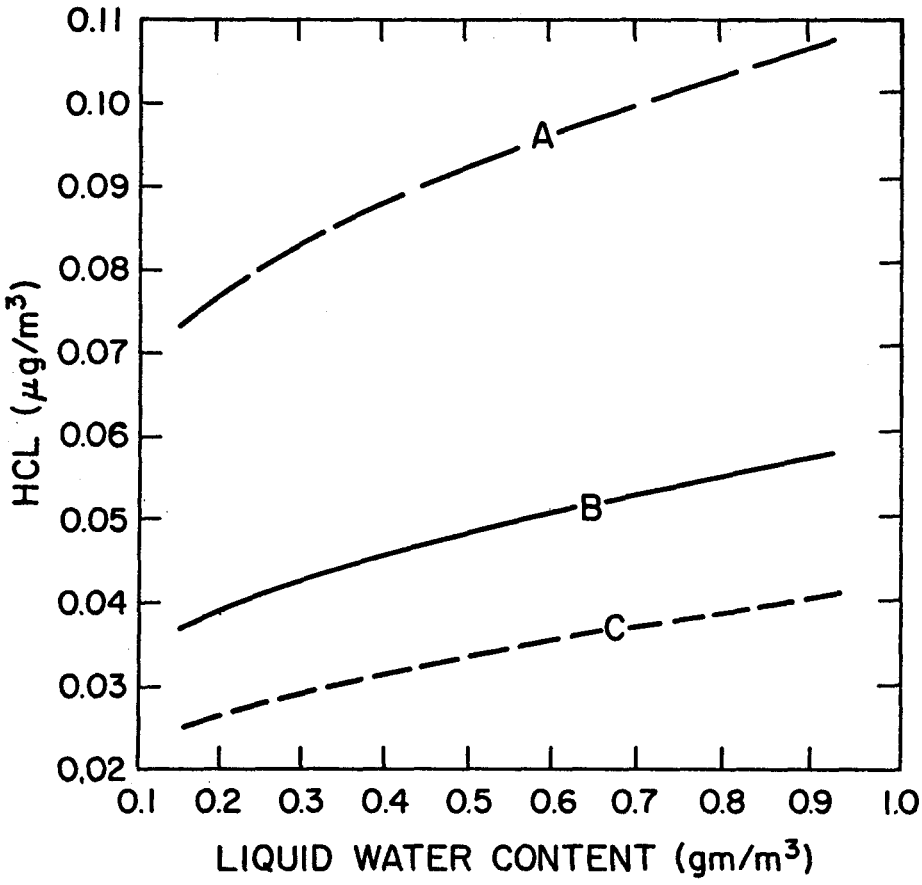

Figure 11. Amount of HCl released into the atmosphere from the cloud as a function of its liquid water content. The environmental SO_2 concentration is 1 ppbv and curves A, B and C correspond to environmental concentration of NH_3 1 ppbv, 2 ppbv and 3 ppbv respectively. Here results are obtained by considering both the liquid and gas phase oxidation of SO_2.

value spectrum depending on the drop size distribution. Generally speaking, the relative importance of these two mechanisms depends on the size distribution of droplets, the time duration of the reaction, the relative abundance of trace gases, and the assumed oxidation rate.

We have demonstrated that non-precipitating clouds containing NaCl can produce a source of free HCl in the atmosphere. The amount of HCl liberated from cloud droplets depends on the following factors: (a) the temperature of the cloud; A higher temperature of the cloud will produce more HCl; (b) the assumed oxidation rate; By using McKay's oxidation rate constant will produce more HCl; (c) the ambient concentration of SO_2 and NH_3; More SO_2 in the environment will produce more HCl, however more NH_3 in the environment will produce less HCl; (d) the

concentration of gaseous acid molecules; More gaseous acid molecules in the environment will produce more HCl; (e) the life cycle of the cloud; More HCl will be released from an "older" cloud; (f) the liquid water content of the cloud; A cloud with higher liquid water content will produce more HCl.

The amount of HCl released into the atmosphere is a combined result of the intricate physical and chemical processes occurring inside the cloud. Due to the complexity of the problem, here we consider only the case in which the droplet is static and does not grow. The macro- and micro-physical processes of a cloud will certainly influence the pH value of the cloud droplets and the effectiveness of HCl production mechanism. Field measurements are urgently needed to reveal the droplet size distribution of the pH value and the spacial distribution of HCl.

ACKNOWLEDGEMENT

This work was supported by the National Science Foundation, Atmospheric Science Section through Grant No. A022760003.

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SO_2-NH_3-PARTICULATE MATTER-H_2O REACTION SYSTEM AS RELATED TO THE RAINFALL ACIDITY

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ABSTRACT

Acidity of rain water is a major concern due to the progressive acidification of soils, its effect of flora and fauna and its corrosiveness to metals. Sulfur dioxide, through chemical transformations and atmospheric scavenging, is thought to be one of the major contributors to the acidity of rainwater. The straightforward oxidation of SO_2 to $SO_4^=$ in the presence of ammonia and metal oxides should lead to a resulting pH higher than what is usually encountered and also to much faster disappearance of SO_2 during rain. These apparently contradictory conclusions may be reconciled by a more complete analysis of the reaction system.

This paper discusses a recent experimental study of the kinetics of a reaction system containing micromolar quantities of SO_2, NH_3 and particulate matter in the presence of a relatively large amount of water. The results indicate that the rain water acidity through atmospheric scavenging must account for the formation of very strong acids, such as dithionate ion as well as sulfate and bisulfate ions, in a very complex reaction system, if the observed mean pH values of 4 to 5 are to be theoretically justified. Some field measurements downwind from a major power plant are also reported to relate the laboratory measurements to the field measurements.

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TIME DEPENDENCE OF THE pH OF RAIN

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ABSTRACT

Standard procedures for determining the pH of rain samples usually involve substantial delays from the time of rainfall to the time of analysis. This assumes that no change in pH occurs during the storage period. We have found that this is not always true. We have determined that individual rain water samples possess a time dependent pH which can be correlated with the surface wind trajectories terminating at our sampling location (Schenectady, New York). Our preliminary investigations have identified four characteristic time dependent behaviors: 1) if the trajectories generally proceeded from the west along the Mohawk Valley the pH gradually increased by about 1/3 in 2 to 4 days; 2) if the trajectories were from the south up the Hudson Valley the pH remained constant; 3) if they came from the east across southern Massachusetts the pH gradually increased by about 1/6; and 4) if they came from the north and west across the southern Adirondack Mountains the pH increased by about 1/5 in a few hours. After these changes occurred, the pH remained constant. No correlations occurred between pH and either surface winds at the time of precipitation or the 500 mb trajectories. This data suggests that for rain water, a time dependent behavior, the [H+] is understated by as much as an order of magnitude.

The samples of rain were collected by a glass funnel. As soon as sufficient water was obtained in glass bottles they were taken inside and a series of pH measurements was immediately started.

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NATURAL DUST AND ACID RAIN

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ABSTRACT

Atmospheric dust originates from three sources, terrestrial airborn matter, volcanic, and cosmic. Terrestrial natural dust makes up the main bulk reflecting the soil composition to 150 miles away. Soil erosion from flood plains, plowed fields and construction sites are the main source. Quartz, feldspar, the carbonates calcite and dolomite, and clay minerals are the components in decreasing order of frequency. Natural dust in the atmosphere interacts with rainwater converting the carbonates to benign gypsum ($CaSO_4.2\ H_2O$). Naturally leached soils produce less calcite than unweathered sediments on flood plains and construction sites, and in granitic and crystalline rocks less than in limestone areas.

Heavy industrialization associated with high emission of CO_2 and SO_2 on the one hand, and excess production of dust on the other appear to counteract man's interference with natural ecosystems in opposite direction.

Acid rain is made responsible for the acceleration of the natural decay of stone, for the accelerated leaching rate of soils and the change of growth rate of vegetation. Likens, Bormann and Johnson (1972) claim that the average pH of rainwater of the Rhine - Ruhr industrial area of West Germany has dropped from about pH=5 to less than pH=4 in the years between 1956 and 1966. The near exponential rate change of weathering of stone monuments for the Rhine-Ruhr area was documented by Winkler (1973) with time-lapse photos of Herten Castle in Westfalia, Germany (Fig. 1) carved from calcite-cemented Baumberg sandstone: one photo was taken in 1908, the second in 1968. Figure 2. shows the semi-quantitative plot for the Herten Castle since its construction in 1702; this curve is believed to be valid also for many other monuments in industrialized areas of the world (Fig. 3). Likens and Bormann (1974) ascribe the decrease of rainwater pH in the last 20 years in New England and other areas of the world to the

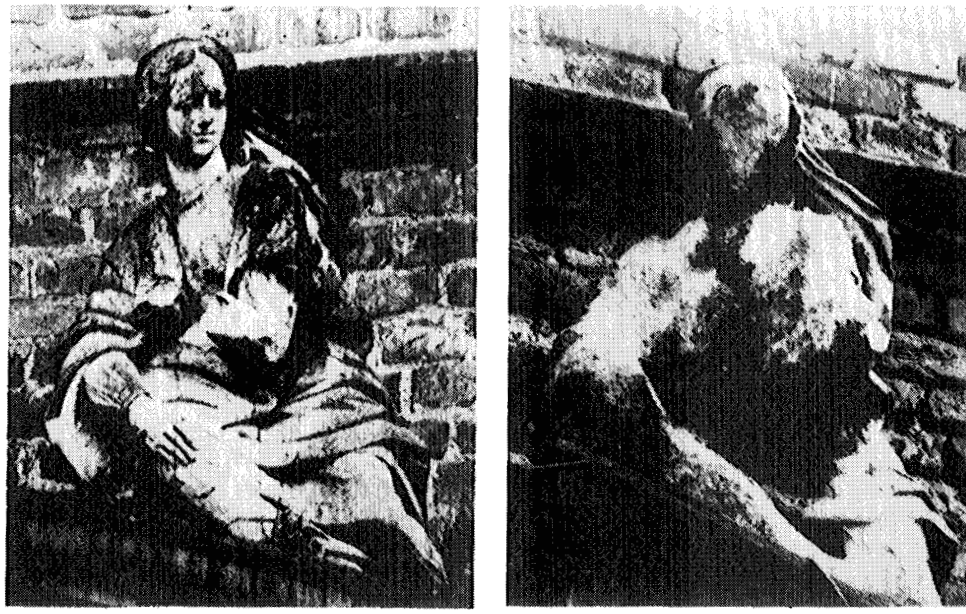

Figure 1. Time-lapse photos of statues at Herten Castle near Reckling-hausen, Westfalia, Germany, built in 1702. The left side picture was taken in 1908, the right side picture 1969, showing almost complete destruction of the surface. Porous Baumberg sandstone is composed of mostly quartz grains which are cemented with soluble calcite. Photos and information were supplied by Mr. Schmidt-Thomsen, Landesdenkmalamt Westfalen-Lippe, Muenster, Germany.

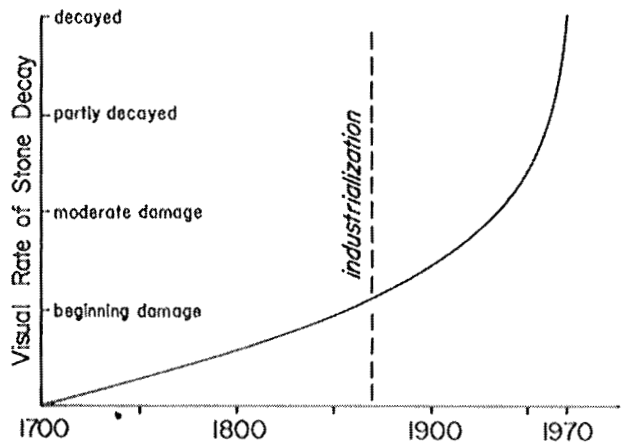

Figure 2. Graphic presentation of approximate weathering rate for picture set of statue at Herten Castle, Westfalia, Germany, illustrated in Figure 1.

Figure 3. Rapid decay towards total destruction of relief on tympanon of parish church in Opherdicke, near Unna, Westfalia. Destruction was severe in 1893, after 600 years of exposure, but catastrophic within the last 80 years. The rate of weathering of Figure 2. appears to apply here too. Stone is Soest Greensandstone with 65% calcite. Photos and information were supplied by Mr. Schmidt-Thomsen, Landesdenkmalamt Westfalia-Lippe, Germany.

increased use of fuel oil and natural gas, also to the reduction of neutralizing alkalic reacting soot by mandatory industrial dust precipitators. The presence and the interaction of natural airborn dust is not mentioned. Winkler (1973) gives three components for natural dust:

1. Windblown dust, from dry river beds, flood plains and beaches, but also from plowed fields and construction sites lacking a protective vegetative cover. Quartz, carbonates, feldspars, and clay minerals are the most important mineral components.

2. Volcanic dust: The explosive eruption of volcanoes has sent dust into the upper atmosphere, essentially as silica glass, where it has travelled for several years before it could settle back to the earth's surface.

3. Extraterrestrial dust or cosmic dust is found in marine sediments of most geological ages as small pellets of iron and silicate glass. Their chemically inactive character and the minute

quantities present make their effect insignificant.

The following table summarizes natural dust, its mineral content and relative reactivity with air pollutants:

COMPOSITION OF NATURAL DUST

Mineral Composition: Approx. Reactivity:

1. Terrestrial Dust, the most essential component of windblown silt:

   a) dust from carbonate rocks (limestone, dolomite):
      agricultural soils... clay, quartz ..... little reactive
      flood plains ..... calcite, some clay .. calcite most reactive
      construction sites ... calcite, clay ..... calcite most reactive

   b) dust from crystalline rocks (granite, gneiss, slate, etc.):
      agricultural soils ... quartz, clay ..... little reactive
      flood plains ..... quartz, clay, silicates.. little reactive
      construction sites ... quartz, clay, silicates.. little reactive

   c) dust from glacial till (moraines):
      agricultural soils ... quartz, clay, (silicates).. little reactive
      flood plains ..... quartz, clay, calcite... reactive (calcite)
      construction sites ... quartz, clay, calcite... reactive (calcite)

   d) dust from glacial outwash (sand and gravel):
      agricultural soils ... quartz, silicates,(calcite). reactive
      flood plains ..... quartz, silicates, calcite.. reactive
      construction sites ... quartz, silicates, calcite.. reactive

2. Volcanic Dust: glassy silicates; about one tenths of terrestrial dust:
      quartz, silicates... very little reactive

3. Cosmic Dust: glassy silicate and glassy metallic; amount is minimal:
      no reaction expected

Quartz, the carbonate minerals calcite and dolomite, the feldspars, ferro-magnesian silicates and various clay minerals are the mineral components of importance. Calcite in dust readily reacts with the acids in the rainwater despite its brief contact between the cloud base and the surface of the terrain. The slow sinking velocity of silt-sized particles in still air ranges from 1 mm to 1 cm per second (fig. 4); calcite has thus enough time to react with the acids in the

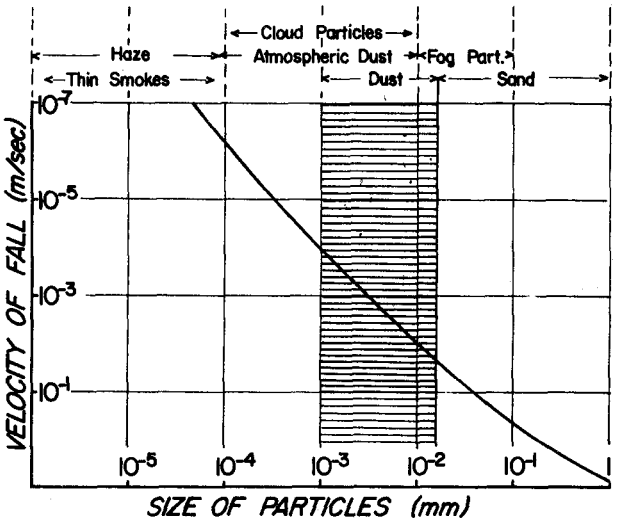

Figure 4. Sinking velocities of particles in still air. The size of natural dust is marked.

air whereby high relative humidity can accelerate the reaction. The sulfate ion is not eliminated from rain but converts from sulfurous or sulfuric acid to relatively harmless gypsum, $CaSO_4$. The sulfate ion tied up in gypsum is not noxious to man. Waters rich in sulfate, however, are known to have severely attacked alkalic cement and concrete. The presence of water-soluble gypsum appears to explain the frequent high calcium content of rainwaters. Sumi et al. (1959) describe gypsum as the chief water-soluble component in the atmosphere of almost all industrialized areas.

The mineral quartz is inert and non-reactive; clay crystals, however, can absorb ingredients and hold them tightly on their crystal surfaces which may help to neutralize some acid components in the air temporarily until they can be released again to the soil. Feldspars and the ferro-magnesian silicates react with the tiny H^+ cation in acid rain producing less acid conditions of the rain when tied up during the weathering process. The time of interaction in the atmosphere appears to be sufficient for the reaction.

The mineral composition of natural dusts depends primarily upon

the area of origin, as well as whether the dust is derived from deeply weathered agricultural soils, from fresh or weathered glacial drift materials, or from flood plains and construction sites. Despite local accumulations of windblown debris of considerable magnitude in the geological past, the rate of dust deposition is believed to have possibly tripled since man has started agricultural activity and construction by scarring the protective sod cover of the American plains. Davitaya (1969) has noticed considerable increase of dust in the firn of the remote mountains of the Caucasus caused by both natural and human recent events, like the eruption of Mt. Krakatoa in 1883, and others. Yaalon and Ganor (1973) discuss in detail dust transport from desert floors, dry flood plains and valley trains of glacial outwash. Dust can be lifted upward from bare ground to a height of 1500 to 2000 m, when turbulent surface winds prevail, common near high-pressure fronts. Theoretically, wind does not lift silt-sized particles off the ground as shown in Figure 5., as the dead air layer affects the

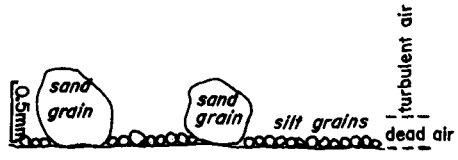

Figure 5. Sand and Silt grains, schematized. Silt grains within the dead air layer are not readily picked up by wind.

silt size. Splashing and bouncing impacts only can mobilize the grains. Soil aggregates smaller than 0.84 mm diameter are subject to sind erosion with a non-linear increase with decreasing grain sizes, whereby air friction can break up the soil grains. Grain diameters larger than 20 µm settle to the ground relatively fast. The plowing and tilling of dry fields, the activity of road graders and soil moving devices on major construction sites stir up clouds of dust eliminating the need for strong air turbulence at the ground surface level. The dust production is also increased by over-grazing and traffic by cattle, like in the Sahel drought belt of Africa today. No reliable data are available for man's participation of natural dust in the air.

Likens and Bormann (1974) report acid rainwaters at near pH = 4 in New England which were also recorded at Geneva and Ithaca, New York; the acidity has increased since about 20 years ago and is believed to have been associated with the increase of natural gas and oil consumption, but also with the compulsory installation of particle-removing devices from flue gasses. The extrapolation of acidity of rain into the near future may raise the question whether or not man's interference in possibly two opposite directions can re-establish

original pre-interference conditions in the acidity of rainwaters: high acidity of the rainwater by air pollution on the one hand and higher production of neutralizing natural dust and soot on the other. The question is thus arising why abnormal acidity arises only in some places. e.g. in New England though the sulfates and other acid ingredients from industrial sources are spreading about equally through atmospheric dispersion throughout the industrial part of the United States. This writer believes that the dense and continuous forest cover of the New England states produces much less natural dust than the agricultural prairie states (Fig. 6); in addition, the area is

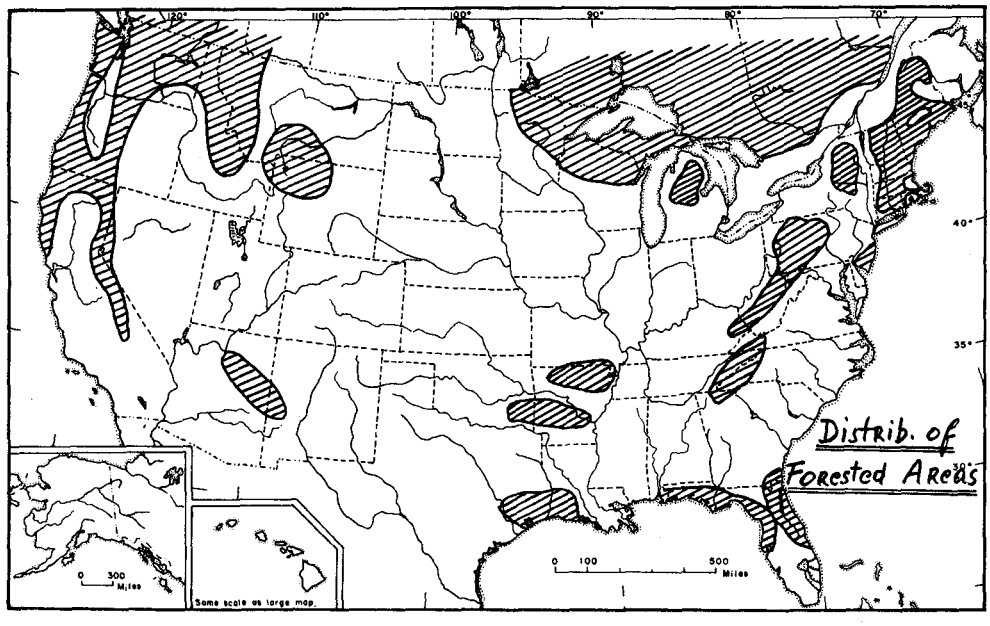

Figure 6. Distribution of forested areas of the United States.

almost entirely underlain by igneous and metamorphic rocks which do not produce acid-neutralizing calcite. Figure 7. shows the distribution of major areas with crystalline rocks exposed at the surface. A tentative range of about 240km (150 miles) from carbonate areas should be allowed, necessary to supply the major bulk of carbonate dust. This author is also convinced that the degree of calcite leaching of the upper soil layer has a strong bearing on the supply of calcite to the dust.

It is difficult to evaluate the true neutralizing strength of both natural and industrial dusts. A closer investigation could give directives where precipitators for industrial dust removal should be employed in order to avoid damage by acid rain in the future. Thus the requirements for future installations of industrial scrubbers should be based upon regional, geological-ecological considerations if

we want to eliminate further damage by acid rains to the environment, and finally to man himself.

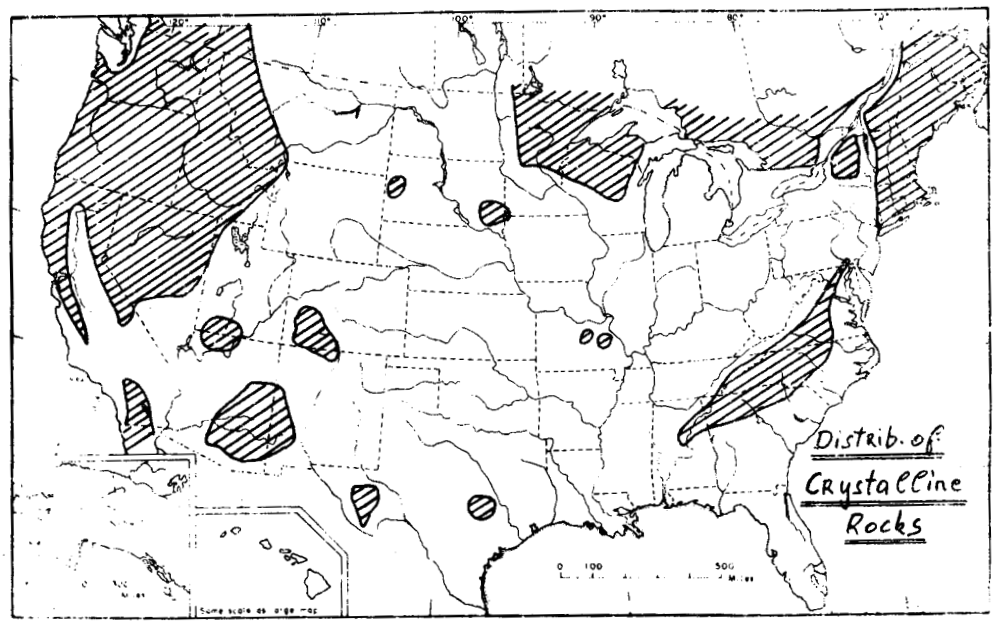

Figure 7. Distribution of non-calcareous crystalline rocks of the United States.

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SOME CONSIDERATIONS ON THE WASHOUT OF SULFATE FROM STACK PLUMES

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ABSTRACT

A theoretical analysis of the contribution to rainwater sulfate concentration by precipitation scavenging of gaseous SO_2 and sulfate containing aerosols is presented. Aspects, such as the proper choice of mean raindrop diameter, are discussed in detail, and guidelines for their use are explored. Sample calculations are provided in which emissions from an hypothetical stack are considered as the source of the gaseous SO_2 and sulfate aerosol. The basic assumption of irreversible sorption behavior is discussed and utilized to obtain an upper limit to the resulting sulfate concentration.

The effect of raindrop diameter on the sulfate concentration is not consistent. However, for a given drop diameter the sulfate concentration decreases as the precipitation rate increases. The sulfate concentration resulting from aerosol scavenging depends on the particle diameter and the precipitation rate. The sulfate concentration shows a maximum with respect to particle size; at moderate distances from the source, it is maximum for particles having aerodynamic equivalent diameter of about 5 μm to 10 μm.

INTRODUCTION

The washout of sulfate from the atmosphere occurs by absorption of gaseous sulfur dioxide or by scavenging of sulfate containing aerosol particles. Both mechanisms have received considerable attention.

The data of Hales, Thorp, and Wolf (1971) showed no strong relationship between mean raindrop size and sulfate washout but did show an inverse relationship with background acidity of the rain (Hales, 1974). Hutcheson and Hall (1974) recently reanalyzed the field experimental data of Ensminger and Martin (1957). They concluded that

aerosol scavenging was not responsible for the sulfate washout, but that SO_2 absorption was the primary mechanism.

In this paper, we will present a theoretical analysis concerning the sulfate concentration of rainwater resulting from precipitation scavenging of gaseous SO_2 and sulfate containing aerosols emitted from an ideal emission source.

THEORETICAL CONSIDERATIONS

As already pointed out, the washout of sulfate from stack plumes occurs by absorption of gaseous SO_2 or by collection of sulfate containing particulates. These mechanisms act in parallel, and their effects on the resulting sulfate content of the rainwater are then additive.

ABSORPTION OF SO_2 BY RAINDROPS

The fundamental considerations of precipitation scavenging of soluble pollutant gases has been nicely summarized by Hales (1972). In that paper the author pointed out that the calculation of precipitation scavenging rates for trace gases is complicated by several factors. Some of these are reversible sorption behavior, liquid phase mixing, and chemical reactions in the liquid phase. Hales considered each of these factors.

If the absorption process is reversible, calculation of this type of scavenging can lead to substantial computational difficulties. Reversible absorption would be operative if the dissolved gas does not undergo any chemical reaction and can be desorbed into the gas phase in its original state. With such phenomena, there can be a redistribution of the pollutant in the atmosphere. Consider for the moment a plume that is approximately gaussian in the vertical. As a particular raindrop enters the plume it experiences an increasing concentration until the plume centerline is reached. For a high mass transfer rate, it is possible that the raindrop is nearly saturated at this point in its travel. As it proceeds below the plume centerline, the raindrop now experiences a decreasing concentration of the species in the gas phase; and the direction of the driving force for mass transfer is out of the drop. Slinn (1974a) has analytically considered reversible sorption behavior and the resulting redistribution of the plume. The influence of the reversible precipitation scavenging is that the plume diffuses about the effective source height corrected for a washdown speed. Slinn's results for small distances of travel (his Eq. 24) are similar to that obtained for irreversible first order scavenging (c.f., Heines and Peters (1973)).

Reversible sorption phenomena can be significant for species that undergo only slow chemical reactions in the liquid phase. This, however, may not be true of SO_2. Liss (1971) has theoretically shown that for waters having a pH > 4, the transfer of SO_2 from air into the liquid phase is gas phase controlled. Brimblecombe and Spedding (1972) have substantiated this for specific experimental conditions, and this is in agreement with the criteria of Hales (1972). He pointed out that the system is mass transfer controlled in the gas phase if $D_c k_r / 3K_g \mathfrak{H} >> 1$, where D_c is the raindrop diameter, k_r is the liquid phase reaction rate, K_g is the overall mass transfer coefficient based on the gas phase, and $\mathfrak{H}$ is Henry's Law constant. For SO_2, the hydration rate constant is on the order of $10^6 s^{-1}$, $\mathfrak{H} \approx 10^{-2}$, $D_c \approx 10^{-3} m$, and $K_g \approx 10^{-1} m/s$. Thus, $D_c k_r / 3K_g \mathfrak{H} \approx 10^6$. If this is the case, the annihilation of SO_2 as a dissolved species within the drop is so rapid that the liquid phase resistance is negligible, and the SO_2 exerts an insignificant back pressure.

However, the liquid phase oxidation cannot be considered infinitely fast, and in the consecutive processes, may be the rate limiting reaction rather than the prior hydrolysis rate of SO_2. As a result, this concept of the irreversible behavior of the SO_2 absorption may not be entirely accurate. The liquid phase oxidation is affected by numerous species. Johnstone and Coughanour (1958) found that the oxidation of SO_2 in a sulfate catalyst solution was relatively fast. However, as the pH was decreased to relatively low values the oxidation slowed. The pH of their acid solutions was probably lower than what one normally anticipates in raindrops. The analysis of Scott and Hobbs (1967), expanding on the experiments of Van den Heuvel and Mason (1963), indicated that the rate determining step is the liquid phase oxidation of the bisulfite (HSO_3^-) to the sulfate. The ammonium ion catalyzes this reaction by maintaining a high pH.

While the question of reversibility of the sorption phenomenon cannot be answered with certainty at this time, it does appear that one cannot consider the scavenging of SO_2 as a simple reversible hydrolysis behavior in pure water (Hales and Sutter, 1973). At this time, it seems more extensive studies on the oxidation of SO_2 in the water phase containing typical contaminants is warranted to answer fully this question of reversible sorption behavior. Nevertheless, the assumption of irreversible absorption provides an upper limit to precipitation scavenging of gaseous SO_2. For this case, the system is first order and irreversible; and the first order loss constant, k, can be described in terms of the gas phase mass transfer coefficient. If each raindrop size contributes to k independently, one can write, considering the normalized distribution of raindrops sizes as $f(D_c)$,

$$k = \int_{D_c^0}^{D_c^\infty} N f(D_c)\ \pi D_c^2 k_g(D_c)\ dD_c \qquad (1)$$

where N is the total number of raindrops per unit volume, $k_g(D_c)$ is the gas phase mass transfer coefficient, and D_c^0 and D_c^∞ represent the smallest and largest raindrop sizes present, respectively. For spherical drops, the Froessling equation (c.f., Skelland, 1974) is most frequently used to estimate k_g,

$$Sh = 2.0 + 0.6\ Re_c^{1/2}\ Sc^{1/3} \qquad (2)$$

where $Sh = k_g D_c/\mathscr{D}$, $Re_c = \rho D_c U_t/\mu$, and $Sc = \mu/\rho\mathscr{D}$. Equation (2) can be imagined to be comprised of a molecular diffusion contribution (2.0) and a convective contribution ($0.6\ Re_c^{1/2}\ Sc^{1/3}$).

It is generally not convenient to use Equation (1) in the integral form but rather to employ some mean diameter. One might ask which mean diameter is appropriate. Equation (2) shows that k_g varies as $1/\sqrt{D_c}$ at high Re_c where the contribution of the constant 2.0 is not substantial. Thus, the appropriate mean diameter is intermediate to the length mean diameter and the area mean diameter. In order to evaluate this factor more completely, Equation (1) was numerically integrated, assuming the raindrop size is logarithmic-normally distributed, and this value of k was compared to the value calculated if the root mean square of the length mean diameter and the area mean diameter ($\bar{D}_{\sqrt{1a}}$) were used.

It should be noted that the raindrops were assumed to be falling at their terminal velocity. The error resulting from this approximation is shown in Table 1 for several values of the number median diameter ($\bar{D}_g^1$) and the geometric standard deviation (σ_g)†. The error is quite small, and it is considerably greater if either the length or area mean diameter is employed. Under the conditions evaluated the absolute error can be 26% using the length or area mean diameter, and as large as 90% if one would use the volume (or mass) mean diameter.

Table 1
Percent Error in Estimating k by Using $D_{\sqrt{1a}}$

σ_g \ $\bar{D}_g^1$	0.6mm	1.0mm	1.4mm	1.8mm	2.2mm
1.2	-1.3	-1.3	0.3	-0.5	-0.6
1.4	-4.4	-2.4	-0.6	-1.7	-2.0
1.6	-7.1	-2.6	-2.1	-3.0	-3.4
1.8	-7.2	-0.6	-2.0	-2.9	-3.3
2.0	-4.2	2.1	0.3	-0.5	-0.8

†$D_{\sqrt{1a}}$ can be obtained from $\bar{D}_g^1$ and σ_g as

$$\ln D_{\sqrt{1a}} = \ln \bar{D}_g^1 + 0.75 \ln^2 \sigma_g.$$

SULFATE AEROSOL SCAVENGING BY RAIN

Sulfates are in the form of aerosol particles, and particulate scavenging by rain is a well known phenomenon. Unlike deposition due to sedimentation which depletes only the lowest layers of the cloud, rain scavenging removes particulates below the entire rain forming layer. The mechanism of particulate capture in below-cloud scavenging can be by inertial impaction, by interception, or by diffusive collection of the dust particles by the raindrops. Let us consider each of these mechanisms separately.

The efficiency of collection by inertial impaction can be characterized in terms of the dimensionless Stokes number; i.e.,

$$St = \frac{C_f \rho_p D_p^2 U_t}{9\mu D_c} \tag{3}$$

where C_f is the Cunningham correction factor for the particulates, ρ_p is the density of the particles, D_p is the diameter of the particles, U_t is the relative velocity of the drops with respect to the particles, and μ is the gas phase viscosity. There have been several correlations suggested to estimate the efficiency of impaction, but one of the simplest is (Walton and Woolcock, 1960)

$$\eta_{Imp} = \frac{1}{(1 + 0.7/St)^2} \tag{4}.$$

This scavenging process is more efficient for larger sized particles, and thus affects the particle size distribution.

In the case of interceptive collection, a simple formula has been suggested for a potential flow field about the spherical raindrop (c.f., Fuchs, 1964); i.e.,

$$\eta_{Int} = (1 + \kappa)^2 - \frac{1}{1 + \kappa} \tag{5}$$

where κ is the interception parameter, and it is the ratio of the particle diameter to the collector raindrop diameter. The applicability of Equation (5) is somewhat limited due to the displacement of the particles by the boundary layer which is not accounted for in the potential flow field assumption. Slinn (1974b) has discussed this limitation. However, Equation (5) does provide a reasonable starting point to estimate η_{Int}.

The collection of particles by diffusion to spherical collectors is frequently based on Equation (2) evaluated for an aerosol system. While the correlation expressed by Equation (2) is, for the most part, based on the low to moderate Schmidt numbers usually experienced in liquid-liquid systems and gas-liquid systems, its applicability has been

generally assumed for the large Schmidt number aerosol case. If this extrapolation can be assumed, the diffusive collection efficiency can be written as (c.f., Strauss, 1966)

$$\eta_{Dif} = \frac{8}{Re_c Sc} + \frac{2.4}{Re_c^{1/2}\ Sc^{2/3}} \qquad (6).$$

Other equations showing similar predictions have been suggested.

The question of how to combine the individual collection efficiency contributions to estimate an overall value is almost always raised. It would be most gratifying if the problem were solved by dimensional analysis in a manner similar to that for cylindrical collectors (Pascari and Friedlander, 1960). In the absence of such a correlation, however, we prefer to assume that the collection mechanisms act in series and write (Strauss, 1966)

$$\eta = 1 - (1 - \eta_{Imp})(1 - \eta_{Int})(1 - \eta_{Dif}) \qquad (7).$$

Equation (7) affords the appropriate limit that $\eta < 1$ if the individual collection efficiencies are all less than unity.

The scavenging of particulates is essentially an irreversible and first order process; and if one assumes that each collision is effective and that the raindrops act independently, the rate constant is

$$k(D_p) = \int_{D_c^0}^{D_c^\infty} Nf(D_c)\ \frac{\pi}{4}\ D_c^2\ \eta(D_c) U_t(D_c)\ dD_c \qquad (8).$$

The question of chemical reaction irreversibility in the liquid phase is generally not considered since the scavenging is of the sulfate.

It should be noted that Equation (8) is written for a single particle size, and if the overall effect of a particle size distribution is sought a second integration is required; i.e.,

$$k = \int_{D_p^0}^{D_p^\infty} N_p g(D_p) k(D_p)\ dD_p \qquad (9).$$

For the moment, however, we will just consider Equation (8) and $k(D_p)$. The error in using a simplified form of Equation (8) with a mean raindrop diameter was also evaluated assuming the raindrop size to be logarithmic-normally distributed. If one uses an appropriate mean diameter, the error can be maintained relatively small. For the smaller particles -- on the order of 1.0 μm aerodynamic equivalent diameter and smaller -- where interceptive collection and to a lesser extent the

diffusive mechanism become increasingly important, $\bar{D}_{\sqrt{1a}}$ seems to be the most appropriate choice. This is understandable since η_{Int} varies roughly as $1/D_c$ and U_t varies roughly as $\sqrt{D_c}$ for the raindrops larger than about 1.3 mm. As a result, the integral is approximately

$$\int_{D_c^0}^{D_c^\infty} f(D_c)\ D_c^{3/2}\ dD_c$$

multiplied by a constant.

On the other hand for the larger particles where inertial impaction dominates, the area mean diameter,† $\bar{D}_a$ appears to be the proper choice. This is also reasonable since $k(D_p)$ is increasing and is in the range where η_{Imp} varies approximately as $1/\sqrt{D_c}$.

CONCENTRATION OF POLLUTANT FROM A POINT SOURCE WITH HOMOGENEOUS SCAVENGING ACTIVE

Chamberlain (1953) performed calculations employing an exponential correction to Sutton's (Sutton, 1932) plume model equation. Other investigators (Engelmann, 1968) have also studied this problem by evaluating the overall washout. However, it is our intent to evaluate the effect of this type of rain scavenging on the resulting sulfate content of the rain.

The eddy diffusion model concept can easily handle scavenging processes occurring either within the plume or at ground level. Consider the behavior to be steady state with the understanding that the eddy diffusivity accounts for the turbulent fluctuations of time scale less than that of the averaging time. Furthermore, presume that the positive x-axis is aligned with the wind field averaged over the same time period. Finally, note that only first order irreversible loss terms are operative. For transport in the x-direction dominated by convection, the governing partial differential equation is (Heines and Peters, 1973)

$$U \frac{\partial c}{\partial x} = A_y\, x^q \frac{\partial^2 c}{\partial y^2} + A_z\, x^n \frac{\partial^2 c}{\partial z^2} - kc \qquad (10).$$

In Equation (10), kc represents any homogeneous first order loss terms. Chemical reaction, of course, is the most obvious example. However, if the time averaged species concentration is considered to be

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†$\bar{D}_a$ can be obtained from $\overline{D_g^1}$ and σ_g as

$$\ln \bar{D}_a = \ln \overline{D_g^1} + 1.0 \ln^2 \sigma_g.$$

averaged over a large spatial volume, then other scavenging and production mechanisms can be treated as being homogeneous even though they are heterogeneous by physico-chemical behavior. A large spatial volume is a relative term. For chemical reactions, one is limited by the number of molecules in the volume, whereas for absorption of a gas by rain the number of raindrops in the volume is limiting. Therefore, the large volume for these two scavenging mechanisms is decidedly different. For example, 40 cm^3 of air will contain on the order of 10^{15} molecules of a species in the ppm concentration range, but only on the order of 10^0 raindrops. As a result, the fluctuation of a species at a concentration of 1 ppm would be due to the turbulence and may only be a few percent, whereas the fluctuation of the number of raindrops could be on the order of fifty percent or so. Thus, the criterion that should be used to establish the volume required for averaging is related to the degree of fluctuation that one might expect in the atmosphere process variable.

Specifically, gas absorption and particulate scavenging by raindrops can be modeled as homogeneous loss terms. We consider k to be based on the appropriate mean diameter as discussed previously. Heines and Peters (1973) have shown the solution to Equation (10) with the appropriate boundary conditions and a deep mixing depth to be

$$c = \frac{Q\sqrt{\frac{(n+1)(q+1)}{A_y A_z}}}{4\pi x \frac{(n+1)+(q+1)}{2}} \exp\left[-\frac{(q+1)Uy^2}{4A_y x^{q+1}}\right]$$

$$\cdot\left\{\exp\left[-\frac{(n+1)U(H-z)^2}{4A_z x^{n+1}}\right] + \exp\left[-\frac{(n+1)U(H+z)^2}{4A_z x^{n+1}}\right]\right\}$$

$$\cdot\exp\left[-\frac{kx}{U}\right] \qquad (11).$$

Some workers have ignored the exp[-kx/U] term in Equation (11) in developing precipitation scavenging models (c.f., Hales et al., 1973).

The rate of irreversible scavenging of a pollutant at a particular point in the x, y, z space is kc. The amount of the species transferred from the air to the rain water in a column having area in the x, y plane of A and below the rain forming layer at altitude H' is

$$R = \int_0^{H'} \int_A kc \, dA dz \qquad (12).$$

It should be noted that using Equation (9) to represent the overall washout coefficient of many particle sizes is only meaningful if the concentration of all aerosol sizes present is the same. Otherwise, one must recognize that both c and k depend on D_p, and a third integration

of the product kc over all particle diameters present is necessary.

In most cases, H' will be large relative to the plume spread in the z-direction, and H' can be assumed to be nearly infinite. Then for k being independent of spatial position, $A \to 0$, and $H' \to \infty$,

$$R = \frac{kAQ\sqrt{\frac{(q+1)}{\pi UA_y}}}{2x^{(q+1)/2}} \exp\left[-\frac{(q+1)Uy^2}{4A_y x^{q+1}}\right] \exp\left[-\frac{kx}{U}\right] \qquad (13).$$

One should note that R does not depend on the source height H nor on the plume spread in the z-direction. This is not unexpected since the total pollutant material above a point in the horizontal plane depends only on the rate of dispersion in the y-direction and the scavenging rate.

SULFATE CONCENTRATION IN THE RAIN WATER

The homogeneous loss constant, k, must account for all washout processes that contribute to the sulfate content of the rain water. Since the effects are first order and parallel, their individual contributions to the sulfate concentration are additive. Consider that the emissions of gaseous SO_2 and sulfate containing particulate from the source can be represented as Q_{SO_2} and Q_p, respectively. It should be noted that Q_{SO_2} will be expressed as mass of SO_2 emitted per unit time. Furthermore, Q_p will consist of aerosol particles of various sizes, D_p. Thus, if $g(D_p^3)$ represents the normalized mass size distribution relationship,

$$Q_{p_i} = Q_p g(D^3_{p_i}) \qquad (14).$$

It should be noted that to readily obtain some indication of the sulfate concentration several idealizations are required at this point. First, we will ignore any gas phase aerosol formation processes by SO_2. In the absence of any other species that can result in gas phase reactions, this seems reasonable. Secondly, it is presumed that the particle size distribution of the sulfate aerosol is only affected by precipitation scavenging. This means that particle size changes by coagulation and/or water vapor condensation growth can be neglected. These assumptions are difficult to completely justify, especially since cooling of the water vapor laden stack plume could lead to supersaturation, and subsequent aerosol growth. However, since the supersaturation, except under extreme circumstances, would be limited by the rapid dilution enhanced by plume dispersion, the submicron size particles should not grow much beyond 0.5 μm. Particle size change by coagulation is most efficient for small aerosol sizes; and again, except for long plume travel times, the particle growth due to rapid coagulation should not be too important

for the larger particles.

We are now in a position to relate Q and k to the individual wash-out processes that are occurring. Let η_i represent the collection efficiency of particles of size D_{pi}. If Q_{SO_2} represents the emissions of gaseous SO_2, then correcting for the molecular weight of $SO_4^=$, the emissions are $1.5Q_{SO_2}$ on a sulfate basis. Therefore, Equation (13) can be written for sulfate removal as

$$R = \frac{\pi D_c^2 NA\sqrt{\frac{q+1}{\pi UA_y}}}{2x^{(q+1)/2}} \exp\left[-\frac{(q+1)Uy^2}{4A_y x^{q+1}}\right]\left\{1.5k_g Q_{SO_2}\right.$$

$$\left.\exp\left[-\frac{\pi D_c^2 Nk_g x}{U}\right] + \frac{U_t}{4}\sum_{i=1}^{m}\eta_i Q_{p_i}\exp\left[-\frac{\pi D_c^2 U_t \eta_i x}{4U}\right]\right\} \qquad (15).$$

Now R mass of $SO_4^=$ is transferred to the rain water by the time the drop reaches ground level. Let P be the precipitation rate. Then R mass of $SO_4^=$ is transferred to PA volume of rainwater in a unit time. Thus, the resulting sulfate concentration of the rainwater, $[SO_4^=]$, is simply R/PA.

P can be easily related to the raindrop size distribution, N, and U_t as

$$P = \int_{D_c^0}^{D_c^\infty} Nf(D_c)\,\frac{\pi}{6}\,D_c U_t(D_c)\,dD_c \qquad (16).$$

Again it is not convenient to use the raindrop size distribution, and it is generally more suitable to base the determination on a mean drop diameter. An appropriate mean diameter can be found by evaluating Equation (16) using the drop size distribution. However, it is not useful to employ different mean diameters as the bases for the first order loss constant and the precipitation rate. We will adopt the mean raindrop diameter appropriate for the first order loss constant as the basis. As a result, the precipitation rate must be corrected by a factor β and is

$$P = \beta N\,\frac{\pi}{6}\,\bar{D}_c^3 U_t(\bar{D}_c) \qquad (17),$$

where $\bar{D}_c$ represents the appropriate mean. A plot of β versus σ_g is shown in Figure 1 for the cases of $\bar{D}_c$ being $\bar{D}_{\sqrt{1a}}$ or $\bar{D}_a$. There is very little dependence of β on $\bar{D}_g^1$, and its effect can be safely ignored if $\bar{D}_g^1$ is between 0.8 mm and 2.4 mm.

By employing Equations (15) and (17), the sulfate concentration can

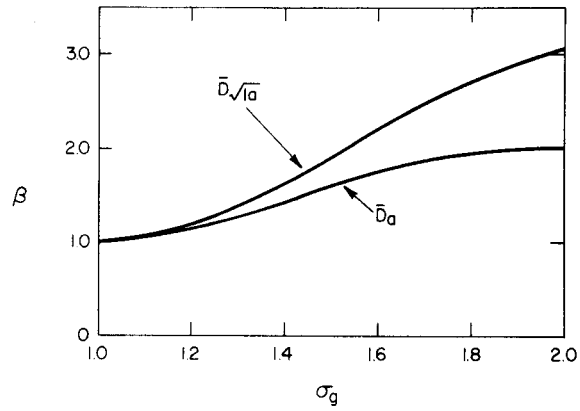

Figure 1. Correction factor to calculate the precipitation rate based on $\bar{D}\sqrt{1a}$ or $\bar{D}_a$ for a logarithmic normal raindrop size distribution.

be obtained assuming gaseous SO_2 emissions and particulate emissions of m discrete aerosol sizes are present.

$$[\overline{SO_4^=}] = \frac{\sqrt{\frac{q+1}{\pi U A_y}}}{D_c U_t x^{(q+1)/2}} \exp\left[-\frac{(q+1)Uy^2}{4A_y x^{q+1}}\right]\left\{4.5\ \frac{k_g Q_{SO_2}}{\beta_g}\right.$$

$$\left.\cdot\exp\left[-\frac{6Pk_g x}{D_c U_t U \beta_g}\right] + \frac{3U_t}{2}\sum_{i=1}^{m}\frac{\eta_i Q_{p_i}}{\beta_{p_i}}\exp\left[-\frac{3P\eta_i x}{D_c U \beta_{p_i}}\right]\right\} \qquad (18)$$

Equation (18) shows that the resulting sulfate concentration of the rainwater should be distributed in a gaussian manner about the direction of the time averaged wind. Furthermore, the maximum sulfate concentration in the rain occurs very close to the stack before significant plume spread in the crosswind direction occurs.

It is believed that the form of the raindrop size distribution should not greatly affect the general conclusions. For example, the single parameter Marshall-Palmer distribution† (Marshall and Palmer, 1948) was also evaluated, and the results indicated that the error introduced by using $\bar{D}\sqrt{1a}$ for gas scavenging is generally within 15% except for extremely small raindrop sizes. In acutality, the use

†The normalized Marshall-Palmer distribution can be written as

$$f(D_c) = \gamma e^{-\gamma D_c}.$$

of $(\bar{D}_1 \bar{D}_a^2)^{1/3}$ predicts a much smaller error, but its use is hardly warranted until a much better predictive model is required. Since the Marshall-Palmer distribution is frequently used, a plot of β versus γ for this distribution is shown in Figure 2.

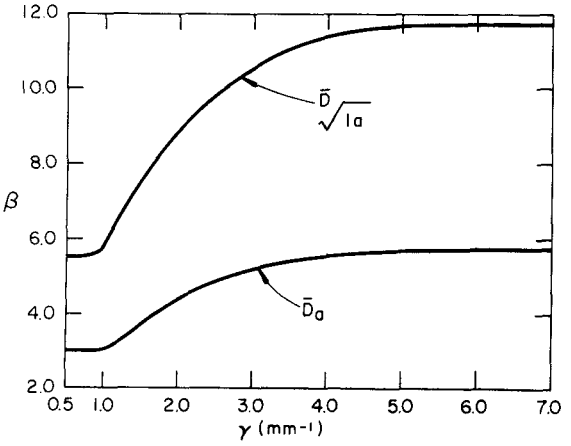

Figure 2. Correction factor to calculate the precipitation rate based on $\bar{D}\sqrt{1a}$ or $\bar{D}_a$ for the Marshall-Palmer Raindrop Size distribution.

DISCUSSION OF THEORETICAL PREDICTIONS

To illustrate the theoretical predictions, we will consider hypothetical meteorological conditions where $q = 0.5$, $A_y = 0.7$, and $U = 4.0$ m/s. Furthermore, let $y = 0$ and for simplicity consider $\beta = 1.0$. This latter consideration implies that the rain consists of a single drop size. While this is an obvious simplification, the results obtained are nevertheless very instructive. Even with this simplification, it will be seen that it is not advisable to make broad generalizations about the effects of raindrop size and precipitation rate on the resulting rainwater sulfate concentration.

In Figure 3, the ratio of the sulfate concentration of the rainwater due to absorption of gaseous SO_2 to the SO_2 source strength is plotted versus distance from the source for raindrop diameters of 0.5 mm, 1.0 mm, and 3.0 mm with precipitation rates of 0.2 μm/s, 1.0 μm/s, and 2.0 μm/s. As expected, the sulfate concentration in the rainwater decreases with distance from the source which is apparently consistent with the data of Ensminger and Martin (1957) and the data of Dana et al. (1973).

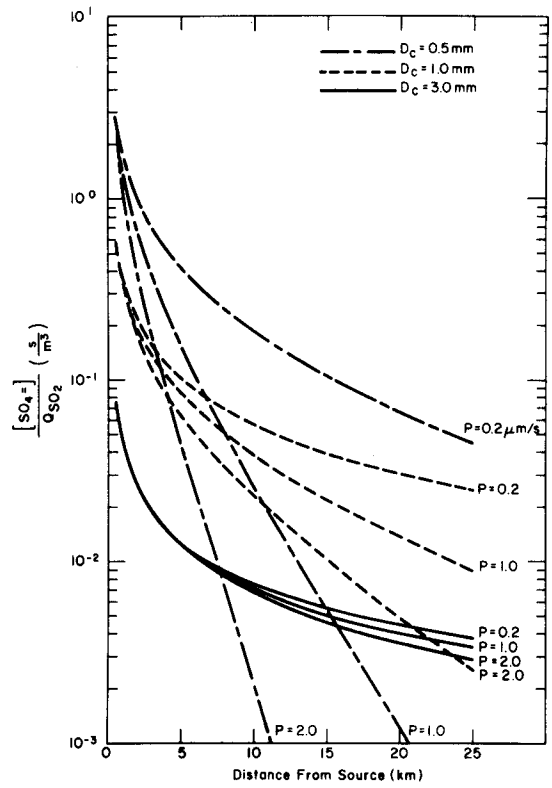

Figure 3. Rainwater sulfate concentration due to precipitation scavenging of gaseous SO_2.

The effect of drop diameter on the sulfate concentration is not always the same; i.e., for a fixed precipitation rate the sulfate concentration with the 0.5 mm drop may or may not be greater than with the 1.0 mm and 3.0 mm drop, depending on the distance from the source. This is consistent, at least qualitatively, with the observations of Hales, Thorp, and Wolf (1971). The effect of increasing the precipitation rate is to decrease the sulfate concentration. This is better illustrated in Figure 4 where the sulfate concentration at x = 10 km is shown as a function of precipitation rate. The dependency of the sulfate concentration on the precipitation rate is more pronounced for the smaller raindrop sizes. The apparent reason for this trend is as follows. For the larger drop, the average volume of air that each drop occupies is so large that it appears essentially infinite in extent. On the other hand, the entire volume occupied by the greater number of smaller raindrops is affected by the absorption process. As the precipitation rate increases, this average volume of air per drop decreases so that the available SO_2 in the volume is limiting.

Typical results of similar calculations for sulfate containing aerosol of size 0.1 μm, 1.0 μm, and 10. μm are shown in Figures 5 thru 8.

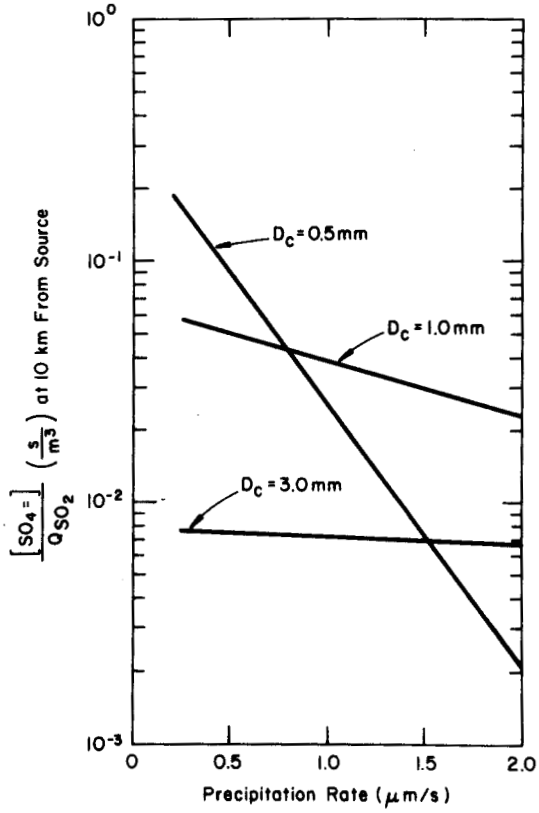

Figure 4. Rainwater sulfate concentration from SO_2 absorption as a function of precipitation rate.

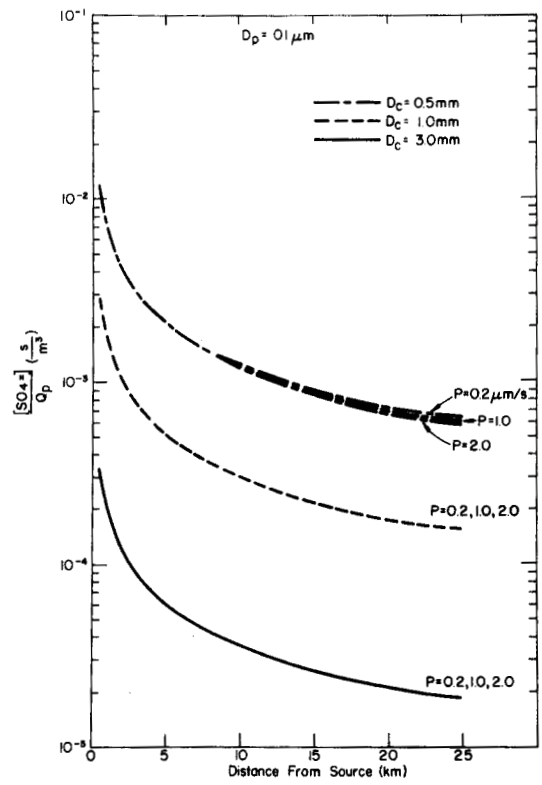

Figure 5. Rainwater sulfate concentration due to precipitation scavenging of 0.1 µm AED sulfate aerosol.

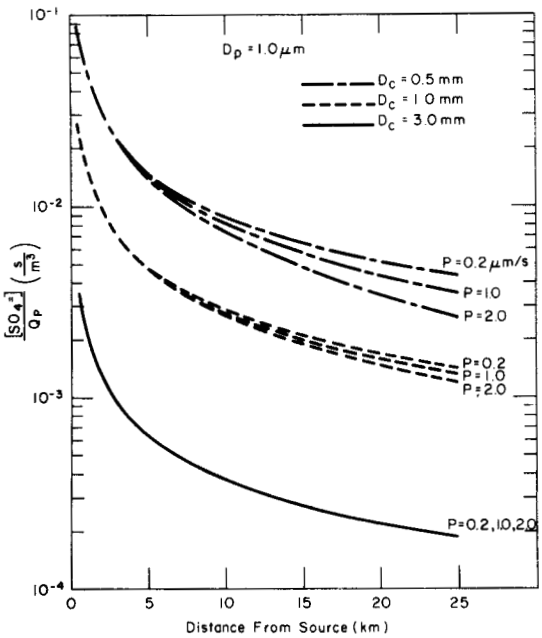

Figure 6. Rainwater sulfate concentration due to precipitation scavenging of 1.0 μm AED sulfate aerosol.

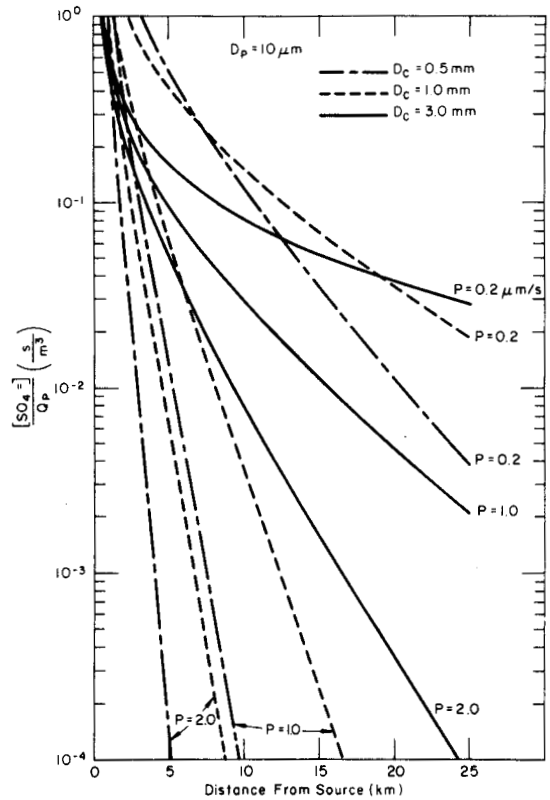

Figure 7. Rainwater sulfate concentration due to precipitation scavenging of 10. μm AED sulfate aerosol.

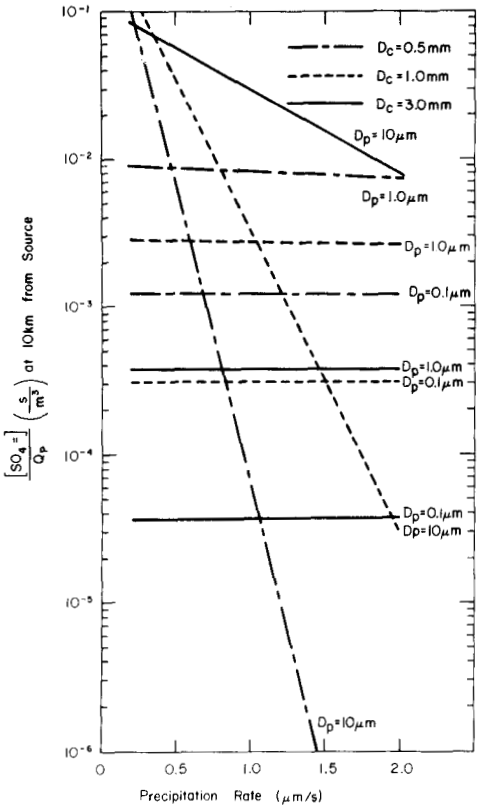

Figure 8. Rainwater sulfate concentration from scavenging of aerosols as a function of precipitation rate.

Effects similar to that observed for gaseous SO_2 absorption are noted. The magnitude of the effect of precipitation rate on the rainwater sulfate concentration is dependent on the raindrop and particle diameters. For the smallest particle size evaluated, the effect of precipitation rate is very slight. This dependence on precipitation rate becomes less as the raindrop size increases and as the particle size decreases. This is more clearly shown in Figure 8.

The dramatic decreases in the rainwater sulfate concentration at moderate distances from the source due to the scavenging of 10. μm aerosol particles is apparently due to the very efficient removal of these particles near the source. Particles of that size are so effectively removed near the source that only very low particle concentrations are present at further distances. Thus, the low numbers of these particles at the 10 to 15 km distance from the source can contribute little to the sulfate concentration. If prior plume washout is ignored, this predicted decrease is not nearly so substantial.

The effect of aerosol particle diameter on the sulfate concentration is more clearly shown in Figure 9 for D_c = 1.0 mm. This shows that

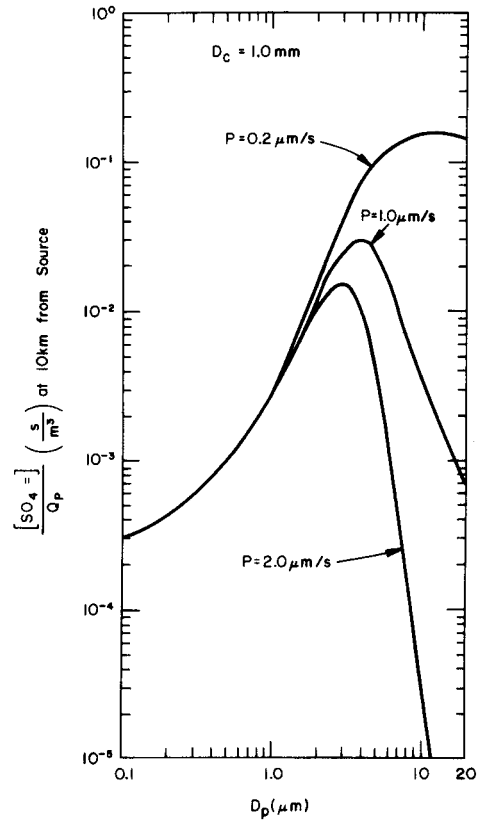

Figure 9. Dependence of rainwater sulfate concentration on aerosol size.

the contribution of particles to the rainwater sulfate concentration is maximum in the 3 μm to 10 μm range at moderate distance from the source. This contribution does not continue to increase with D_p as other workers have suggested. This is due to prior plume washout and the very efficient particulate removal near the source for these particle sizes. For equivalent rates of sulfate emission from the source, the contribution to the sulfate concentration at 10 km from the source by 1.0 μm aerosol particles can be two orders of magnitude less than that from 5 μm to 10 μm particles for low precipitation rates. Furthermore, the sulfate concentration is maximum for scavenging particles of 4 μm to 6 μm diameter at the high precipitation rates.

SUMMARY

Results of calculations are presented that show the effect of precipitation rate and raindrop size on sulfate washout from stack plumes. Both gaseous SO_2 absorption and scavenging of sulfate aerosols are considered. For equivalent mass emission rates both effects are important and neither can apparently be ignored, especially if the emitted sulfate containing particles are in the 3 μm to 10 μm range.

One must remember that these theoretical calculations are based on several idealizations and should recognize the limitations of the results. For example, aerosol coagulation, growth and formation processes in the plume have been neglected. Furthermore, ideal plume behavior and constant precipitation rates were used in the analysis. Nevertheless, the underlying physico-chemical treatment is sound, and the author feels that the model should provide reasonable guidelines for the refinement of such calculations. In addition, one should note that realistic confirmation of precipitation scavenging models is only possible when the physical parameters such as raindrop size distribution, particle size distribution, and precipitation rate are accurately known. Inaccuracies in these parameters of twenty to thirty percent and even higher are not unexpected in field evaluations, and these can result in order of magnitude errors in the rainwater sulfate concentration.

NOMENCLATURE

Latin Letters

A_y	coefficient in y-direction eddy diffusivity
A_z	coefficient in z-direction eddy diffusivity
c	concentration in the air
C_f	Cunningham correction factor
D_c	diameter of collector raindrop
$\bar{D}_a$	area mean diameter
$\bar{D}_l$	length mean diameter
$\bar{D}_{\sqrt{la}}$	root mean square of the length mean and area mean diameters
$\bar{D}_g^l$	number median diameter in logarithmic-normal distribution
D_p	diameter of particle
$\mathcal{D}$	molecular diffusivity of pollutant species in air
H	effective stack height

H'	height of rain forming layer
$\mathcal{H}$	Henry's law constant
k	first order homogeneous loss constant
k_g	gas phase mass transfer coefficient
k_r	first order reaction rate constant
K_g	overall mass transfer coefficient based on overall gas phase driving force
n	exponent in z-direction eddy diffusivity
N	number density of raindrops
q	exponent in y-direction eddy diffusivity
Q	strength of point source emissions
R	amount of pollutant species transferred from the air to the rain
Re_c	collector raindrop Reynolds number
Sc	Schmidt number
Sh	Sherwood number
St	Stokes number
U	wind velocity in the positive x-direction
U_t	relative velocity of the raindrops with respect to particles
x	downwind direction
y	crosswind direction
z	vertical direction

Greek Letters

β	correction factor defined by Equation (17)
γ	parameter in Marshall-Palmer distribution
μ	viscosity of the air
ρ	density of air
ρ_p	density of particle
σ_g	geometric standard deviation in logarithmic normal distribution

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A SULPHUR BUDGET FOR SOUR GAS PLANTS

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ABSTRACT

The principal aim of this project is to produce a mass balance for the SO_2 that is emitted into the atmosphere from sour gas plants in various localities in Alberta. Partial sulphur budgets for two plants at dissimilar locations are shown to exhibit major differences.

The rise and dispersion of sour gas plant plumes have been investigated in detail. In order to investigate the chemical transformation of SO_2 within these plumes, the use of a conserved tracer that can be detected by neutron activation is discussed.

1. INTRODUCTION

There are certain peculiarities about sour gas plant plumes and the climate of Alberta which may enable us to shed a different light on the seemingly intractable problem of atmospheric sulphur budgets. The effluent from a sour gas plant sulphur recovery unit can be considered to be relatively "clean" in the sense that the only pollutant emitted is SO_2 without a significant loading of particulates or other contaminants. The water content has a high value of approximately 25 mole per cent, but the effluent is emitted from the stack at temperatures in excess of 800K so that the plume is normally invisible, except when the ambient winter temperature is below -15°C (Havlena et al., 1975). Thus this effluent is markedly different from that emitted from a coal-burning power plant, a smelter or an oil sands coke-burning power plant, and may have a greater potential to acidify soils and water, because there appears to be less opportunity to form neutral sulphates.

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*UNISUL Project 4 leader; UNISUL is an acronym for the University of Calgary Interdisciplinary Sulphur Research Group. The other members of Project 4 are: K. Aziz, S. Benjamin, H. Brown, D. Exall, R. Klemm, J. Havlena, G. Hodgson, H. Krouse, A. Legge, P. Lester, M. Mohtadi and M. Nyborg.

Over 80% of the natural gas produced in Canada comes from Alberta, about one half of which is exported to the U.S.A. Over 50% of these gas fields are sour, i.e. they contain an appreciable percentage of H_2S. The sour gas processing plants are mainly located alongside the Rocky Mountains in the so-called sour gas corridor; see Figure 1. The H_2S is

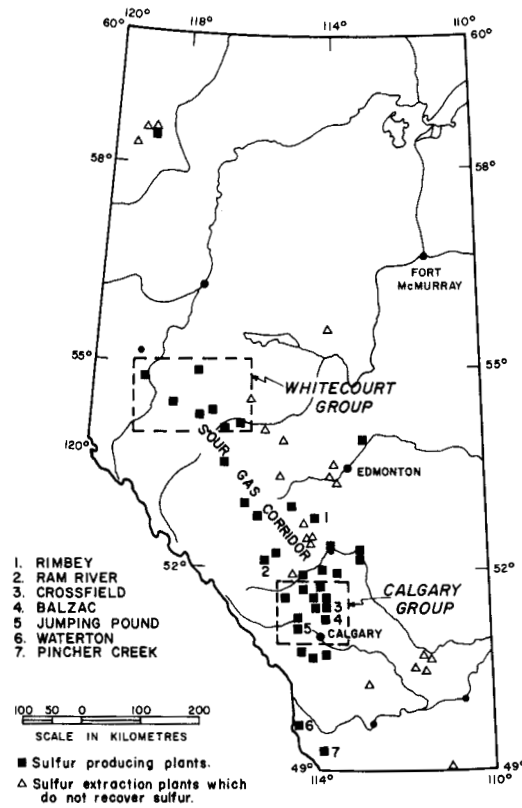

Figure 1. Location of Sulfur Extraction Gas Plants in Alberta (Reproduced from a report by Klemm, 1972)

removed from the natural gas and is then converted to elemental sulphur by the Claus process, but a small percentage (approximately 10^6 kg of SO_2/day in total) has to be incinerated and released to the atmosphere as SO_2. There are a few large sulphur recovery units which emit about 10^5kg of SO_2/day.

Public hearings were held in October, 1972 by the Alberta Environment Conservation Authority (1973) on "The Environmental Effects of the

Operation of Sulphur Extraction Gas Plants in Alberta." One result of these hearings was that it became much more widely appreciated that only a few per cent of the SO_2 emitted from these plants is accounted for by sulphation monitors (lead candles) within a 10 km radius of each plant. The project reported in this paper was established in order to attempt to answer the question: "Where does the rest of the SO_2 go to?" This is not to say that no experiments have been performed prior to this paper or even prior to 1972.

2. PREVIOUS WORK

A pioneering effort to determine the fate of SO_2 from sour gas plants is described by Summers and Hitchon (1973). They inferred that approximately 40% of the SO_2 emitted from the Rimbey sour gas plant (Figure 1) during a summer was returned by convective storms in the near vicinity of this plant. This is a somewhat surprising result as it does not rain for more than 10% of the time! This paradox, which was not discussed in their paper, can perhaps be explained by the normal diurnal wind pattern next to a mountain range on relatively calm days. Soon after sunrise an upslope wind sets in which could entrain the Rimbey plume into the convective storm cells that form for most of the day over the mountains. In the late afternoon the storm clouds move away from the mountains and heavy rain and/or hail often occurs at approximately the same distance from the mountains as that of the Rimbey plant.

An investigation of wind statistics by Benjamin (1975), using the technique of Paterson and Benjamin (1975), supports the idea of air currents moving to and fro within the sour gas corridor. Similar diurnal variation of the wind direction has also been reported for Calgary by Longley (1969). These air movements may well lead to a build up of pollutant concentration as well as explaining the observations of Summers and Hitchon (1973).

The ground level SO_2 concentrations recorded by 7 continuous monitors around the Balzac plant have been investigated (Mohtadi and Rowe, 1973) to test the applicability of various dispersion correlations for sour gas plant plumes and to ascertain the meteorological conditions which cause pollution episodes. An episode was defined as an hourly average ground level SO_2 concentration of 0.15 ppm or greater. Twenty-eight pollution episodes occurred during the twelve month period of this investigation. Twenty of these episodes can be definitively classified into the following categories:

(a) uniform atmosphere - 5 cases;
(b) inversion breakdown - 6 cases;
(c) plume trapping - 9 cases.

Inversion breakdowns and plume trapping, which are associated with clear

skies and low winds, are by no means rare or unusual east of the Rocky Mountains and are part of the normal variation in the meteorological dispersion conditions of Alberta.

Sour gas plant plume rise and diffusion has been investigated in detail, using airborne rapid response SO_2 monitors, by many workers; see, for example, Lee et al. (1973) and ERA Sciences (1974). All of these investigations have been carried out over relatively flat terrain, and have shown that sour gas plant plumes disperse in a manner similar to any other industrial stack plume. However, the problem of plume dispersion in complex mountainous terrain still requires much further study. Plume flow across a long ridge has been studied at the Jumping Pound plant (Figure 1), and an acceptable engineering model for this distinct topographical feature, involving the concept of potential flow, has been developed (Leahey and Rowe, 1974). Computer dispersion models for complex terrain have been applied to sour gas plant plumes by Lantz et al. (1972) and Wallis et al. (1975).

A number of plume marking techniques, e.g. the incomplete combustion of a hydraulic cluid, have been used in order to visualize the rise stage of these plumes. A novel technique for photographing SO_2 plumes using the ultraviolet light from the sun and exploiting the UV absorption properties of SO_2 has been under development for some time, and this method appears to be an almost ideal way to photograph sour gas plant plumes (Havlena et al., 1975).

H_2S from different sour gas pools varies considerably in its S^{34}/S^{32} abundance ratios. Krouse (1974) has investigated whether sulphur isotope abundances can be used to monitor gas industry emissions of sulphur compounds and their effects on the environment. He examined the sulphur isotope abundances of lead candle sulphation monitors, and found that he could readily identify the major source of emission in a neighborhood but the "background" isotopic composition appears to vary significantly from site to site and with season.

The fate of SO_2 in the atmosphere has to be experimentally determined, in part, by monitoring what arrives at the ground. For the past three years, Nyborg (1975) has been investigating the pH and SO_4-S content of: rainfall, snowfall, dryfall (particulates), water (protected), soils, grasses and barks. These data are being taken at over 70 sites, which are concentrated just north of Calgary, and around the Ram River and Waterton sour gas plants, and scattered throughout the southern half of the Province (Figure 1). These observations (Nyborg, 1975) suggest that direct absorption of sulphur gases is more important than deposition in rain and snow.

Nyborg's sites are mainly located on agricultural lands. An investigation of the uptake of sulphur gases by pine trees is being undertaken by Legge et al. (1975), their data are quite fascinating because they indicate that the concentration of a sulphur compound can

be an order of magnitude lower within a forest canopy than above it; see, also, ERA Sciences (1974).

3. FATE OF SO_2

Examination of the data collected to date reveals that the sulphur budget for an individual sour gas plant is very dependent on its particular location and on the climatology of that area. For example, Nyborg (1974) conducted experiments around the Waterton plant, where he placed pots of soil with barley plants at distances up to 40 km downwind from the stack. His findings show that during a three month summer period the soil and barley gained at least an order of magnitude more sulphur by absorption than that deposited by rain, which contrasts markedly with the findings of Summers and Hitchon (1973) at the Rimbey plant.

Besides the drier climate, Nyborg's data are determined in part by the topography of the Rocky Mountains to the west of the Waterton plant (Figure 1), which is shaped like vanes and gives rise to extremely persistent westerly winds. A high level of mechanical turbulence is generated by these mountain vanes, which reduces the rise and increases the diffusion of the plume bringing it rapidly to the ground, with resultant high levels of absorption in a narrow downwind sector (Wallis et al., 1975).

The effect of wind directional persistence at the Waterton plant is also clearly evident in the total sulphation monthly averages taken by lead candles. Oval shaped isopleths can be readily drawn for these sulphation data on the downwind (easterly) side of the Waterton plant, and also for those of the much smaller nearby Pincher Creek plant. Interestingly enough, this information was used to resolve the division between the gas plant operators of the settlement of damages awarded to ranchers as a result of emissions from these two plants. At all other plants investigated the lead candle data do not yield such definitive trends; in fact the values indicate that the contribution from the background is of the same order of magnitude as that due to the stack; see, for example, Rowe (1974). Although the airborne background concentrations are normally much lower than those due to the stack, the plume is infrequently carried by the wind to the monitor.

Simple calculations (Benjamin, 1975) similar to those of Scriven and Fisher (1975), but using a Gaussian plume model rather than solving the diffusion equation (K theory), and using a constant deposition velocity of 1 $cm.s^{-1}$ and a mixing layer of limited depth show that as much as 30% of the sulphur emission from a sour gas plant could be accounted for by dry deposition within 100 km of the plant. The predictions of this model can be made to agree reasonably well with Nyborg's data for sites close to both the Waterton plant and the Calgary group of

plants. However, this model is not able to reconcile Nyborg's values at remote sites (greater than 100 km) as well as those near to the sour gas plants; the reason for this anomaly remains to be determined.

An interdisciplinary project at the University of Calgary has been established in order to attempt to solve the sulphur budget for sour gas plants. A schematic presentation of this project in the form of an SO_2 mass balance equation for the atmosphere showing the principal areas of interest of each of the (original) co-workers is given below:

$$\begin{bmatrix}SO_2 \text{ emitted from} \\ \text{local sources}\end{bmatrix} + \begin{bmatrix}\text{Background } SO_2 \\ \text{(Krouse)}\end{bmatrix}$$

$$= \begin{bmatrix}SO_2 \text{ transported by} \\ \text{convective diffusion} \\ \text{(Aziz and Rowe)}\end{bmatrix} + \begin{bmatrix}SO_2 \text{ transformed by} \\ \text{chemical reactions} \\ \text{(Mohtadi)}\end{bmatrix}$$

$$+ \begin{bmatrix}SO_2 \text{ absorption at} \\ \text{ground surfaces} \\ \text{(Hodgson)}\end{bmatrix} + \begin{bmatrix}SO_2 \text{ rainout and} \\ \text{washout}\end{bmatrix}$$

As reviewed above, much work has already been done on all aspects of the sulphur budget for sour gas plants except for the question of possible chemical transformations of the SO_2 within the plumes.

4. PLUME TRACERS

An extensive literature exists on the atmospheric chemistry of SO_2 and a survey of this information as it pertains to sour gas plant plumes has been completed by Mohtadi and Gyuse (1975). A few plume chemistry field experiments have been reported in the literature, almost entirely for power plants, which have yielded conflicting evidence about the rate of oxidation of SO_2; see, for example, Wilson (1975). Only the ratios of SO_2 to sulphates at various downwind distances have so far been reported, and the oxidation rate of SO_2 has then been inferred from these data. It is not possible to determine directly the mass flux of a plume component, such as SO_2, through a downwind cross-section by airborne sampling because of the turbulent nature of the atmosphere (Brown et al., 1972). A conserved tracer needs to be injected into the stack gases in order to obtain an additional check of the oxidation rate and to verify that the total sulphur mass flux is conserved, assuming that the sulphates do not fall out (Manowitz et al., 1972).

A review by Exall (1975) of conserved tracers that can be detected at extremely low concentrations (of order 10^{-12}) revealed two main contenders: SF_6 gas with electron-capture gas chromatography, or

elements with low natural abundance but high thermal neutron capture cross-sections. SF_6 has been rejected because of a variety of chemical reactions that appear likely to proceed with the high temperature sour gas plant stack gases. The high sensitivity obtainable by combining neutron activation with gamma-spectrometry in the determination of microquantities of elements suggests that this technique should be most suitable for plume chemistry experiments. The criteria governing the choice of element are: nuclear properties, natural abundance, price and suitability as a tracer of air movements. Gold, indium and lanthanum are among the more suitable elements. Due to its very short half-life, indium would have to be chemically separated soon after irradiation before counting. Atmospheric dust can contain significant quantities of lanthanum, which leaves gold as apparently the most suitable element for this conserved tracer technique.

Airborne high-volume filter samples have been obtained (Exall, 1975), both within a sour gas plant plume and upwind of the plant. This experiment was performed shortly after rain had fallen and the ambient air dust levels were presumably low at that time. After neutron activation, the only significant elements found on all filters were sodium and bromine. A nozzle apparatus to inject a fine spray of a solution of gold into the incinerator of a sour gas plant is currently being developed.

In conclusion, sour gas plant effluents in Alberta offer a unique opportunity to study SO_2 transformations in plumes that are almost completely devoid of particulates in a non-industrial clean air environment. Furthermore, a sulphur recovery unit could be used as an experimental reactor since the heat emission rate and particulate loading could be varied rapidly during a given meteorological event.

ACKNOWLEDGEMENT

This work is supported by a National Research Council of Canada Negotiated Development Grant to The University of Calgary Interdisciplinary Sulphur Research Group (UNISUL).

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TRANSPORT OF POLLUTANTS CONSIDERED FROM THE POINT OF VIEW OF A SHORT AND MEDIUM RANGE-MATERIAL BALANCE

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ABSTRACT

Episodical long-range transport is the quasi-instantaneous peak event. It does not express the total dosage of pollutant carried over from the source area to some distant place. The purpose of the present paper is to obtain an average material balance of a pollutant leaving a given area. Available information from the OECD "Long Range Transport of Air Pollutants" is being used for this purpose. The IRCHA is one of the laboratories participating in this project.

Our main sampling station is 37 km from the center of the Paris district. This position allows us to compute, based on emission data from the area and air pollution survey records, the amount of pollutant (total sulfur) leaving the region. We worked out this specific example because we had the first-hand, checked data.

Out of a total emission of about 300 kT SO_2/year (1972 figure), over 50% may be accounted for as remaining inside the 37 km-radius circle. Gaseous and particulate dry deposition mechanisms are considered mainly responsible for this fact. Less than half of the total sulfur emission seems to be transported beyond the 37 km-radius limit. The exact aspect of the deposition function within the national territory is currently being researched.

1. ACKNOWLEDGEMENT

This paper discusses a few aspects and results of the OECD Long Range Transport of Air Pollutants project. Ten European nations participate actively in this program and provide financial support. Their results are being centralized and disseminated by the Norwegian Institute for Air Research. Most of the figures used here come from the OECD project and are largely unpublished. I am expressing herewith my gratitude towards the ten participating laboratories and their staff for the possibility of using a few selected results out of the enormous amount of data gathered.

I am also grateful to Dr. Eric G. Walther of the Charles F. Kettering Foundation, Dayton, Ohio for his assistance in translation of this paper into English.

Episodical long-range transport of pollutants, such as red Sahara dust falling out over Europe, has been known since antiquity. Recently much attention is being paid to episodical long range transport, mainly considering radioactive fallout and acid rains.

2. MATERIAL BALANCE OF THE PARIS REGION

Great attention has hitherto been directed towards "episode analysis" i.e. the scrutiny of the not-to-frequent pollution episodes at remote, slightly polluted stations. If and when such a station records a concentration peak, be it as gaseous pollutant, dry or wet fallout, the cloud can be traced back to its origin. This approach may be termed "receptor-oriented". An alternate way, albeit not original, because it is frequently and almost exclusively used in calculations regarding industrial stacks, is source-oriented. Here, an attempt is made to establish a material balance at and around the emission source.

The Paris district provides a ready example for this approach. It's well-documented emission inventory for 1973 (C.I.T.E.P.A., 1973) amounts to 300 kT SO_2 per year. This emission takes place within a rather well defined, almost circular area of 30 km diameter. No other comparable emission is to be found within 300 km and excepting the North and North-East directions where emissions are nearer, all other directions are altogether free of sources for many hundreds of km and also of geographical relief of any importance.

The area is well-monitored (40 stations) by the Laboratoire d'Hygiène de la Ville de Paris, assisted in this task by other laboratories (EdF; CSTB, etc). One of the OECD-LRTAP ground stations, FO1 is operated by the IRCHA 37 km due South from the center of the district, at VERT-le-PETIT.

The siting of this station is singular, because of the clear possibility of distinguishing between Paris (urban) plume pollution situations and background values. Following from the urban geometry and the wind rose, (information gathered at the Brétigny-sur-Orge airfield, at 6 km distance as well as ours') FO1 is swept by the plume of Paris 13% of the time. Between the 1.1.1972 and 31.5.1974, we could pick out 28 episodes, when the wind and concentration patterns showed clearly that Vert-Le-Petit was for at least 24 hours inside the plume from Paris. During these episodes, the average of the measured SO_2 concentrations was 108 $\mu g\ m^{-3}$. The number of episodes when the plume swept over FO1

for less than 24 hours at one time, was 41 during the same 29 month period. In the absence of a North wind (or a sampling period with a North-wind component) the SO_2 concentration was found on average to be below or near 10 μg m^{-3}. See Table I.

TABLE I

Average concentrations of the SO_2 in the air at FO1 during the summer months of 1973, in the absence of NNE-N-NNW winds, compared with corresponding values at IC1, CH1, NO1 and SF1.

Monthly average SO_2 conc. in the air μg m^{-3}

Code	Country**	May	June	July	Aug.	Sept.
FO1	France	12.1	21.3*	9.6	8.1	7.7
IC1	Iceland	9.3	0.8	1.2	1.7	2.4
CH1	Switzerland	3.7	2.5	2.3	2.4	2.2
NO1	Norway	7.2	8.4	8.4	8.7	5.7
SF1	Finland	10.0	6.1	4.6	5.7	5.0

*The relatively high June average is accounted for by a North wind during the day of 13.6.73, when a 24 h mean of 116 μg m^{-3} was recorded.

**See also Table III.

Thus the yearly average at FO1 may be computed as:

$$0.13 \times 108 \text{ μg } m^{-3} + 0.87 \times 10 \text{ μg } m^{-3} = 22.7 \text{ μg } m^{-3}$$

The 1973 experimental average at FO1 was 24.2 μg m^{-3}

The material balance may be established in the following way. The downtown average SO_2 concentration in Paris during the reference period was 154 μg m^{-3}. With a vertical deposition velocity of 0.8 cm s^{-1}, as is assumed throughout the OECD program, taking into account the radial decrease in concentration from 154 to 24 μg m^{-3}, the dry deposition integrates to 110 kT yr^{-1} inside the 37-km-radius circle.

The SO_2 leaves the 37-km-radius circle at the average concentration of 24.2 μg m^{-3}, at an average mixed height of 690 m (Benarie 1975) and a "plume width" of 45 km. This latter dimension was established by recording about 1000 SO_2 concentrations and plotting them against the observed average wind direction, also measured at our laboratory

(Fig. 1). The average plume is quite distinct between compass direction

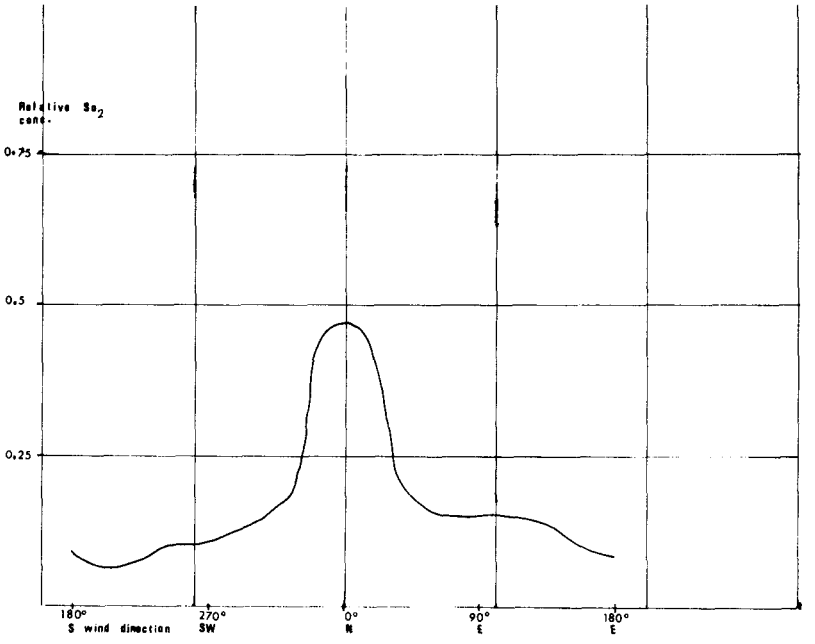

Figure 1. Average SO_2 conc. PARIS divided into the SO_2 conc. at FOl plotted against prevailing wind direction.

of 330° and 40°. This produces an estimate of average plume width of 70°, corresponding to a 45 km front at 37 km radial distance. This estimate is in fair agreement with the St. Louis, Mo. urban plume width measured by Stampfer and Anderson (1975) by aerial sampling. Thus $4.5 \cdot 10^6$ cm (plume width) × $6.9 \cdot 10^4$ cm (plume height) × $24.2 \cdot 10^{-6}$ g m^{-3} (concentration) × $4.1 \cdot 10^2$ cm s^{-1} (average wind speed) × $31.5 \cdot 10^6$ s (year) ≈ $100 \cdot 10^9$ g yr^{-1} = 100 kT yr^{-1}.

Out of the 300 kT yr^{-1} SO_2 emission of the area, 100 kT (≈33%) leave the 37 km radius circle and 110 kT (≈37%) are accounted for by dry and wet deposition inside the area. The remainder, 30% probably undergoes transformation into sulfate during the average residence time (37 km/4.1 m s^{-1} 2.5h) of the emission inside the control area and undergoes partially dry deposition. This figure seems quite realistic in the light of the findings of Benarie et al. (1973) further bibliography and estimates in the reference).

As the average concentration of suspended sulfate at Vert-le-Petit was found to be 13.5 µg m^{-3}, the same reasoning as above gives as an upper estimate of sulfur transport over the 37 km radius boundary, 36 kT yr^{-1} (counted as SO_2). The wet and dry mechanisms account for a deposition of 64 kT yr^{-1} inside the circle. Thus the material balance

(in SO_2 kT yr^{-1}) may be summed up as follows:

	Deposited inside the 37 km radius circle	Transported beyond the 37 km radius circle
Sulfur Dioxide	110	100
Suspended sulfate (as SO_2)	64	36
	174 = 57%	136 = 44%

Total: 310 kT, estimated from the material budget.

Emission: 300 kT, estimated from the source inventory.

This deposition-to-transport ratio is in excellent agreement with that found by Hogstrom (1973) from Uppsala data. He estimated the yearly sulfur deposition originating from "local sources" at about 50 per cent for the Stockholm and Gothenburg areas. To quote Hogstrom: "... high deposition figures are not especially concentrated in the central city area, but occur rather in an area with a radius of 50-100 km around the city".

Attempting to pursue the plume at greater distance, we are handicapped (1) by the scarcity of ground stations; (2) by the appearance of non-background concentrations at the sampling site not caused by the source area (Paris) for which we are attempting to determine a material balance. However, concerning this second objection our purpose is to obtain a maximum estimate of the sulfur leaving the area. Hence the non-background concentrations can only increase this estimate, so it is not of much concern.

At La Crouzille (FO3) we could identify at least one period when wind direction and concentration pattern made the Paris plume clearly identifiable. La Crouzille is 320 km due South from Paris with no obstacles and no important emissions all the way. The annual average SO_2 concentration at FO3 in 1973 was 4.2 $\mu g\ m^{-3}$, while the suspended sulfates were 4.26 $\mu g\ m^{-3}$. From 18.2.74 to 20.2.74, the wind blew on the average at 3.1 to 3.7 ms^{-1} steadily from the northern sector and no precipitation recorded at all. During this period, the following sulfate and SO_2 concentrations were observed: Table 2.

During the three significant days of the episode (18 -20.2) the wind direction did not deviate by more than ± 15° from its mean direction. In these conditions, a 30° plume width at La Crouzille is a good guess; it agrees also with the recent St. Louis study of Stampfer and Anderson (1975). The average sulfur content (accounted for as SO_2) decreased from 148 $\mu g\ m^{-3}$ at FO1 to about 1/4 of this value (=35 $\mu g\ m^{-3}$) at FO3.

Table 2

Sulfur dioxide in the air and suspended sulfate concentrations ($\mu g\ m^{-3}$) observed during February 1974 with a steady North wind blowing from the 17th to the 22nd and no rain.

	February							
	16	17	18	19	20	21	22	23
Paris, average SO_2	135	251	170	180	140	276	216	181
FO1 Vert-le-Petit SO_2*	48	48	123	49	152	37	57	166
Sulfate	0.9	3.6	92	52	42	40	12	13
FO3 La Crouzille SO_2	0	0	19	23	14	14	6	10
Sulfate	2.4	7.1	23	25	20	20	6.5	1.8

At Vert-le-Petit, these averages relate only to the hours during which the North wind was actually recorded. All other figures are for the whole 24-hour sampling period, containing variable wind directions.

We assume, as usual in plume calculations that, at distances which are large compared to the vertical diffusion coefficient and in the presence of a restriciting "lid", the vertical concentration gradients disappear.

With this information, we may formulate the following conditional hypotheses: (1) If the plume does not broaden at all between 37 and 320 km most of the difference 148-35 = 113 $\mu g\ m^{-3}$ was deposited between the two distances. That seems an obvious over-estimation of the deposit, and consequently, an underestimtion of the sulfur leaving the control radius. (2) The effective width of the plume cannot be more than $4 \times 45 = 180$ km, because that would mean that more sulfur leaves the 320 km limit than enters at 37 km, which is obviously impossible. Thus 180 km (which incidentally agrees well with the above 30° estimate, because $\frac{2\pi\ (320\ km)}{12} \approx 170$ km is an upper limit of the width of a plume that meanders as little as possible. In this case, no deposition would have taken place between FO1 and FO3 and all the material entering the 37 km circle would have left the 320 km circle.

As this second hypothesis must overestimate the amount of sulfur leaving the 320 km radius, we can adopt it as the basis of the following estimate. With a plume section of 180 km by 690 m (average mixing height), on the average $4.2 + 2/3\ 4.26 = 7.0\ \mu g\ m^{-3}$ SO_2 are "emitted" throughout the 320 km radius. As the concentration figure contains the (unknown) background sulfur transported from elsewhere than the Paris region, we have a second element of overestimation. A third element of

overestimation follows from the fact that during the period under consideration it did not rain, thus rainy days included, the deposition inside the control circle can only be more, not less than our estimate. With the above data, we estimate that as an upper limit, 115 kT SO_2, (accounting for the SO_2 and the suspended sulfate, i.e. less than 40% of the originally emitted amount) leave the 320 km-circle around the Paris district. The decrease i.e. the deposition between the 37 and 320 km circles does not seem too high but we must bear in mind that the 320 km guess is an overestimate for at least three reasons.

By different reasoning, Raynor et al. (1974) arrive at the same conclusion about New York City: the mean SO_2 concentration is exceeded by local contributions at 70 km from mid-Manhattan and approaches zero at a distance of 112 km.

3. IMPLICATIONS FOR LONG-RANGE TRANSPORT

Admitting as a first estimate the result we derived in the previous section, i.e. that about 150 kT SO_2 per year leave the Paris region, we may ask, how much of it will be available for deposition in some remote area. Some of it will obviously be deposited en route following, on the average, an exponential law. The available best estimate for the decay constant in the exponent is $3 \cdot 10^{-5} s^{-1}$, obtained recently by Eliassen and Saltbones (1975), also from the OECD data. To be rather on the side of overestimation of the remote deposition instead of its probable value, we will consider that the decay constant is equal to zero, i.e. no loss by deposition en route is assumed.

From Northern Central Europe, the end points of trajectories of "particles" (small clouds) released every third day for a period of about one year were calculated following the 850 mb-trajectory by Rodhe (1972). The end points of the trajectories are nearly equally distributed in the four quadrants. For example, we find the following number of end points after 60 hours of travel within 3000 km of the release:

	Quadrant			
Number of 60-hr trajectory ends, after Rodhe (1972)	First	Second	Third	Fourth
	25	19	24	21

We may conclude that there is an approximate directional equipartition on an annual basis. If we admit that the *whole* emission is deposition within the 1000 and 3000 km limits (*no* deposition before; no transport beyond) this circular zone receives on the average an amount of sulfur deposit equivalent to $1.5 \cdot 10^{-2}$ g SO_4 m^{-2} y^{-1}. If we take into account instead of the 150 kT y^{-1} of the Paris area, 50% of the SO_2

emission of France, Great Britain and the Federal Republic of Germany not deposited at short range, i.e. $1/2 \cdot 13400$ kT y^{-1}, this amounts to 0.6 g SO_4 $m^{-2}y^{-1}$ on the average within the boundaries. Not withstanding all the overestimation made, this still is less than the half of the global background (See sect. 5.).

An area of $0.75 \cdot 10^6$ km (roughly the area of Sweden and Norway) within the 1000 to 3000 km limits from Western Europe thus can receive a total yearly deposit of 450 kT sulfate. The 1973 yearly SO_2 emission of these two countries was 1000 kT SO_2, out of which, following the arguments of Sect. 2, 500 kT are deposited at short range, corresponding to 750 kT sulfate. This budget agrees closely with the estimation of Rodhe (1972) "that about half of the sulfur (deposition in Sweden) originates from foreign anthropogenic emission, whilst the other half is caused by Swedish emissions and a natural background".

4. THE PERCENTAGE BREAKDOWN OF THE DRY AND WET DEPOSITION MECHANISMS IN A NUMBER OF GROUND STATIONS

Table 3 presents comparatively the percentage breakdown of the total sulfur deposited (fifth column) for a few ground sampling stations from June 1972 to Dec. 1973. The choice is somewhat haphazard, because of the incomplete measurements and the uncompleted records. Nevertheless, some conclusions seem clear. A group of stations show overwhelming dry SO_2 deposition. These are mostly to be found in the more densely populated areas, and the local SO_2 concentrations must be held responsible for the relatively high dry SO_2 deposition. These network stations are obviously DK2, 3, 4, 5, 6; FO1, NL1, 2, 3, and UK1, 2. It seems surprising but not less clear that IC1, SO4, O5, and SF 1, 2, 3, 4, 5 belong on basis of this statistic also to this group, and thus seem to be influenced by relatively near SO_2 emissions.

On the other hand, in the second group: DK1; NO3; O9; and SO3 the wet mechanism dominates: here the rain precipitates more than 50 percent of the total deposited sulfates.

Table 3 shows that a distinction among ground stations influenced by nearby emission sources can be made on the basis of the ratio of deposition due to the main mechanisms.

Table 3

Percentage breakdown of the sulfate deposition according to the three main deposition mechanisms, June 1972 - Dec. 1973; total deposition in sulfate in g m^{-2} compared with the average emission figures for nearby areas (about 1° by 1°). For the stations marked with an *, fragmentary records (i.e. less than 18 months) were extrapolated.

Station	Dry deposition of SO_2, accounted for as SO_4%	Dry deposition of SO_4, %	Wet deposition SO_4, %	Total deposition of SO_4, gm^{-2} yr^{-1}	Average yearly sulfur emission T $km^{-2}yr^{-1}$
DK 1* Faroe Isl.	30	3	67	3	0
DKZ Hanstholm	60	12	28	4.5	4
DK3 Tange	58	18	24	4.7	6
DK4 Keldsnor	61	18	20	4.4	10
DK5 Gniben	69	16	15	5.0	3
DK6 Dueodde	47	19	33	4.7	1.3
FOl Vert-le-Petit	68	16	15	12.8	30
ICl Rjupnahaed	50	3	47	4.8	0.6
NO3 Finsland	35	7	58	5.0	0.6
NO9 Soyland	25	6	70	6.0	0.6
NLl Wageningen	65	14	21	13.6	30
NL2 Witteven	60	17	23	8.0	18
NL3 Den Helder	58	14	27	9.2	20
SO3* Sjöängen	35	19	46	3	1
SO4* Ryda	49	15	36	5	2
SO5* Bredkälen	44	15	28	6	0
SFl Jomala	62	11	28	5.6	0.2
SF2 Jokioinen	66	7	28	6.8	6
SF3 Puumala	63	8	30	5.5	2
SF4 Ahtäri	50	11	39	4.2	1
SF5 Sodankylä	68	10	32	2.5	0
UKl* Cottered	80	7	13	16	40
UK2 Eskdalemuir	66	10	24	6.0	11

DK = Danemark; F = France; IC = Iceland; N = Norway

NL = Netherlands; S = Sweden; SF = Finland; UK = United Kingdom

5. REGRESSION ANALYSIS

It seems obvious that the material balance method outlined in Section 2 should also be applied to areas other than Paris. Nevertheless, this meets some difficulties. Isolated emission areas in the 10^2 kT yr^{-1} range do not abound in Europe. At least one ground station must

be within a range of clearly distinguishing the plume, as was shown in Fig. 1. This plume should not be confused by other emissions. To meet these criteria, new ground stations may have to be erected, or at least all the OECD results must be accessible in computer compatible form, which is not yet the case.

An attempt which may be made at the present time is to correlate the total per area sulfur deposition rate (fifth column) with the typical nearby regional sulfur emission figures per square kilometer, as reported in the last OECD emission inventories. The regression line

$$\text{Total deposited sulfate (g m}^{-2}\text{ yr}^{-1}\text{)} = 0.28 \text{ emission } (TSO_{12}\text{km}^{-2}\text{ yr}^{-1}) + 4.06$$

represents the data with a correlation coefficient of).91, i.e. with the 21 D.F., largely beyond the 0.0001 α level of significance.

There seems to exist a very narrow correlation between neighbouring area emission and total sulfate deposition. The intercept is an estimate of the background deposition in the area. Very exceptional stations report less that this amount. Very remote and anthropogenically uninfluenced stations show values near 4 g SO_4 $m^{-2}yr^{-1}$: DK1, SO3, SF4.

This estimate of the global background level should be compared to Rodhe's (1972) figure, 250 mg S m^{-2} yr^{-1} (=0.75 g SO_4 m^{-2} yr^{-1}) for the wet deposition.

Considering from Table 3 the four relatively umpolluted stations, where the wet precipitation predominates (these are the four stations belonging to the "second group" Sect. 4) one can see that this mechanism accounts on the average for 60% of the total deposition. Thus from Rodhe's estimated figure we arrive at 1.25 g SO_4 m^{-2} yr^{-1}. On the other hand, after Wolaver and Lieth (1972), throughout the anthropogenically uninfluenced areas of the continental U.S. the total deposition extrapolated in the same way as above is between 1.3 and 2.6 g SO_4 m^{-2} yr^{-1}. Thus the present estimate of global background based on European data comes near to the upper limit of Wolaver and Lieth. The data of Selesneva (1966) concur with these findings.

6. CLIMATOLOGICAL EFFECTS ON THE RECEPTOR-ORIENTED OBSERVATIONS

The emission-oriented mass-balance approach has the added advantage of being less sensitive to the prevailing weather conditions during the reference period than episode-analysis. If the meteorological conditions conducive to high pollution were frequent during a given period, a given deposition might look dramatically high, though on the average

it would not be. This point was proven by Munn and Rodhe (1970). These authors demonstrate a remarkable statistical relation between the deposition of chloride and sulfate at Plönninge (south-western Swedish coast) and Flahault (centrally land-locked in southern Sweden. and the frequency of occurence of rainbearing winds in the SE-S-SW-W-NW sectors.

Qualitatively, the agreement is excellent, all the curves showing peaks in the middle fifties, larger peaks in the middle sixties, and minima at the end of fifties. This behavior is in agreement with that found by Eriksson (1970) for the entire European (Scandinavian, Dutch, Belgian, French, and English) network of stations. All these stations show variations more or less in phase. The amplitude of variations is such that at several stations, the deposited sulfur was less by a factor of ten between a minimum and a maximum year. A factor of five is found in most stations. However, five Irish stations agreeing amongst themselves, do not show the maxima and minima observed in all others. This is somewhat bewildering. Perhaps the single, circumspect conclusion to be drawn from the present Sect. 6 is, to point out the danger of evaluating trends or of generalizing from one or two years of receptor-oriented observations. One doesn't know climatologically if this year is a peak or a low. Thus, extrapolation might be far off the target.

7. CONCLUSIONS

It was shown by example, that a credible source oriented material balance of an urban district may be derived. A shortcoming of the argument is that it concerns just one urban district, the Paris region. For the time being, this could not be checked elsewhere, because of the lack of appropriate emission-receptor topography. Work is now being done to obtain more similar material-balances.

The material balance of the Paris region shows, that at a yearly average, not more than half of the sulfur emission leaves the 37 km radius boundary. The material balance at the 320 km radius is more tentative, but at least does not contradict this conclusion.

According to the ratios for the SO_2-sulfate-wet deposition, ground stations seem to group themselves into those which are influenced by nearby sources, and others where wet deposition prevails and sources farther away must be sought.

There exists a very strong correlation in Europe between overall deposition and (nearby) area emission. The intercept of the regression line is near to the global background.

Finally, previous research has shown that the range of wet deposition of sulfates, and also of other material, has changed by a factor of ten over the years. This change is not geographically uniform, and may have an opposite direction in ground stations only a few thousands of

km apart. Thus fallout-research during a few months or years may show up memorable episodes, but not uncover real trends.

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THE WASH-OUT OF EMISSIONS FROM THE ATMOSPHERE BY PRECIPITATION

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ABSTRACT

We investigated the mechanism and dynamics of solid particles, emissions, and the concentrations of sulphur dioxide as integral components of the contamination of atmosphere. The only way of decontamination is the wash-out by precipitation (solid - snow, liquid - rain). We started from the items of information acquired during the studies of snow acidity in mountain regions heavily polluted by industrial exhalations (NOVÁKOVÁ and TOLLINGER 1971). It was necessary to choose a quite new methodical process, as required and enabled by the existing conditions of our investigation. The investigations of analogous character, carried out mainly in Scandinavia (e.g., BARRETT et al. 1955, ERIKSSON 1955, etc.), approached to the solving of involved problematics from another point of view.

We investigated the separated samples of diurnal precipitation, collected in two sites, the first of which was situated in the centre of an industrial agglomeration in the open landscape, the second one in a wooded mountain valley at a distance of 10 km to the northwest with an elevation of 250 m in relation to the sources of emission.

We found that in the mountain valley the concentrations of SO_2 achieved in 63% of all cases the values up to 0.08 mg/m^3, but the hydrogen-ion-concentrations (pH) in precipitation showed distinctly more acid reaction than in the centre of industrial agglomeration, immediately in the vicinity of emissions source. Here almost 60% of all samples exceeded the concentration of 0.15 mg/m^3 SO_2 in the atmosphere, but the pH values were distinctly shifted to the right (54% of pH values were between 4.5 and 6.0, where as in the remote wooded valley 66% of pH values lay between 3.5 and 5.0).

The differences are, basing on the number of cases investigated, statistically significant. Therefore, it is necessary to define the potential carrier of acidity. There is confirmed the so-called "aerosol theory" (HANUSKA 1971, HRUBÝ 1973, HANUSKA and NOVAKOVA 1975), viz. that the increase of acidity of precipitation is caused mainly by fine particles of maximally 5 μm size.

ACIDIC PRECIPITATION AT A SITE WITHIN THE NORTHEASTERN CONURBATION

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ABSTRACT

Rain and snow were collected in plastic beakers either manually or with a Wong sampler during 58 precipitation events in 1974 at Yonkers, New York approximately 24 km north of the center of New York City. Determinations were made of total dissolved ionic species, free hydrogen ions, total hydrogen ions, sulfate, nitrate, chloride, and fluoride. Conductivity measurements ranged from 618 to 162 umhos, pH from 3.4 to 4.9, total acidity from 36 to 557 ueq/l sulfate from less than 1 to 20 mg/l, nitrate from less than 1 to 14 mg/l, and chloride from less than 1 to 7 mg/l. All fluoride concentrations were less than 0.1 mg/l.

The results indicate that precipitation at this suburban location adjacent to New York City is consistently acidic and contains concentrations of sulfate, nitrate, and chloride which are similar to values found for other locations in the northeastern United States. Positive correlations were found between nitrate and sulfate concentrations and acidity suggesting that the atmospheric contaminants, sulfur and nitrogen dioxide, are causally-related to the occurrence of acidic precipitation. Further research will be necessary to clarify the relative influence of natural and man-made sources of nitrogen and sulfur compounds and the contributions of gaseous and particulate contaminants in the atmosphere to the acidity of precipitation at this location.

INTRODUCTION

Acidic precipitation is a well-known phenomenon in northern Europe and some of its actual and potential environmental effects have been described (Sweden, 1971) but explanations for its occurrence still are debated. Although a similar problem exists in the northeastern United States, the available data are primarily for bulk deposition (wet and dry) (Pearson and Fisher, 1971; Likens, 1972; Frizzola and

Baier, 1975) and relatively few estimates of the composition of individual precipitation events are available (Cogbill and Likens, 1974; Frohliger and Kane, 1975). This report presents results of the first phase of a program designed to characterize some of the chemical and physical properties and environmental effects of acidic precipitation. The data include the acidity and anionic composition of individual rain and snow samples collected during 1974 at a site in Yonkers, New York, about 24 km north of the geographical center of New York City.

EXPERIMENTAL

COLLECTION

Wet deposition was collected during 58 events from January through December 1974 at a height of 1.2 m above ground either manually or with an automatic rain sampler (Wong Labs.) with minimum collection of dry deposition between precipitation events. The sampling device consisted of a polyethylene funnel of 25 cm outer diameter placed over a polyethylene beaker of 0.6-liter capacity; two-liter beakers were used later in the study to avoid overflow during heavy precipitation. Samples were stored in tightly-closed polyethylene bottles at 1 to 5° C for periods of up to four weeks prior to analysis.

Precipitation was collected in an open field at an elevation of approximately 100 m above sea level, latitude 40°58'45" north, longitude 73°52'57" west (Figure 1). The nearest bodies of salt water were

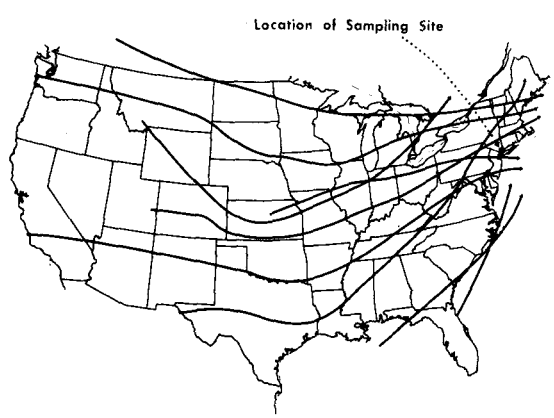

Figure 1. Location of precipitation sampling site in relation to prevailing storm trajectories in the United States.

the lower estuary of the Hudson River (about 1 km to the west) and Long Island Sound (about 11 km to the south-southeast).

Precipitation occurred as snow or a mixture of snow and rain in five of the 58 events sampled. No data are available for several events because they occurred on weekends or because liquid volumes were too low. Partial data were obtained for 16 events because the volume of liquid was insufficient for all analyses.

ANALYSIS OF CONDUCTIVITY AND FREE AND TOTAL HYDROGEN ION CONCENTRATION

Conductivity was measured using a conductivity bridge and pH with an expanded-scale pH meter*. During the measurement of pH and subsequent titration, the surface of the sample was swept with pure nitrogen gas. Samples were stirred during addition of standardized CO_2-free sodium hydroxide (0.008 N) but not during actual pH measurement. Sodium hydroxide was added in 0.06 ml aliquots and pH recorded after each addition until a reading of 9.4 to 9.5 was obtained. Nitrogen was bubbled through representative samples to determine the changes in free and total acidity occurring when volatile gases such as CO_2 are purged from solution.

Free hydrogen ion concentration was calculated from the initial pH; total hydrogen ion concentration was computed from the difference between equivalents of alkali added during titration and the equivalents of hydroxyl ions present at the final pH. The latter value included free hydrogen ions and titratable hydrogen ions of substances with pK values less than about 9.5 (e.g., carbonic acid). Titration curves were constructed both for precipitation samples and for standard samples of pure sulfuric and nitric acids and pure SO_2 and CO_2 bubbled through deionized water.

ANALYSIS OF ANIONS

Sulfate was measured by addition of barium perchlorate to precipitate barium sulfate and spectrophotometric determination of excess barium (II) ions with thorin reagent (Norwegian Institute for Air Research, 1974). Initially, nitrate was measured spectrophotometrically by reaction with brucine (Jenkins and Medsker, 1964). Chloride was determined by the mercury thiocyanate method (Florence and Farrar, 1971) and fluoride with a selective ion electrode (American Society for Testing and Materials, 1973).

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*Conductivity measurements were performed with a Model 31 Yellow Springs Instrument Co. meter and pH with either a Model 12 Corning or Model 801 Orion digital electrometer. A No. 14073 Instrumentation Lab. combination electrode or a No. 476139 Corning pH electrode and No. 90-01-00 Orion reference electrode were used for pH measurements.

1971) and fluoride with a selective ion electrode (American Society for Testing and Materials, 1973).

Selected samples were titrated before and after addition of hydrogen peroxide solution to detect the presence of partially oxidized components. Conversion of a weak into a strong acid was clearly shown by titrating SO_2 in water before and after addition of hydrogen peroxide.

DATA ANALYSIS

Frequency distributions of measurements were constructed and joint distribution of paired variates was investigated by plotting one variate against another for all events on an arithmetic scale and by calculating partial correlation coefficients and testing for significance using the *t*-test.

Total deposition of components in rain and snow for the year were calculated from the measured concentrations and the volume of rainfall for each event. These values represent lower limits of deposition because analyses were not obtained on all events and, infrequently, measurement of rainfall volume was negatively biased due to overflow of the collector.

RESULTS

The minimum, maximum, and mean values for components of precipitation and total wet deposition for 1974 are summarized in Table I. Precipitation at Yonkers was consistently acidic; some samples had hydrogen ion concentrations more than two orders of magnitude greater than expected for a solution of pure water in equilibrium with the atmospheric concentrations of CO_2. The concentrations of total available hydrogen ions were consistently greater than free hydrogen ions (Figure 2) and the ratio of total to free hydrogen ions tended to rise as pH increased. Free hydrogen ions usually comprised more than half of the total acidity in samples with pH values below 4.2. Values for total deposition of sulfate, nitrate and hydrogen ions (Table I) are similar to those found in northern Europe.

Sulfate was the anion generally in greatest concentration (Table I), but in some samples, concentrations of nitrate were greater than sulfate. On an equivalent basis, the ratio of sulfate to nitrate generally was more than two when the value of sample pH values was greater than 4; when the pH of the precipitation was less than 4, the ratio of sulfate to nitrate was usually less than 2.

Table I. Composition of precipitation collected at Yonkers, New York during 1974

Measurement	Minimum	Mean	Maximum	Total deposition[1]
Amount of precipitation, cm	0.03	1.49	7.1	85.9
Conductance, μmhos	6.8	47.7	162	-
pH	3.4	4.1	4.9	-
Free H^+, μeq/l	13	103	380	0.88
Total H^+, μeq/l	36	148	557	1.27
Ratio of total H^+ to free H^+	1.2	1.7[2]	2.9	-
Sulfate, mg/l	<1	4.8	20	4.12
Nitrate, mg/l	<1	4.4	14	3.78
Chloride, mg/l	<1	1.2	7	1.03
Fluoride, mg/l	<0.1	-	<0.1	-

[1] Data in this column given in kg/hectare except for amount of precipitation (cm).

[2] Mean ratio calculated only for those events in which both free and total hydrogen ions were measured (47 of 58 samples collected).

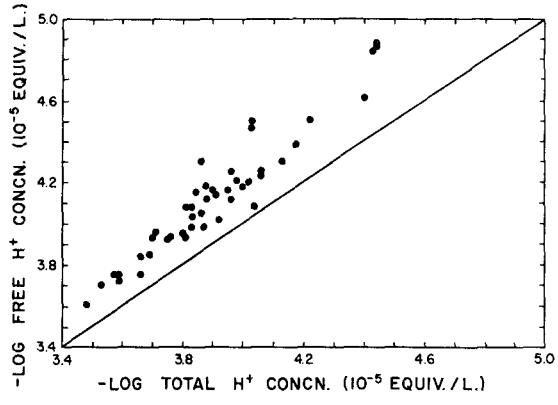

Figure 2. Joint distribution of free and total hydrogen ion concentrations of precipitation samples. The solid line indicates the expected distribution if there were no bound hydrogen ions.

Chloride was present usually in concentrations less than 2 mg/l and the concentration of fluoride seldom exceeded the precision of analyses (± 0.05 mg/l) and never was greater than 0.1 mg/l (Table I).

Frequency distributions for all measurements were skewed with a few data points at high concentrations; cumulative frequency distributions tended to be linear either on arithmetic or on logarithmic scales (free and total hydrogen ion concentrations).

Graphical analysis of the data indicated that there was a similarity between the distributions of certain variates. Free hydrogen ion concentration was positively correlated with total hydrogen ion concentration (Figure 2), conductance (Figure 3), nitrate concentration (Figure 4), and sulfate concentration (Figure 5); but inversely correlated with volume of precipitation event (not shown). Statistical

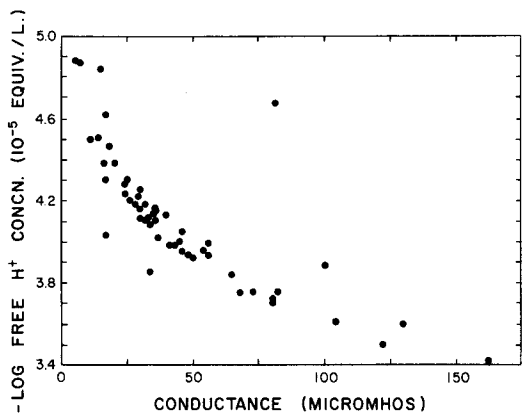

Figure 3. Joint distribution of free hydrogen ion concentrations and conductivity of precipitation samples.

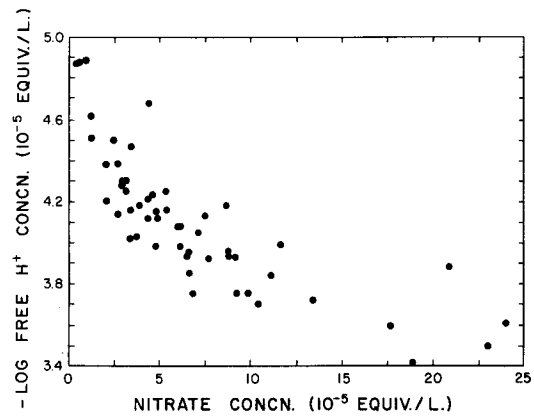

Figure 4. Joint distribution of free hydrogen ion and nitrate concentrations in precipitation samples.

analysis of the data using partial correlation coefficients demonstrated that the most significant correlations with free hydrogen ion concentrations were: volume, conductance, total hydrogen ion concentrations, and nitrate concentrations. Nitrate and sulfate concentrations also were significantly correlated.

All rain samples titrated as though they contained a monoprotic acid with an equivalence point in the vicinity of pH 7 (Figure 6). Synthetic aqueous solutions of carbon dioxide and sulfur dioxide, before and after oxidation to sulfuric acid with hydrogen peroxide, displayed titration curves (Figure 7) typical of carbonic acid (A), a combination of sulfurous and sulfuric acid (B), and sulfuric acid (C).

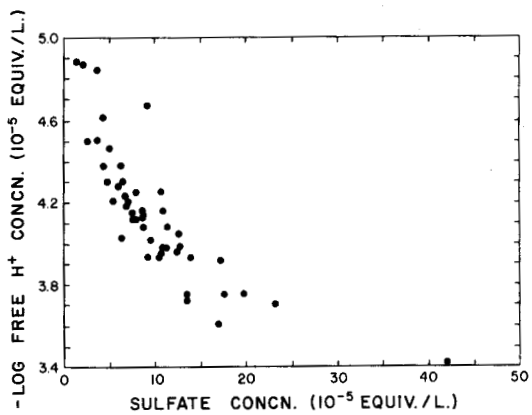

Figure 5. Joint distribution of free hydrogen ion and sulfate concentrations in precipitation samples.

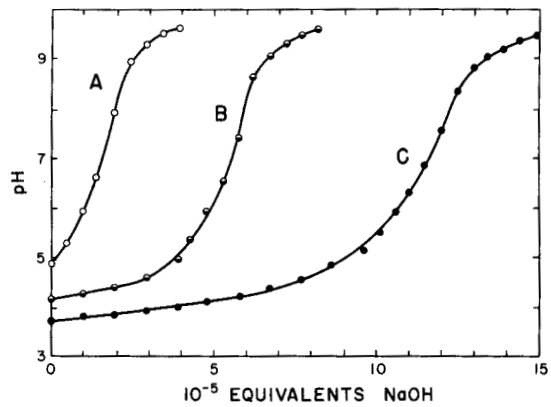

Figure 6. pH titration curves for three representative rain samples (50 ml aliquots) collected at Yonkers, New York in September (A), July (B) and August (C), 1974.

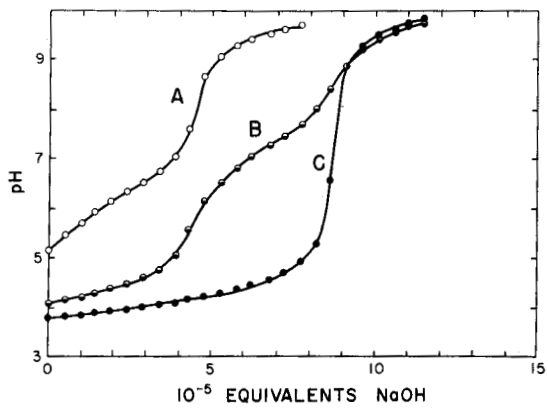

Figure 7. pH titration curves for solutions of carbon dioxide in water (A), sulfur dioxide in water (B), and sulfur dioxide in water (50 ml. aliquots) containing approximately 0.003% hydrogen peroxide v/v (C).

Purging rain samples of volatile gases with nitrogen gas produced only minor changes in free acidity but total hydrogen ion concentrations were reduced by 15 to 25% in different samples.

DISCUSSION AND CONCLUSIONS

The data in Table I demonstrate that precipitation of a consistently acidic nature falls in Yonkers, New York, a suburban site within the northeastern conurbation immediately adjacent to New York City (Figure 1). The sulfate, nitrate, and chloride as well as hydrogen ion concentrations in precipitation at this location (Table I) are similar to those found at other sites in the northeastern United States (Junge, 1963; Fisher et al, 1968; Pearson and Fisher, 1971; Likens and Bormann, 1974). However, the mean sulfate concentration of 4.8 mg/l tends to be toward the upper end of the ranges reported by others and the mean nitrate concentration of 4.4 mg/l is above that reported by others. According to Likens and Bormann (1974), nitrate concentrations in precipitation have increased since 1945. The mean chloride concentration of 1.2 mg/l is intermediate between coastal and continental sites (Pearson and Fisher, 1971).

The range of values found for hydrogen, sulfate, and chloride ion concentrations in precipitation tends to be narrower in previous reports than for Yonkers because bulk sampling for weekly or monthly periods tends to average out the storm by storm variations. In addition, bulk samples contain both wet and dry deposition and are not strictly comparable to event samples which contain only wet deposition.

The chemical form and physical state of sulfur and nitrogen compounds at the time of scavenging by rain are important factors in determining the acidity of precipitation because protons are formed during hydrolysis and oxidation of SO_2 and NO_2. The correlations found between acidity and nitrate and sulfate concentrations in precipitation at Yonkers (Figures 4 and 5) tend to support the hypothesis that SO_2 and NO_2 are largely responsible for the acidity of precipitation (Junge, 1963; Pearson and Fisher, 1971; Johnson et al, 1972; Cogbill and Likens, 1974). Pearson and Fisher (1974) also have reported a correlation between hydrogen and sulfate ions in precipitation. In addition to entering precipitation in the gaseous form, sulfate and nitrate are components of aerosols and particulate matter. Granat (1972) and Likens and Bormann (1974) have suggested that atmospheric particulate matter has a neutralizing influence on the acidity of rain; however, Frizzola and Baier (1974) found that bulk samples (wet and dry deposition) are more acidic than event samples (wet deposition only) at coastal sites in New York. In addition, Brosset et al (1975) have found that particulate matter on the Swedish west coast is acidic. There is as yet no clear understanding of the relative contributions of atmospheric gases and particulate matter to the composition of precipitation in the northeastern United States.

Alkalimetric titrations of precipitation collected in Yonkers demonstrated the presence of substantial quantities of bound as well as free hydrogen ions (Table I and Figure 2). A portion of this weak

acidity probably was due to the presence of carbonic acid because decreases in total acidity of 15 to 25% were found after removal of volatile gases by bubbling nitrogen gas through rain samples. Other substances such as complexes of heavy metals, organic acids, and clay particles which dissociate weakly to produce protons in aqueous solution may account for the remaining bound hydrogen ion. The ratios of total to free hydrogen ions for precipitation in Yonkers ranged from 1.2 to 2.9 (Table I). Frohliger and Kane (1975) found ratios of 2 to 100 for rainfall in a rural area of Pennsylvania and have interpreted this to mean that strong acids do not play a major role in determining the pH of rainwater. The high total to free hydrogen ion ratios found by Frohliger and Kane may be due, in part, to the lower free hydrogen ion concentrations of precipitation in Pennsylvania (pH values ranged from 4.12 to 5.78). Differences in techniques used for titration may also be involved because the latter authors heated their samples and then titrated slowly without using an inert gas to prevent possible absorption of CO_2 from the ambient atmosphere.

Precautions to be taken during the measurement of pH have been published (Barnes, 1964) but there is no agreement or standardization among laboratories in the United States measuring the total acidity of precipitation. The sources of error vary with the method used and each method appears to have some disadvantages. Depending on vapor pressure gradients, volatile components may diffuse out of or into solution during storage or titration. Heating of samples and slow titration procedures may enhance gas exchange with the surrounding atmosphere. Titrations carried out in a laboratory atmosphere may result in absorption of CO_2 because CO_2 partial pressures are frequently above normal indoors. CO_2 also may diffuse into solution from the atmosphere especially when the sample being titrated becomes alkaline. On the other hand, efforts to purge acidic precipitation samples of CO_2 using an inert gas may cause loss of volatile acids including CO_2 derived from bicarbonate or carbonate in atmospheric particulate matter.

In this study we used an inert atmosphere during titration with no purging of CO_2 from samples even though CO_2 will slowly diffuse from solution during the titration. Even if all of the carbonic acid present in rain samples had been lost during these titrations, the maximum negative bias produced in total acidity measurements by this procedure would have been 15 to 25%.

Calculations of free and total hydrogen ions from the titration curves in Figure 6 indicate that strong acids comprise approximately 37% of sample A, 59% of sample B, and 66% of sample C. The lower pH rain samples collected at Yonkers contain the highest proportion of strong acids. Similar calculations for titrations of known substances displayed in Figure 7 indicate that strong acids comprise approximately 7% of sample A (CO_2 in water), 48% of sample B (SO_2 in water), and 97% of sample C (SO_2 in water oxidized to sulfuric acid with hydrogen peroxide). The evidence clearly implies that strong acids are largely responsible for the free hydrogen ion concentrations of rain samples at

this location. The measured concentrations of sulfate and nitrate found in these samples are more than sufficient to account for the accompanying free hydrogen ion concentrations assuming that SO_2 and NO_2 are the original sources of most of the sulfate and nitrate found.

Despite the emissions of fluorides from combustion of coal and other industrial operations in the United States (Committee on Biological Effects of Atmospheric Pollutants, 1971), the fluoride concentration of precipitation in Yonkers was consistently less than 0.1 mg/l (Table I). Fluorides in concentrations as high as 14 mg/l have been found in rain at other locations but mainly in the vicinity of specific industrial operations or where bituminous coal was being used for space heating (Garber, 1970; MacIntire et al, 1952; Harriss, 1969). There are no specific fluoride-emitting industries in Yonkers and bituminous coal has been replaced by anthracite coal, oil, and natural gas in the United States.

Comparisons between concentrations of measured components and conductivity (Table I) indicate that over 90% of the dissolved ionic species are accounted for by hydrogen, sulfate, nitrate, and chloride ions. The remaining conductivity is probably due to cationic species such as calcium, magnesium, sodium, and ammonium ions (Pearson and Fisher, 1971). The correlation between conductivity and acidity (Figure 3) largely reflects the influence of the high concentrations of hydrogen ions in precipitation. Conductivity of precipitation samples also may be influenced by volume of rain because dilution decreases the concentrations of ionic species.

The results of this study indicate that precipitation in Yonkers is equivalent to a dilute solution of sulfuric and nitric acids containing salts of sulfate, nitrate, and chloride in addition to smaller amounts of other inorganic and organic substances. A complete inventory of the composition of rain and snow may require analyses for hundreds of components because of the wide variety of materials present in trace quantities in the atmosphere. Further investigations are needed in order to evaluate the relationships between conductivity, volume of rain events, and cation and anion concentrations. The results of 1974 analyses suggest that there may be a more direct relationship between nitrate concentrations and acidity than between sulfate and acidity but data for at least several years is needed to evaluate these observations and to discover differences in composition with season and type of meteorological event.

The relative contribution of natural vs. anthropogenic sources of pollutants to the composition of precipitation in the northeastern United States is not clear. Junge (1963) has reported that the major sources of naturally-occurring sulfur compounds in the atmosphere are of maritime and coastal origin. The relatively low concentrations of chloride in the majority of precipitation samples taken at Yonkers (Table I) implies a predominately terrestrial origin for precipitation.

The prevailing movement of storm systems and air masses from west to east (Figure 1) also suggests that the major sources of components of rain at Yonkers are terrestrial rather than maritime in origin. However, this information does not indicate the actual course taken by air masses in their anti-cyclonic movement around storm centers. Cogbill and Likens (1975), using wind trajectory data, found that the mid-western region of the country is a major source of components of precipitation in the northeast. This suggestion needs additional verification.

ACKNOWLEDGMENTS

The authors thank L. H. Weinstein for several useful discussions and D. C. McCune for calculation of partial correlation coefficients. This study was financed in part with Federal funds from the Environmental Protection Agency under Grant No. 801070. The contents do not necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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CHEMICAL COMPOSITION OF ACID PRECIPITATION IN CENTRAL TEXAS

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ABSTRACT

Studies were undertaken to determine factors affecting composition of acidic precipitation formation in the Austin area of Central Texas. The study was initiated to determine background levels of acid and alkalinity producing constituents in an area with elevated natural dust levels from nearby limestone rock formations. Results showed normal rainfall pH values of 6.5 to 6.6 in the area, with extreme variations from 5.8 to 7.3. Significant calcium levels of 1 to 4 mg per liter were observed from probably natural origin which appeared to have a buffering effect on acidity. Significant sulfate and nitrate ion concentrations occurred during the early stages of rainfall where rainfall pH was dependent on calcium-sulfate ratio.

INTRODUCTION

The increasingly serious problems of availability of domestic petroleum energy resources is causing increasing interest in coal burning for electric power generation. It is estimated that the coal-fired generating capacity in the United States will increase from 166,000 megawatts in 1973 to over 400,000 megawatts by 1990. Coal fired generating capacity in the State of Texas is expected to increase from 1,100 megawatts to almost 17,000 megawatts by the year 1990. Major increases in oil-fired electric generating capacities in Texas are expected to occur from 900 megawatts in 1973 to above 24,000 megawatts by 1990 by replacement of natural gas as a boiler fuel.

The burning of coal and oil as boiler fuels for electric power generation and industrial process heating will result in major increases of sulfur oxides and nitrogen oxides emissions to the atmosphere. Sulfur oxides emissions on a worldwide basis are expected to increase from 47 million tons in 1968 to 94 million tons by 1980. Sulfur oxides emissions in the United States are projected to increase from 33 million tons in 1968 to 50 million tons by 1980, and nitrogen oxides emissions are projected to increase from the present 20 million to 30 million tons per year. The burning of coal and oil for electric power generation in Texas is expected to increase sulfur oxides emissions by more than one million tons per year by 1990.

The selective application of particulate controls on electric power plants in the eastern United States burning high sulfur coals has occurred simultaneously with the construction of tall stacks for dispersion of sulfur dioxide in ambient air without attempting to reduce the quantities emitted to the atmosphere. The result has been to minimize the ambient sulfur dioxide concentrations immediately downwind of these power plants but also to create the less obvious but insidious problem of acid rainfall formation at remote locations many miles away. This acid rainfall can create hazards in terms of forestry, agriculture, materials, aquatic life and humans through potential adverse effects.

BACKGROUND

The problem of acid rainfall formation appears to be associated with the presence of sulfur oxides and nitrogen oxides emitted to the atmosphere from combustion of fossil fuels. Acid rainfall was reported to be a problem in the city of Leeds, England by Crowther and Rustan (1911) who measured rain acidity levels equivalent to pH 3.2. Rainfall acidity values in some areas of Sweden and Norway have been reported from pH 3 to 5, with increasing acidity levels observed beginning in the early 1950's by Barrett and Brodin (1955).

Recent studies by Likens and Bormann (1972) (1974) indicate increasing rainfall acidity values in the northeastern United States over the past 20 years as compared to the rest of the country. Average rainfall pH's of 3 to 4 have been observed at several locations in the states of New York and New Hampshire, with extreme values measured as low as 2.1 in 1964 by Fisher et al. (1968). Rainfall acidity values were observed to increase beginning about 1950 even though total sulfur levels in the rainfall began to decrease, ostensibly because of the selective implementation of emission controls for alkaline particulate fly ash without simultaneous controls on acidic sulfur and nitrogen oxides on combustion sources.

Previous studies of rainfall acidity in a nonindustrialized area of northern Florida along the Gulf of Mexico by Brezonik (1968) indicated pH values ranging from 5.3 to 6.8 in 1967 and 1968. Previous studies by the Texas Air Control Board of rainfall acidity showed pH values of 6.0 in downtown Houston and 6.5 in Austin. Recent studies by the Clear Creek School District located between industrial areas along the Houston Ship Channel and in Texas City showed average rainfall pH values of 4.0 to 4.5. Extreme values as low as 3.5 were measured on two occasions, where it was desired to determine potential impacts on drinking water quality.

CHEMISTRY

The relative acidity or alkalinity of rainfall is affected by the presence of both acid-producing and alkali-producing constituents in rainfall. These constitutents may be present in either the gaseous or particulate forms and may be derived from either natural or manmade sources. In the absence of major manmade pollutants, raindrops falling through the atmosphere will reach an equilibrium with carbon dioxide which dissolves in water to produce the slightly acidic carbonic acid with an equilibrium pH of approximately 5.7.

The major constituent from manmade sources tending to produce acid rainfall is sulfur oxides emitted from combustion of coal or oil, where the amount released is directly proportional to the sulfur content of the fuel. The sulfur present in coal or oil is converted to sulfur dioxide during combustion, which can then be oxidized to form sulfuric acid either in the gaseous or liquid phase, as shown in Figure 1. The sulfuric acid formed either by hydrolysis of sulfur trioxide or oxidation of sulfurous acid can then react with the alkaline ammonia gas or calcium carbonate particulate matter to form ammonium sulfate or calcium sulfate, respectively.

Nitrogen oxides constitute an additional major source of rainfall acidity from combustion processes. Nitric oxide is formed at elevated temperatures by reaction of nitrogen and oxygen to produce nitric oxide, which can then be oxidized to form nitrogen dioxide in either the combustion zone or the atmosphere. The nitrogen dioxide can be hydrolized in the presence of water to form both nitrous and nitric acids. These acids can then react with either ammonia gas or calcium carbonate to form the respective ammonium or calcium nitrite or nitrate salts, as shown in Figure 1.

Other constituents present in the fuels can also affect the acidity levels of rainfall once the materials are emitted to the atmosphere. Chlorine and fluorine present in trace quantities of some coals react during combustion to produce their respective hydrochloric and

SULFUR OXIDES

$$S + O_2 \longrightarrow SO_2$$

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$H_2SO_3 + \tfrac{1}{2}O_2 \xrightarrow{\text{Catalyst}} H_2SO_4$$

$$2SO_2 + O_2 \xrightarrow{\text{Catalyst}} 2SO_3$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$$

$$H_2SO_4 + CaCO_3 \longrightarrow CaSO_4 + H_2O + CO_2$$

NITROGEN OXIDES

$$N_2 + O_2 \longrightarrow 2NO$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

$$HNO_2 + NH_3 \longrightarrow NH_4NO_2$$

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3$$

$$2HNO_2 + CaCO_3 \longrightarrow Ca(NO_2)_2 + H_2O + CO_2$$

$$2HNO_3 + CaCO_3 \longrightarrow Ca(NO_3)_2 + H_2O + CO_2$$

Figure 1. Chemical Mechanisms of Acid Rainfall Formation in the Atmosphere

hydrofluoric acids. Trace metals present in coals such as iron, copper, manganese, vanadium and others can act as catalysts to promote the oxidation of sulfite to sulfate ion in solution, or of nitrite to nitrate ion. Other constituents present particularly in the fly ash released from combustion contain calcium, aluminium or silicon or other ions which are associated with the carbonate, silicate or oxide forms which can contribute to the alkalinity of rainfall. The ammonia present in the atmosphere from natural sources or from oil combustion can also act as a weak alkaline constituent.

METHODOLOGY

The purpose of the study was to determine background levels of rainfall acidity and factors affecting rainfall acidity in Austin, Texas in a city of about 300,000 population to provide a baseline for observing future changes. Existing rainfall chemical properties were measured in an area with little existing heavy industry, negligible sulfur oxides emission sources, and high natural background limestone (calcium carbonate) dust levels from adjacent deposits. The study was performed to obtain background information regarding rainfall composition affecting acidity prior to construction of a large coal-fired

power plant 35 miles southeast and upwind in the prevailing directions, and also prior to implementation of catalytic converter exhaust controls on new motor vehicles.

Rainfall collection stations were located at three points in Austin in a generally south-north line at a residence along Town Lake, atop the Civil Engineering Building at the University of Texas, and at the Texas Air Control Board. Sequential static units were used for collection of rainfall samples through funnels consecutively into 300 milliliter plastic collection bottles, as shown in Figure 2. Following

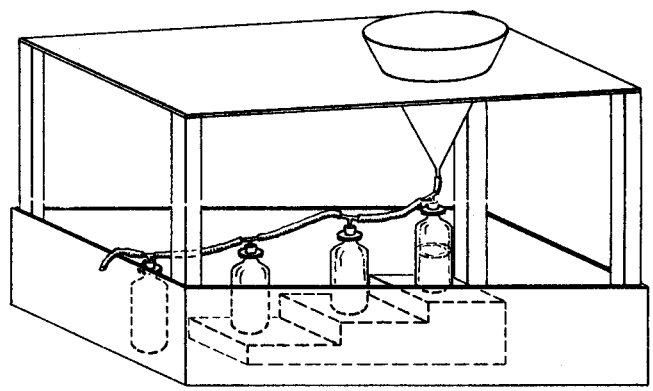

Figure 2. Sequential Rainfall Sample Collection Unit

collection, the rainfall samples were taken to the laboratory for subsequent chemical analyses. Collection bottles could also be removed for intermittent analysis of liquid pH.

Chemical measurements during the studies were made for liquid pH, total solids, total dissolved solids, sulfate ion, nitrate ion, nitrite ion, calcium ion and trace metals using established analytical techniques. The barium chloride turbidometric method was used for sulfate ion determination. While the reduction-diazotization method was used for nitrate and nitrite ion measurements. Calcium ion measurements were made by means of atomic absorption spectrophotometry while trace metal measurements were made using X-ray fluorescence.

RESULTS

Rainfall samples were collected during rainstorms in Austin, Texas on February 1-4, March 1-3 and April 28-29, 1975. An additional rain

sample was taken in Laredo, Texas on March 11-12, 1975 and a snow sample was collected in Austin, Texas on January 8, 1975.

Rainfall pH measurements were made periodically at the Town Lake sampling station during a prolonged four day rainstorm which began on January 31st and ended on February 4th of 1975. Initial rainfall pH values were about 6.6 at the start of the rain which gradually increased to 7.4 and then dropped dramatically to almost 5.7 during a heavy rain with a strong north wind. The rain pH then gradually increased to 6.6 over the next two days with a reduced rainfall intensity and a return to southerly winds, as shown in Figure 3. Soils to the

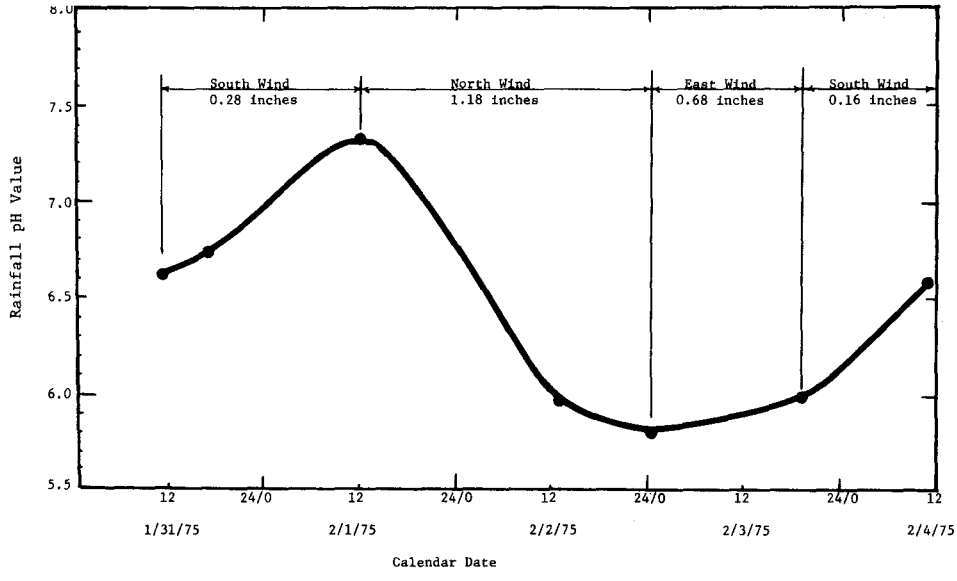

Figure 3. Variation of Rainfall pH during a Storm in Austin, Texas January 31 - February 4, 1975

South and West of the sampling location generally contained high calcium carbonate contents which probably increased the entrained limestone dust and resultant rainfall pH values.

The pH of the rainfall during a second storm on March 1-4, 1975 varied between 6.6 and 7.7. Samples taken at the University sampling station showed a decrease in pH from 6.6 to 5.9 during the course of a recent rainstorm on April 28-29, 1975 characterized by thunderstorms and medium rainfall intensity. An additional rainfall sample taken during a thunderstorm in Laredo, Texas indicated a pH value 6.66 while a snowfall sample taken in Austin showed a pH of 7.65.

A series of chemical analyses were made to characterize the chemical composition of rainfall samples taken during the February and March rainstorms. Sulfate ion levels observed during the February rainstorm generally decreased from 7.5 to 2.0 milligrams per liter during the storm as shown in Table I. Sulfate ion levels in the March rainstorm generally decreased from 12.5 to 3.0 milligrams per liter. The

TABLE 1

CHEMICAL COMPOSITION OF RAINFALL COLLECTED IN AUSTIN, TEXAS

January 31 - February 4, 1975

SAMPLE DATE	TIME INTERVAL	DISSOLVED SOLIDS mg/liter	TOTAL SOLIDS mg/liter	CALCIUM ION mg/liter	SULFATE ION mg/liter	NITRATE + NITRITE mg/liter
1/31/75	1030-1700	136.0	140.0	4.10	7.50	1.74
1/31/75	1700-2400	110.0	114.0	2.30	4.25	1.63
2/1/75	0000-0900	138.0	138.0	1.35	2.00	0.88
2/1/75	0900-2300	---	140.0	3.32	3.50	0.64
2/2/75	0100-1030	96.0	100.0	3.80	6.00	1.08
2/2/75	1100-2400	---	96.0	2.10	3.00	1.36
2/3/75	0030-1930	92.0	92.0	1.70	0.00	0.80
2/3/75	1930-0400 (2/3)	---	94.0	1.00	2.00	0.45
2/4/75	0400-1200	---	92.0	0.20	2.00	0.17
2/4/75	0400-1200	---	---	0.20	---	0.17

sulfate ion concentration in snow was 21.5 milligrams per liter as shown in Table II. This trend corresponded to the higher total solids level in snow of 210 milligrams per liter, which was significantly higher than the initial value of 140 milligrams per liter reported for the February rain.

The calcium ion concentrations in rain generally decreased from a maximum of 4.1 to a minimum of 0.2 milligrams per liter during the progress of the rainstorm on February 1-4, 1975. Significantly higher calcium levels were observed during the March rainstorm, which may have occurred because of the prolonged air stagnation period prior to the rain. A general decrease in pH of rainfall was observed during the progress of rains as the weight ratio of calcium-to-sulfate contents of rainfall decreased, as shown in Figure 4. These results showed that decreases in the amount of available calcium associated with the alkaline calcium carbonate in relation to the sulfate content of rainfall caused a decrease in the pH.

TABLE 2

CHEMICAL COMPOSITION OF RAIN COLLECTED IN AUSTIN, TEXAS

March 1-4, 1975

SAMPLE	LIQUID pH	TOTAL SOLIDS mg/liter	CALCIUM ION mg/liter	SULFATE ION mg/liter	NITRATE + NITRITE mg/liter
1A	7.72	206	15.0	12.5	1.28
2A	7.17	100	4.5	3.0	0.44
3A	—	96	3.4	—	—
1B	—	—	8.7	8.5	2.54
2B	7.52	138	10.5	3.5	1.12
3B	—	92	2.5	3.5	0.36
1C	6.69	—	—	4.0	0.84
1D	6.65	—	—	—	—
Laredo	6.66	—	—	5.0	0.00
Snow	7.65	210.0	11.0	21.5	2.52

Values for total nitrite plus nitrate content of rainfall decreased from 1.74 to 0.17 milligrams per liter during the February

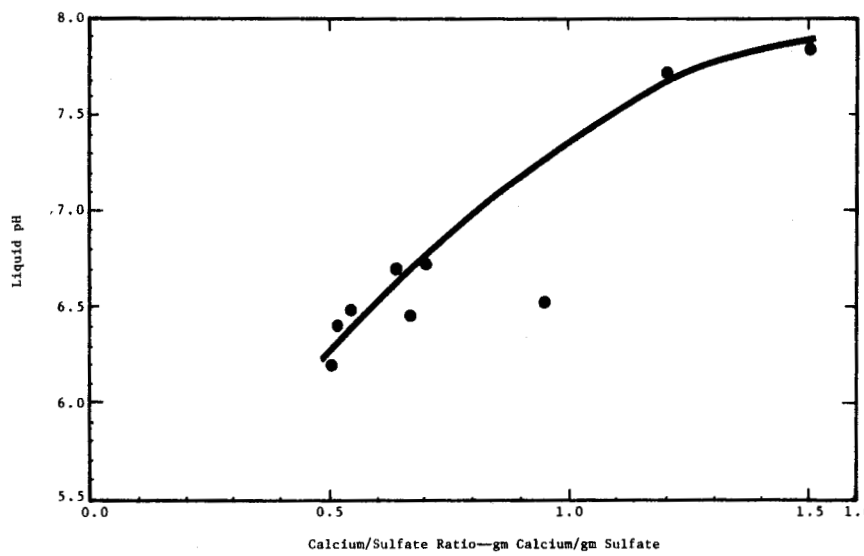

Figure 4. Effect of Calcium/Sulfate Concentration on Final Rainfall pH Value.

rainstorm as the nitrogen was gradually removed from the atmosphere, with a similar trend noted during the March rain. Further analyses showed that the major portion of the nitrogen was present in the nitrate ion form, with only a residual 0.1 milligrams per liter present in the nitrite ion form as shown in Table III. The nitrate ion is

TABLE 3

NITRITE AND NITRATE ION CONTENTS OF RAINFALL

IN AUSTIN, FEBRUARY 1-4, 1975

RAIN SAMPLE	Ionic Concentration—mg/liter		
	NO_2^-	NO_3^-	$NO_2^- + NO_3^-$
1A	0.10	1.80	1.90
4A	0.10	0.70	0.80
1B	0.10	1.10	1.20
4B	0.10	0.35	0.45
1C	0.10	0.00	0.10
2C	0.10	0.00	0.10

significant not only for acid rainfall formation, but also as a nutrient for algae and for soils, while the nitrite ion is significant in terms of potential oxygen demands in receiving waters.

A limited number of measurements have been made of the trace metal contents of rainfall samples using both atomic absorption spectrophotometry and X-ray fluorescence techniques. Analyses for calcium using cationic and anionic membrane ion exchange filters showed that materials tended to leach from the cationic filter and tended to be uncollected with the anionic filter. It was noted that small amounts of lead and bromine from automobile exhaust were detected, as well as trace quantities of vanadium, arsenic, copper, iron, potassium and zinc, as shown in Table IV. Additional work is necessary to evaluate the potential suitability of X-ray fluorescence for trace metal analyses in rainfall.

TABLE 4

COMPOSITION OF AUSTIN RAINFALL ON SAMPLE 1A

February 1-4, 1975

	METAL COMPOSITION mg/liter		
METAL	ATOMIC ABSORPTION	X-RAY CATIONIC	X-RAY ANIONIC
Calcium	2.72	2.850	0.042
Arsenic	——	——	0.004
Copper	——	——	0.002
Bromine	——	——	0.008
Iron	——	0.060	0.083
Lead	——	0.016	0.004
Potassium	——	0.230	0.054
Vanadium	——	——	0.002
Zinc	——	0.190	0.003

CONCLUSIONS

Existing rainfall acidity levels in Austin, Texas were determined through a series of measurements taken during the period January-April, 1975 to determine background levels in an area removed from major industrial activity. Results showed rainfall pH values to vary between 5.7 and 7.7 with average values of 6.6, where the pH tended to decrease during the progress of rainstorms as the alkaline calcium carbonate-bearing particulate materials were gradually removed. Sulfate ion levels in rain and snow ranged from 2.0 to 21.5 milligrams per liter while nitrate levels ranged from 0.2 to 2.5 milligrams per liter. Small quantities of lead and bromine from automobile exhausts, plus vanadium and other trace metals were also noted in the rain.

A possible solution to the problem of acid rainfall lies in the removal of sulfur dioxide from flue gas streams through regenerative emission control systems followed by conversion to liquid sulfur dioxide, sulfuric acid or elemental sulfur. The sulfur byproducts could then be transported from surplus generation points in the eastern United States by railroad to arid areas of the western United States. The sulfur byproducts could be added as sulfuric acid or sulfurous acid either through irrigation water or directly to these alkaline soils as neutralization agents to enhance agricultural productivity in these

areas. Recovery of the sulfur dioxide as elemental sulfur is indicated to minimize the amounts of material moved, and to enable the sulfur to be loaded into the same hopper cars used for the shipment of coal to be returned by unit trains to points adjacent to mining areas.

ACKNOWLEDGEMENT

The authors are indebted to the Bureau of Engineering Research at the University of Texas at Austin and the Texas Air Control Board for their support of the present research project.

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NUTRIENT CONTENT OF PRECIPITATION OVER IOWA[1]

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ABSTRACT

Nutrient content and pH of precipitation samples collected at six sites during 1971-1973 were studied to determine the reaction of rainfall and snowmelt and the amounts of N, S, and P added by precipitation over Iowa. The amount of NH_4-N added by precipitation per hectare annually at each site was about equal to that added as NO_3-N. The amounts of inorganic N added per hectare per year ranged from 10 kg in north-central to 14 kg in west-central Iowa, and the annual amounts of SO_4-S added per hectare ranged from 13 kg in northeastern to 17 kg in north-central Iowa. It is estimated that, on average, precipitation adds about 0.6 kg of NH_4-N, 0.6 kg of NO_3-N, and 1.5 kg of SO_4-S per hectare monthly in Iowa. However, the data indicated that, on an annual basis, the contribution of precipitation to P in soil is very small; at the most, about 0.1 kg of water-soluble PO_4-P was added per hectare annually in Iowa. No NO_2-N could be detected in any of the precipitation samples analyzed.

Average pH value of the rainfall and snowmelt samples collected at each site during each year was about 6, individual samples seldom reached as low as pH 4. The data indicate that the concentration of SO_4-S in precipitation in this region is seasonal, high during fall and winter and low during spring and summer.

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[1]Journal Paper J-8229 of the Iowa Agriculture and Home Economics Experiment Station, Ames, Iowa, Project 1845; and the North Central Region, Agricultural Research Service, U.S. Dept. of Agriculture.

INTRODUCTION

The many facets of nutrients (e.g., C, N, and S) in the biosphere have become major environmental issues occupying the scientific and public sectors of our society for the past decade. Although this concern is justified by the increasing contamination of air and water resources by various substances on local levels, information on the amounts and concentrations of some of the substances present in air and natural water under normal conditions is needed. Such information is essential for our better understanding of the sources and fates of pollutants in the biosphere.

The atmospheric component of the cycles of nitrogen and sulfur often can be a significant part of the various pools of their respective cycles (Allison, 1965; Erickson, 1963; Feth, 1966; Gambell and Fisher, 1964; Meetham, 1950; Robinson and Robbins, 1970), but the atmospheric component of the phosphorus cycle seems to be of minor significance to the cycling of this element in the environment. Among the various chemical elements present in precipitation (e.g., N, S, K, Cl, and Ca), N and S deserve special attention because N added by precipitation may contribute to nitrate pollution of surface and ground water. Sulfur may cause acid rain that can lead to increased leaching from soils of Ca and other nutrient elements, deterioration of aquatic ecosystems, damage to vegetation and buildings, and other agricultural and urban problems. On the other hand, the limited amount of N and S brought down by precipitation might be useful to meet the requirements of crops for these elements in areas where soils have limited supplies of N and S (Allway et al., 1937; Erdman, 1923; Tabatabai and Bremner, 1972; Walker, 1969; Widdowson and Hanway, 1974).

Normal water in the atmosphere in equilibrium with prevailing CO_2 pressure will have a pH of about 5.7 (Barrett and Brodin, 1955), but much lower pH values (ca. 2) have been reported for precipitation in the northeastern United States. The low pH values of precipitation have been considered to indicate air pollution (Likens and Bormann, 1974).

Nitrogen is the most plentiful element in the atmosphere. It plays a key role in the life of all living organisms. There are several nitrogen compounds in the atmosphere. These include N_2O, NO, NO_2, NH_3, and ammonium (NH_4^+) and nitrate (NO_3^-) aerosol. Large portions of the ammonia and nitrogen oxides (NO_x) in the atmosphere may originate from biological processes, but the concentrations of these gases in the air are greatly affected by industrial activities, automobile traffic, and feedlot operations (Elliott et al., 1971; Hutchinson and Viets, 1969; Robinson and Robbins, 1970). Of the eight possible oxides of nitrogen (N_2O, NO, N_2O_3, NO_2, N_2O_4, N_2O_5, NO_3, and N_2O_6) only three are important constituents of the atmosphere. Of these -- nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2) -- the most plentiful in the atmosphere is the relatively inert nitrous oxide. Nitrogen dioxide

present in the atmosphere, however, can react with water vapor to form nitric acid, which, in turn, reacts with ammonia or particles in the air and forms nitrate salts, such as ammonium nitrate, which is brought down by precipitation. The major reactions involving the various gaseous nitrogen compounds are oxidation reactions of both NH_3 and NO_2 to form nitrates and neutralization of NH_3 to form ammonium sulfate and ammonium nitrate aerosols. Atmospheric particles are frequently found to contain $(NH_4)_2SO_4$, and its formation from NH_3 and SO_2 in the atmosphere is probably a significant factor in the scavenging of SO_2. The major sources for the gaseous nitrogen compounds are biological action and organic decomposition in the soil and, to a lesser extent, in the ocean. Only NO and NO_2 are emitted as pollutants, at an estimated annual world-wide rate of about 50 million tons (Robinson and Robbins, 1968). It has been estimated that, on a global basis, about 99% of the total atmospheric N is derived from biological processes and only 1% from combustion (Robinson and Robbins, 1970). The residence times for all the nitrogen compounds except N_2O are only a few days. For N_2O the residence time has been calculated to be 70 years if there was no loss in the biosphere. Biological reaction, however, may reduce the residence time to about one to three years (Robinson and Robbins, 1968).

Stewart (1970) found that a significant portion (90%) of the urea N excreted by animals in feedlots may find its way to the air as ammonia. An appreciable fraction of atmospheric ammonia, in turn, is absorbed by soil, plant, and water surfaces in the vicinity of feedlots (Elliott et al., 1971; Hutchinson and Viets, 1969). It has been shown that there is a tendency for more NH_3 to be contained in precipitation near feedlots, but it seems that the amounts brought down by precipitation are insignificant compared with those directly absorbed by soil and water surfaces (Hoeft et al., 1972; Hutchinson and Viets, 1969).

Sulfur is one of the trace substances always found in the atmosphere. Sulfur enters the atmosphere as sulfur dioxide (SO_2), hydrogen sulfide (H_2S), sulfuric acid (H_2SO_4), and various sulfates ($SO_4^=$). In unpolluted air, S occurs primarily in three compounds; $SO_4^=$ in aerosol and SO_2 and H_2S gases. Hydrogen sulfide in the air is normally oxidized to SO_2, which, in turn, is oxidized to $SO_3^=$. Sulfur trioxide dissolves in water droplets to form sulfuric acid, which may react further to form sulfate salts, such as ammonium sulfate. Both the sulfuric acid and sulfate salts thus formed exist in air as an aerosol and are removed by precipitation and, to a lesser extent, by gravitational settling. It is estimated that a given volume of SO_2 that enters the air will be removed by these mechanisms, as acid or salt, in a time ranging from five days to two weeks (Erickson, 1963).

There are several sources for atmospheric S, these include sea spray, H_2S and volatile sulfides released from marshlands and sea, and S released by burning S-containing fuels (Coleman, 1966 ; Erickson, 1963). Junge's (1960) work on the S budget of the global atmosphere indicates that, excluding the $SO_4^=$ in sea salt particles, 30% of the

atmospheric S is of anthropogenic origin. Other estimates indicate that the S released from sea spray and S-containing fuels accounts for about 12 and 11%, respectively, and that the other 77% is released as H_2S from marshlands and sea (Erickson, 1963). Hoeft et al. (1972) have shown that atmospheric SO_2 levels in both rural and urban locations in Wisconsin tend to be seasonal, low in summer and increased markedly in winter. They attributed this to the burning of S-containing fuels in winter months and slow release of S from soil and biological reactions during this time.

This paper reports results obtained from a monitoring program to assess the pH and concentrations of NH_4-N, NO_3-N, SO_4-S, and PO_4-P in precipitation over Iowa, to determine the quantities of these nutrients added annually by precipitation to land surfaces in this region, and to compare the values obtained in Iowa with those reported for other regions.[2]

MATERIALS AND METHODS

Six sampling stations were established in Iowa in September 1971. The sites selected were located on a line extending across the state from the northeast to the southwest. The sites were selected so that no major industrial activity directly influenced the nitrogen, sulfur, and phosphorus concentrations of the atmosphere of the sample-collection sites. Table I shows the sites, counties, and the general area where precipitation samples were collected for 27 months during 1971-1973.

The procedure used to collect precipitation samples and the methods used for the analyses reported are described by Tabatabai and Laflen (1976).

RESULTS AND DISCUSSION

The six sites selected for this study were located on a line extending from northeast to southwest of Iowa (Table I). The precipitation samples collected were analyzed for pH, NH_4-N, NO_3-N, NO_2-N, PO_4-P, and SO_4-S. Because the concentrations of PO_4-P were very small, ranging from 0 to 10 ppb, the results obtained were not summarized. Use of

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[2]A summary of part of the results presented in this paper was submitted for publication in Journal of Environmental Quality (Tabatabai and Laflen, 1976).

TABLE I

Description of sampling sites.

Site				
Nearest city	County	Area of Iowa	Proximity to nearest urban area	Classification*
			km	
Ames	Story	Central	0	U
Boone	Boone	Central	10	R
Charles City	Floyd	NE	15**	R
Creston	Union	SW	4	R
Eldora	Hardin	N. Central	3	R
Guthrie Center	Guthrie	W. Central	12	R

*U, urban; R, rural.

**Late 1972 and all of 1973 samples were collected within 1 km of Charles City.

the maximum value to calculate the amount of inorganic P added by precipitation, however, indicated that, at the most, about 0.1 kg of P is added per hectare annually in Iowa. No NO_2-N could be detected in any of the precipitation samples analyzed.

pH OF PRECIPITATION

Table II shows the average of pH values obtained for precipitation samples collected at the six sites for 27 months. The averages of pH values ranged from 5.8 ± 0.8 to 6.5 ± 0.3, and the overall average pH value of the samples collected was 6.2 ± 0.5. Although a pH value of 4 was measured occasionally, no seasonal variation in pH values was observed. The pH values obtained in this study were markedly different from those reported for samples from northeastern United States and Sweden where pH values as low as 2 and 3 were measured (Likens and Bormann, 1974).

Normal water in the atmosphere in equilibrium with CO_2 will have a pH of 5.7 (Barrett and Brodin, 1955), and, if this pH value is considered as the neutral point for atmospheric water, most of the precipitation samples that we collected showed a slight net alkalinity; most pH values were above 5.7. The results obtained indicate that concentrations of SO_4-S in precipitation over Iowa were much higher than those found in samples from the northeastern United States (Likens and Bormann, 1974). Because no consistent low pH values were found for

TABLE II

Annual means of some chemical properties of precipitation collected at six sites in Iowa.

Period	Site	Annual mean of chemical property specified*			
		pH	NH_4-N	NO_3-N	SO_4-S
			ppm		
1971	Ames	6.11(0.38)	0.43(0.56)	0.36(0.24)	1.23(0.74)
	Boone	6.18(0.28)	0.38(0.48)	0.60(0.42)	1.08(0.58)
	Charles City	5.91(0.36)	0.61(0.41)	0.67(0.38)	1.70(0.70)
	Creston	6.15(0.48)	0.43(0.28)	0.59(0.32)	1.22(0.50)
	Eldora	6.33(0.20)	0.48(0.37)	0.43(0.28)	1.16(0.50)
	Guthrie Center	5.94(0.49)	0.64(0.59)	0.99(0.98)	1.37(0.97)
1972	Ames	6.21(0.66)	0.64(0.37)	0.74(0.36)	2.06(1.14)
	Boone	6.33(0.29)	0.55(0.29)	0.78(0.40)	1.81(1.05)
	Charles City	6.17(0.47)	0.79(0.78)	0.98(0.29)	1.44(0.82)
	Creston	6.15(0.48)	0.73(0.65)	0.59(0.30)	1.72(1.25)
	Eldora	6.46(0.30)	0.54(0.56)	0.50(0.33)	2.31(1.52)
	Guthrie Center	6.24(0.50)	0.76(0.94)	0.59(0.32)	1.44(0.82)
1973	Ames	6.00(0.39)	0.49(0.36)	0.57(0.29)	1.49(1.15)
	Boone	5.78(0.82)	0.53(0.24)	0.60(0.26)	1.48(0.96)
	Charles City	6.03(0.74)	0.86(0.53)	0.58(0.40)	1.19(0.90)
	Creston	6.53(0.29)	0.52(0.33)	0.44(0.28)	1.16(1.00)
	Eldora	6.25(0.36)	0.66(0.42)	0.55(0.29)	1.41(0.90)
	Guthrie Center	5.81(0.87)	0.70(0.51)	0.54(0.34)	1.50(1.12)
1971-1973 (all samples)	Ames	6.12(0.54)	0.55(0.42)	0.60(0.34)	1.68(1.11)
	Boone	5.97(1.20)	0.51(0.32)	0.69(0.38)	1.55(1.02)
	Charles City	5.98(0.95)	0.80(0.64)	0.60(0.35)	1.43(0.86)
	Creston	6.26(0.46)	0.62(0.54)	0.55(0.30)	1.48(1.09)
	Eldora	6.36(0.32)	0.57(0.48)	0.50(0.30)	1.81(1.25)
	Guthrie Center	6.05(0.67)	0.72(0.76)	0.62(0.47)	1.43(0.92)
	All sites	6.15(0.55)	0.63(0.55)	0.60(0.37)	1.55(1.04)

*Figure in parentheses indicates standard deviation.

precipitation in this region, it seems that SO_4-S in precipitation in Iowa exists as un-ionized particulate SO_4 or as ionized forms neutralized by equivalent amounts of bases. Also, the results obtained showed that the occasional low pH values were not associated with high concentrations of SO_4-S in those samples. Data reported by Likens and Bormann (1974) for SO_4-S content of rain and snow in New York indicate that present-day precipitation contains about 70% less S than precipitation preceding 1950, but it has lower pH values. From the results obtained for concentrations of SO_4-S and pH values of precipitation in Iowa and those reported by Likens and Bormann (1974) for samples in the state of New York, it seems that a factor other than SO_4-S is responsible for low pH values of some precipitation samples or that sufficient cations (e.g., NH_4^+) are not present in precipitation where acid rain is found.

INORGANIC N IN PRECIPITATION

The monthly average concentrations of NH_4-N and NO_3-4 for the six sites studied ranged from 0.1 to 2.1 ppm and from 0.1 to 2.2 ppm, respectively. Figure 1 shows the monthly average concentrations of NH_4-N

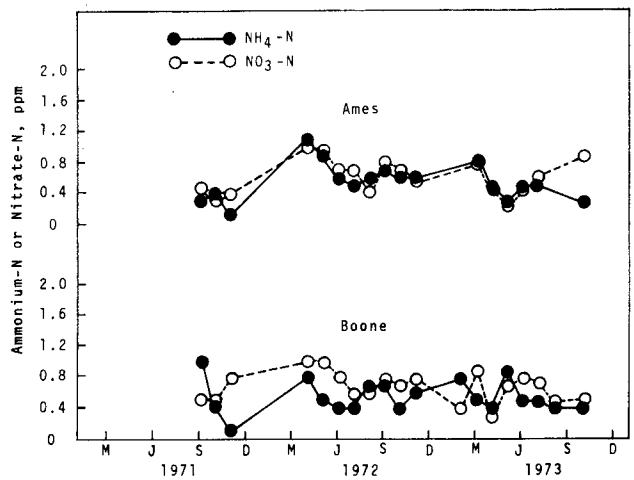

Figure 1. Monthly average concentrations of ammonium-N and nitrate-N in precipitation at two sites in Iowa.

and NO_3-N of precipitation samples from two of the six sites studied. The results indicate no seasonal variation in concentration of precipitation N over Iowa. The results were similar for the other sites studied.

The average annual NH_4-N concentrations in the precipitation samples studied ranged from 0.38 ± 0.48 to 0.86 ± 0.53 ppm, and the NO_3-N concentrations ranged from 0.36 ± 0.24 to 0.99 ± 0.98 ppm. The overall average of NH_4-N and NO_3-N concentrations of the six sites were 0.63 ± 0.55 and 0.60 ± 0.37 ppm, respectively (Table II). Generally, the concentration of NH_4-N was about equal to that of NO_3-N. The concentrations of inorganic N found in this study are similar to those reported by Taylor et al. (1971) for rainfall in Coshocton, Ohio. The highest NO_3-N concentration found for precipitation in Iowa (2.2 ppm) is similar to that reported for precipitation in Nebraska (Olson et al., 1973), but the highest value of NH_4-N (2.1 ppm) found in Iowa is much lower than that (3.3 ppm) reported for Nebraska (Olson et al., 1973) and for Wisconsin precipitation collected from sites removed from barnyards (Hoeft et al., 1972).

The ratio of NH_4-N to NO_3-N in precipitation samples studied was about 1:1. A similar ratio has been reported for precipitation samples

from urban areas and rural areas removed from barnyards in Wisconsin (Hoeft et al., 1972). Other studies, however, indicated a ratio of 2:1 for these forms of inorganic N in precipitation samples from Nebraska (Olson et al., 1973). The relative concentrations of NH_4-N and NO_3-N in precipitation samples in the Midwest are strikingly different from those found for coastal areas of the United States (Likens and Bormann, 1974; Tarrant et al., 1968). In studies of organic and inorganic N in precipitation samples in coastal Oregon, Tarrant et al., (1968) found very little (0-0.1 ppm) of NO_3-N and no trace of NH_4-N. The results obtained for inorganic N in precipitation samples from New Hampshire and New York, however, indicate significantly higher concentration of NO_3-N than NH_4-N (Likens and Bormann, 1974). This high concentration of of NO_3-N in precipitation has been attributed to increased combustion of natural gas and motor fuels.

Table III shows the correlation coefficients (r) for paired relationships of some of the chemical properties of precipitation over Iowa. Statistical analyses indicated that, with a few exceptions, total inorganic N, $(NH_4 + NO_3)$-N, concentration in the precipitation collected during each year was significantly correlated with SO_4-S concentration, and NH_4-N was significantly correlated with NO_3-N. Statistical analyses of the pooled data collected at each site during the study period indicated that $(NH_4 + NO_3)$-N concentrations in the samples were also significantly correlated with SO_4-S. Statistical analyses of the relationship between pH and SO_4-S, NH_4-N, or NO_3-N, however indicated that, with a few exceptions, pH was not correlated with NH_4-N, NO_3-N, or SO_4-S. The strong relationship between inorganic N and SO_4-S and between NH_4-N and NO_3-N in precipitation over Iowa may indicate that nitrogen and sulfur in precipitation in this region are originating from similar source(s) or that chemical reactions of these elements in the atmosphere are producing compounds containing N and S. The strong relationship between NH_4-N and NO_3-N suggests presence of NH_4NO_3, and the strong relationship between inorganic N and SO_4-S suggests presence of $(NH_4)_2SO_4$ along with ammonium nitrate in precipitation in this region. Use of the seasonal averages of NH_4-N and NO_3-N and of long-term annual precipitation (average annual precipitation in Iowa is 80 cm) to calculate the seasonal deposition of N by precipitation indicated that, on the average, between 9 and 12 kg of inorganic N/ha is deposited annually (Figure 2). Use of the measured annual precipitation for the study period indicated, however, that the annual amounts of inorganic N added by precipitation ranged from 10 kg/ha in north-central to 14 kg/ha in west-central Iowa (Table IV). Of these amounts, between 70 and 82% is deposited during spring and summer. The data also indicate that the amount of NH_4-N deposited annually at each site was equal to the amount of NO_3-N. The overall average annual addition of inorganic N (13 kg/ha) by precipitation in Iowa is similar to that in Nebraska and Wisconsin rural areas (Hoeft et al., 1972; Olson et al., 1973). In addition to these amounts of inorganic N added by precipitation in Iowas, NH_4-N could be directly absorbed by soil and water surfaces, especially in areas near feedlots.

TABLE III

Simple correlation coefficients (r) for paired relationships of some chemical properties of precipitation over Iowa.

Period	Variables	Site					
		Ames	Boone	Charles City	Creston	Eldora	Guthrie Center
1971	$(NO_3 + NH_4)$-N vs. SO_4-S	0.60*	0.85**	0.51	0.81**	0.54	0.96**
	NO_3-N vs. NH_4-N	0.52*	0	0.68*	0.39	0.79**	0.88**
	pH vs. SO_4-S	0.50*	0.39	0	0.71**	0.54	0.84**
	pH vs. NH_4-N	0.52*	0.17	0.17	0.66*	0.17	0
	pH vs. NO_3-N	0.73**	0.22	0.28	0.83**	0.51	0.76*
1972	$(NO_3 + NH_4)$-N vs. SO_4-S	0.70**	0.72**	0.53**	0.36*	0.45*	0.66**
	NO_3-N vs. NH_4-N	0.79**	0.42*	0.41*	0.48**	0.84**	0.42*
	pH vs. SO_4-S	0.14	0.10	0.17	0.10	0	0
	pH vs. NH_4-N	0	0.30	0.25	0.14	0.30	0.30
	pH vs. NO_3-N	0	0.30	0.25	0	0.22	0
1973	$(NO_3 + NH_4)$-N vs. SO_4-S	0.82**	0.39*	0.69**	0	0.10	0.76**
	NO_3-N vs. NH_4-N	0.57**	0.51**	0.28	0.35	0.28	0.77**
	pH vs. SO_4-S	0.35	0.14	0.17	0.22	0.69**	0
	pH vs. NH_4-N	0.51**	0.17	0.35	0.40	0.33	0.17
	pH vs. NO_3-N	0.10	0	0.54**	0.25	0.41	0.10
1971-1973 (all samples)	$(NO_3 + NH_4)$-N vs. SO_4-S	0.75**	0.65**	0.57**	0.36**	0.33*	0.70**
	NO_3-N vs. NH_4-N	0.65**	0.33**	0.36**	0.42**	0.66**	0.46**
	pH vs. SO_4-S	0.25*	0.10	0.64	0	0.37**	0.10
	pH vs. NH_4-N	0.27*	0	0.25	0.14	0.25	0.20
	pH vs. NO_3-N	0.17	0.14	0.28	0.17	0.30**	0

*Significant at $P < 0.05$. **Significant at $P < 0.01$.

Junge (1958) conducted a nationwide survey of NH_4-N and NO_3-N in rainwater samples of 60 sites in the United States during 1955 and 1956. He found an uneven distribution of both these forms of inorganic N in rainwater. Also, he found no correlation between these inorganic N forms in precipitation and thunderstorm activity, density of industry, population, or agricultural activity. He found, however, that areas

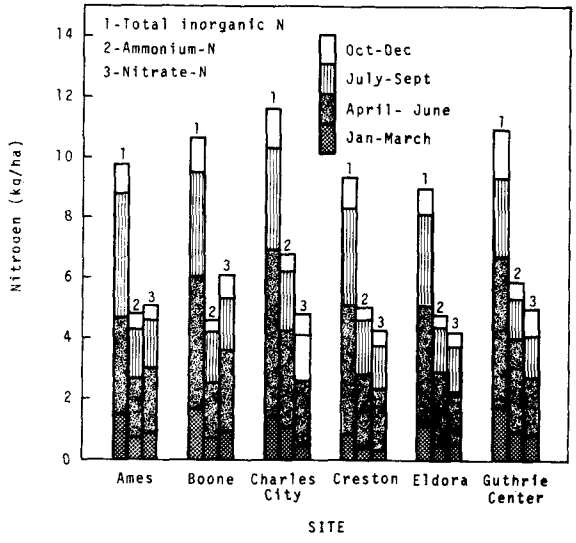

Figure 2. Seasonal addition by precipitation of total inorganic N, ammonium-N, and nitrate-N as six sites in Iowa.

having soils of low pH values correlated with areas having low concentrations of NH_4-N in precipitation and that alkaline-soils regions seemed associated with high concentration of NH_4-N in rainwater. The results obtained in our study were not aimed toward investigating such relationships, but the results obtained for concentrations of NH_4-N in precipitation samples at the six sites in Iowa do not seem to show any general trend to indicate such relationships.

SULFUR IN PRECIPITATION

The concentrations of SO_4-S found in the precipitation collected at the six sites during the study period ranged from 0.1 to 4.9 ppm, and the monthly average concentrations of SO_4-S in precipitation samples from the six sites ranged from 0.3 to 4.6 ppm. The annual average concentration of SO_4-S ranged from 1.08 $\pm$ 0.58 to 2.31 $\pm$ 1.52 ppm, and the overall average for the six sites was 1.55 $\pm$ 1.04 ppm (Table II). The monthly average concentrations of SO_4-S in the samples collected at two of the sites studied are reported in Figure 3. These results show that the concentrations of SO_4-S in precipitation in Iowa is seasonal and inversely related to the amount of monthly precipitation. The inverse relationship between average monthly SO_4-S in precipitation and monthly addition of precipitation is shown in Figure 4 for three of the sites studied. The data obtained for the other sites showed similar relationships. The highest concentration of SO_4-S was found during the fall and winter when precipitation is low, and the

TABLE IV

Amounts of ammonium-N, nitrate-N, and sulfate-S added annually by precipitation at six sites in Iowa

Site	NH_4-N	NO_3-N	SO_4-S
	---------- kg/ha/year* ----------		
Ames	6.0	6.0	16.8
Boone	6.0	7.2	15.6
Charles City	7.2	6.0	13.2
Creston	6.7	6.0	16.7
Eldora	5.0	4.8	17.3
Guthrie Center	7.1	7.2	16.1
Avg.	6.3	6.2	16.0

*The values obtained for Creston, Eldora, and Guthrie Center were calculated from average annual nutrient concentration and percentage of the annual precipitation received during sampling period.

lowest concentration during the summer and spring when precipitation is high. Atmospheric S levels in Wisconsin at rural and urban sites also

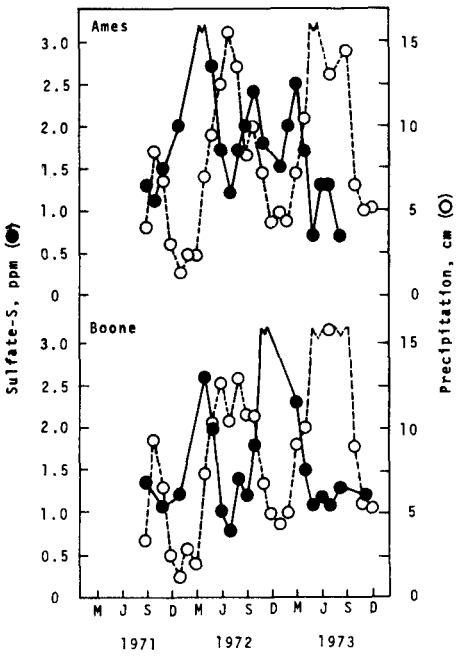

Figure 3. Relationship of monthly average concentration of sulfate-S in precipitation to amount of monthly precipitation at two sites in Iowa.

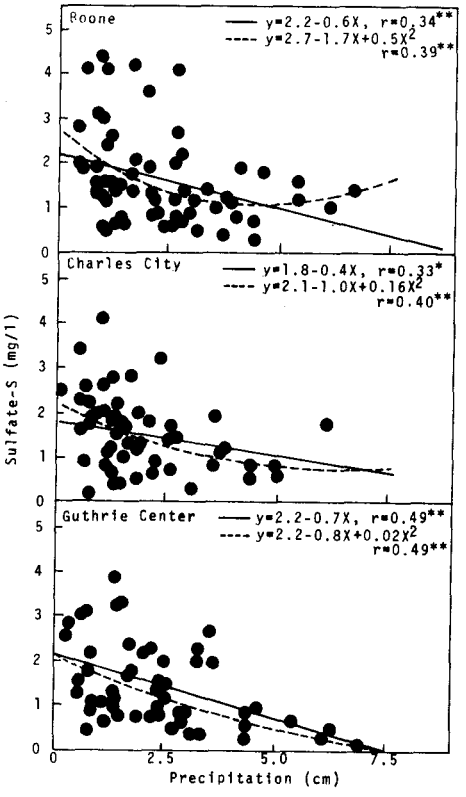

Figure 4. Relationship between monthly average concentration of sulfate-S in precipitation and amount of monthly precipitation at three sites in Iowa.

were found to be low in the summer and high in the winter (Hoeft et al., 1972). The high concentration of SO_4-S in precipitation during the fall and winter in Iowa could be due to home and business heating during these months. The low concentrations during spring and summer could be due to washing by precipitation and to lower concentration of S gases in the atmosphere resulted from direct absorption of SO_2 and other S gases by the exposed soil and plant surfaces. These processes of addition and removal of S gases into and from the atmosphere seem to play major roles in the observed seasonal concentrations of SO_4-S in precipitation in Iowa. Use of the seasonal averages of SO_4-S and of long-term average of precipitation (80 cm) to calculate the seasonal deposition of S by precipitation indicated that, on the average, between 12 and 15 kg of S/ha is deposited annually. As was true of N, between 62 and 78% of these amounts of S are deposited during spring and summer (Figure 5).

Precipitation during 1971-1973 was abnormally higher than the normal annual average of each of the six sites studied. During the study period, the averages of annual precipitation of the six sites were between 10 and 45% higher than the long-term annual average. Use of the measured monthly precipitation and concentration of SO_4-S indicated that the monthly deposition of S ranged from 1.1 to 1.8 kg/ha (ave. 1.5 kg/ha). On this basis, the annual addition of S by precipitation at

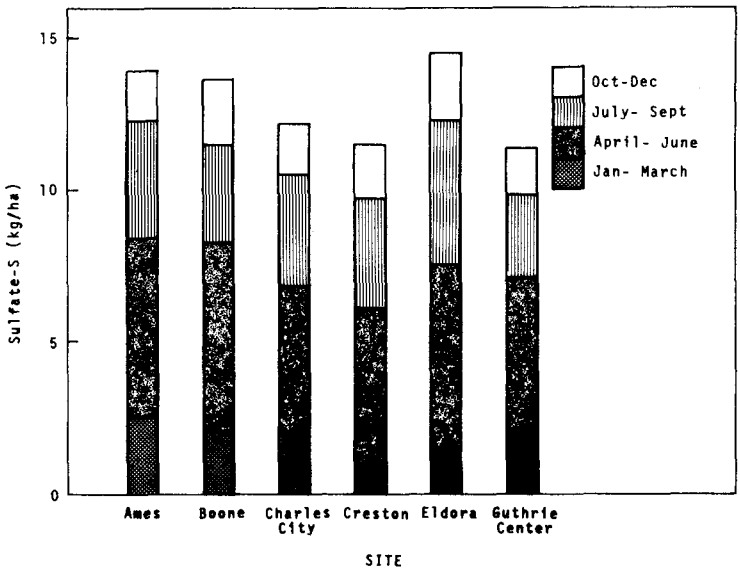

Figure 5. Seasonal addition by precipitation of sulfate-S at six sites in Iowa.

the six sites varied from 13 kg/ha in northeastern to 17 kg/ha in north-central Iowa. The average annual additions of S by precipitation (16 kg/ha) during the study period in Iowa (Table IV) is similar to that reported (17 kg/ha) for rural areas in Wisconsin (Hoeft et al., 1972). Present-day addition of S by precipitation in Iowa is similar to that reported a half-century ago. Erdman (1923) estimated the annual precipitation-originated S in Ames in 1923 to be 17 kg/ha, and the present estimate for this site is 17 kg/ha. Also, Harper (1942) summarized the data that were available before 1942, indicating that rural areas of the United States were receiving precipitation-originated S in amounts similar to those found in this study.

The 13 to 17 kg/ha of S added by precipitation in Iowa are of importance to crop production in this region because laboratory tests and greenhouse experiments have shown that Iowa soils do not contain sufficient plant-available S to meet crop requirements of this element (Tabatabai and Bremner, 1972; Widdowson and Hanway, 1974), yet no S-deficiency symptoms have been reported for crops grown under field conditions. In previous studies on S in soils, Tabatabai and Bremner (1972) found that Iowa soils have low reserve of plant-available S, and they suggested that studies to assess atmospheric contribution of S to crops and soils in Iowa be performed before recommending S fertilization of Iowa soils. From the results obtained in this work, it is evident that precipitation adds the small amounts of S required by many crops in this region. Also, some S gases are likely absorbed directly by soils and plants in Iowa because it is known that soils and plants absorb SO_2 directly from the atmosphere (Allway et al., 1937; Coleman,

1966; Faller, 1970; Olsen, 1957; Ulrich et al., 1967). A recent study in Wisconsin showed that, under optimum yield, 44% of the S in alfalfa was derived from atmospheric sources (Hoeft et al., 1972). The results of concentrations of S in precipitation and those reported for S in Iowa soils (Tabatabai and Bremner, 1972; Widdowson and Hanway, 1974) indicate that current concentrations of S in precipitation in Iowa are beneficial to crop production in this region.

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THE EFFECT OF A LOCAL SOURCE ON THE COMPOSITION OF PRECIPITATION IN SOUTH-CENTRAL MAINE

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ABSTRACT

Bulk precipitation samples were collected from ten sites in south-central Maine during the period 18 June to 30 September 1974. Data from the chemical analyses of the precipitation were used to determine regional deposition patterns of the ionic constituents. Acidic pH values ranging from 3.8 to 5.0 are characteristic of the region, but relatively alkaline pH values of 5.5 to 7.0 were observed in the precipitation from one collection site. Systematic increases in sulphate and sodium deposition in the samples from this site suggest a local source.

The observations of the bulk precipitation analysis lead to a study of the chemical composition of precipitation near a kraft paper mill. Samples were collected during single precipitation events. The results indicate that this source can affect background levels of composition up to a distance of at least 20 km and that considerable care must be taken in the selection of sites for sampling background precipitation.

INTRODUCTION

Long-range transport of anthropogenic sulfur dioxide and sulfate aerosols from industrial emissions in Great Britain and Northern Europe has been shown to significantly influence the chemical composition of precipitation over regions of Scandinavia (Rodhe et al. 1972). The State of Maine represents a situation which in some respects is similar to that of southern Scandinavia. During periods of prevailing southerly and southwesterly winds common in May through September (Court 1974), Maine lies downwind of major industrial development.

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Little intensive precipitation monitoring has been initiated in New England, except the work at Hubbard Brook in New Hampshire by Likens et al. (1975). Two collection sites established in Maine by the United States Geological Survey comprised a small component of a large-scale northeastern regional study by Pearson and Fisher (1971).

In the present study, a network of collection sites was developed in south-central Maine for the sampling and analysis of bulk precipitation. Analyses included conductivity, pH, sulfate, nitrate, sodium, and calcium determinations. Data from this phase of the investigation provides preliminary information on the relationship between acidity and the chemical composition of the precipitation and to some extent distinguished the contributions of rainfall and dry deposition.

The results of this brief regional study are shown to be unexpectedly conditioned by local sources, and a more detailed study was undertaken in the vicinity of a large kraft-process pulpmill.

EXPERIMENTAL PROCEDURES

COLLECTION OF PRECIPITATION SAMPLES

Ten sites in south-central Maine were selected for sampling bulk precipitation during the summer of 1974 (fig. 1). The locations for the collectors were chosen to provide a representative picture of regional variations in precipitation chemistry. A wide variety of terrain was included: coastal, urban, and inland rural areas. Collectors were placed well away from heavily traveled roads, buildings, and trees. Each collector was exposed for 2 or 4 week intervals during the period 18 June to 30 September 1974. Sampling periods included 2 week intervals between 18 June and 12 August and a 4 week span from 12 August to 10 September. Insufficient volumes of precipitation were obtained during a 2 week dry spell from 31 July to 12 August, so data for this interval have been omitted.

Two-liter plastic milk bottles were used as collection containers. A 15-cm diameter polyethylene funnel was inserted into the bottle, creating an effective sampling surface of about 175 cm^2. The funnels were placed 0.4 to 1.0 m above ground level. Packaged presterilized bottles were cleansed thoroughly with a brush and detergent and then rinsed several times with distilled water. The rinse water from several containers had no measurable levels of the ions studied here.

After collection, the samples were subjected to crude filtration, using glass wool to remove odd bits of organic matter. The filtration step was included in the treatment of the blank. Subsequent analysis indicated that use of this collection procedure did not contaminate the precipitation samples.

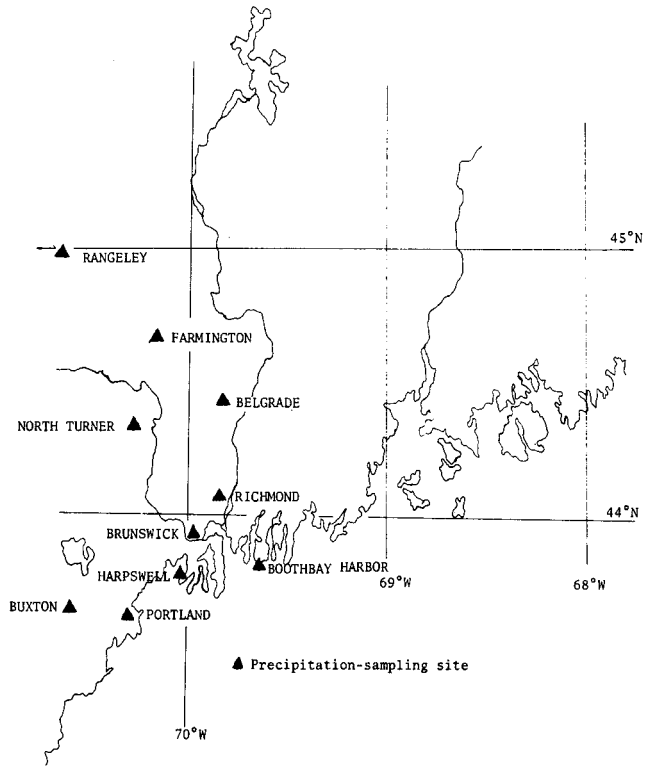

Figure 1. Locations of bulk precipitation sampling sites in Maine.

A slight modification of the sampling procedure was required during the second phase of the study. Twenty-five-centimeter glass funnels were used to increase the effective collection surface to about 500 cm^2. These collectors were placed at 10 locations around the pulpmill in Jay, Maine, as illustrated in figure 2. The glass funnels were washed and rinsed in the manner described previously and covered with a sheet of polyethylene until time of sampling. This prevented contamination of the collector by dry deposition prior to the precipitation events. Samples were capped and transported immediately following termination of the rainfall. Precipitation was collected in this manner on 13 and 15 November. Control experiments demonstrated that leaching of sodium from the glass funnels did not introduce significant levels of contamination.

Snow samples associated with the precipitation of 13 January and 5 February 1975 were also obtained. The snow was collected in the immediate proximity of the rain collectors. Sites were selected at a distance greater than 50 meters from roadways to avoid contamination from salting and sanding operations. After removal of the top 3 to 4 cm of snow, samples were taken from an area of about 1 m^2 to a depth of 6 to 8 cm. Forland and Gjessing (1970) demonstrated that constituents arising from dry deposition and absorption of gases contaminate only the

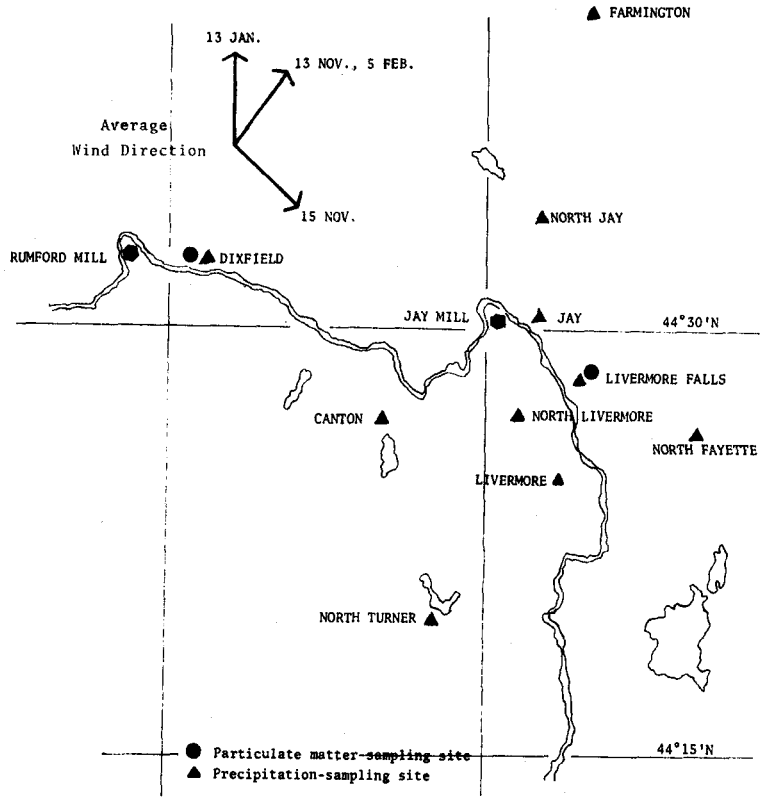

Figure 2. Locations of rain and snowfall sampling sites around the kraft paper mill at Jay, Maine.

upper 2 to 3 cm of snowfall. Samples were collected with a clean plastic shovel, stored in polyethylene bags, and allowed to melt prior to analysis.

COLLECTION OF PARTICULATE MATTER SAMPLES

Samples of suspended particulate matter were collected from areas near the pulpmill during each precipitation period. In addition to the principal source under investigation, a second kraft-process mill is located in Rumford, about 30 km west of Jay. Two high-volume air samplers were used to collect particulate matter associated with both sources. One sampler was placed at Livermore Falls, 5 km south of the Jay facility. The second was placed in Dixfield, about 15 km northwest of Jay and between the two sources. Precipitation collectors were placed next to the high-volume samplers at each location.

Each high-volume filter was cut into quarters, and the soluble matter was extracted with 300 ml of distilled water for a 24 hour period, using a Soxhlet extractor. Extraction thimbles were not used due to the

high concentrations of sodium found to result from their use. To determine the contribution of ions from the glass fiber filters, the extraction from several clean filters was used as a blank.

METEOROLOGICAL MEASUREMENTS

Meteorological data for the precipitation of 13 and 15 November were obtained with a portable recording instrument. Wind speed, direction, and temperature were recorded from the summit of a hill located about 5 km south of the Jay mill. Due to servicing of the equipment, hourly observations 13 January and 5 February 1975 were obtained from the Brunswick Naval Air Station, located about 60 km south of the Jay mill.

CHEMICAL ANALYSES

The pH and electrical conductivity of the samples were determined at the time of filtration. Conductivity was measured with an Industrial Instruments Model 16B1 Wheatstone Bridge. The pH was measured with a London Instruments Model PHM Research pH Meter. Nitrate ion was determined, using the cadmium reduction method described by Gleason (1973). Sulfate was determined by the barium sulfate turbidity method outlined in *Standard Methods for the Examination of Water and Wastewater* (Amer. Public Health Assoc., 1971). To achieve the desired sensitivity for sulfate, the samples were concentrated by evaporation by a factor of 10 before analysis. Metal analyses were performed with a Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer.

DATA

EMISSION DATA

There are two sources of sulfur dioxide and particulate matter in the rain-collection area: the kraft-process mill at Jay, Maine and a second, similar mill located about 30 km to the west in Rumford. The emission data were based on 1973 figures obtained from the Bureau of Air Quality Control of the Maine Department of Environmental Protection. The pulpmill at Jay emits an average of 1570 kg h^{-1} of sulfur dioxide and 665 kg h^{-1} of particulate matter. The Rumford facility emits about 880 kg h^{-1} of sulfur dioxide and 442 kg h^{-1} of particulate matter. Particulate emissions from the Jay mill include significant amounts of sodium sulfate and other sodium salts.

METEOROLOGICAL DATA

A prevailing northeasterly wind accompanied the precipitation of 13 November 1974 and 5 February 1975. The rainfall of 14 and 15 November was associated with surface winds from the south and southeast, while northerly winds occurred during the snowfall of 13 January 1975.

PARTICULATE MATTER ANALYSES

Results of the chemical analyses of total suspended particulate matter for each sampling period are shown in Table I. A significant

TABLE I. Data Summary for Particulate Matter Samples ($\mu g\ m^{-3}$)

Sample	Date	Total Mass. Conc.	$[Na^+]$	$[Ca^{2+}]$	$[SO_4^{2-}]$	$[NO_3^-]$
Livermore Falls	11/13	39	5.42	<0.05	3.19	0.92
Livermore Falls	11/15	14	3.33	<0.05	8.80	1.55
Livermore Falls	1/13	50	4.16	0.05	24.57	3.80
Livermore Falls	2/5	43	3.35	0.22	11.09	1.79
Dixfield	11/13	43	2.00	<0.05	5.15	0.10
Dixfield	11/15	41	1.60	0.22	11.50	0.74
Dixfield	1/13	87	0.67	0.42	12.43	0.36
Dixfield	2/5	57	10.22	0.51	21.07	0.42

decrease in concentration for the Livermore Falls sample of 15 November reflects the upwind location of this site. The high particulate matter concentration at Dixfield on 5 February very likely results from the consistent easterly wind between 1600 and 2400 hours on that date, which placed this site downwind from the Jay mill.

PRECIPITATION ANALYSES

Expression of chemical composition of precipitation in terms of concentration is not always the most useful parameter for a discussion of regional variations. Ionic concentrations in precipitation are subject to changes resulting from evaporation during sampling, which can become particularly significant over a 2 week sampling period. Losses due to sample evaporation may vary from site to site. These losses have not been evaluated in this study; thus only the deposition of ions for the period 18 June to 31 July are presented in table II.

TABLE II. Total Deposition in Bulk Precipitation (Mg m^{-2})

Sample	Na^+	Ca^{2+}	SO_4^{2-}	NO_3^-	Rainfall (cm)	$[H^+]$ [b]
Boothbay Harbor	146	49	156	198	10.0	6.73
Harpswell	76	30	109	155	8.7	3.26
Portland	82	61	175	177	10.1	3.99
Brunswick	49	45	139	146	7.4	2.83
Richmond [a]	13	17	67	93	4.1	3.59
Buxton [a]	7	9	71	89	3.6	6.62
North Turner	79	46	185	220	12.3	1.75
Belgrade	103	54	152	248	14.8	1.65
Farmington	165	151	295	315	21.7	0.14
Rangeley	66	27	122	61	14.2	2.62

[a] Deposition based on Two Sampling periods.

[b] Evaluated from pH = - log $[H^+]$

RESULTS AND DISCUSSION

Sodium deposition shows a sharp gradient with increasing distance from the ocean. Such a distribution is clearly attributable to sea salt aerosols which become incorporated into coastal precipitation. Sulfate, nitrate, and calcium content is fairly constant over much of the sampling network. This uniformity seems to suggest that most of these ions originate from distant or natural sources.

Unusually high sodium deposition values were evident in precipitation samples from each site during 18 June to 2 July. The ion loads for this period constitute between 55 and 90% of the six week total even though rainfall amounts were of equal magnitude to those during other bi-weekly periods. Examination of synoptic surface weather charts reveals the passage of a series of low pressure troughs off the Maine coast during 22 to 27 June. Constant east to northeasterly winds associated with these systems produced an influx of marine air into the region, resulting in a prolonged period of rain and fog. A network average pH of 5.8 was observed during this two week period. For the rest of the six week sampling period, precipitation originated mainly from convective showers associated with frequent frontal passages through the region. The pH values for these periods ranged from 4.0

to 5.0.

Total depositions of Na^+, Ca^{2+}, $SO_4^{=}$, and NO_3^- are plotted as a function of precipitation amount in order to examine the origin of each constituent (Figures 3 and 4). Pearson and Fisher (1971) note that dry

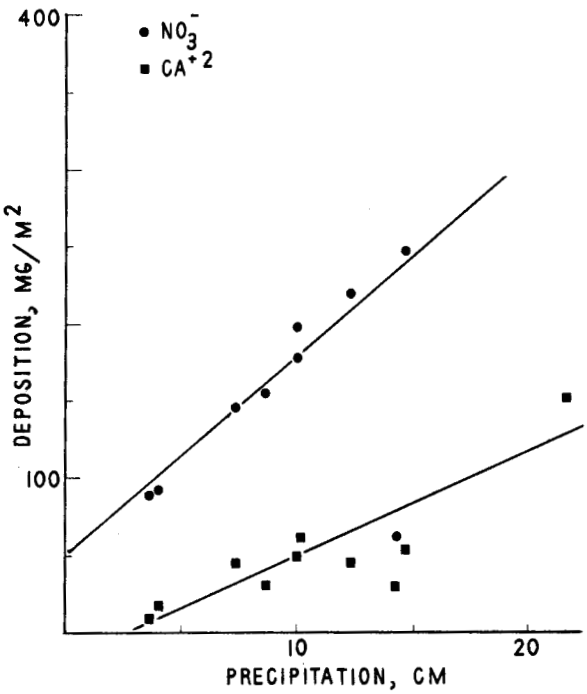

Figure 3. Deposition of nitrate and calcium versus precipitation amount for the period of 18 June to 31 July, 1974.

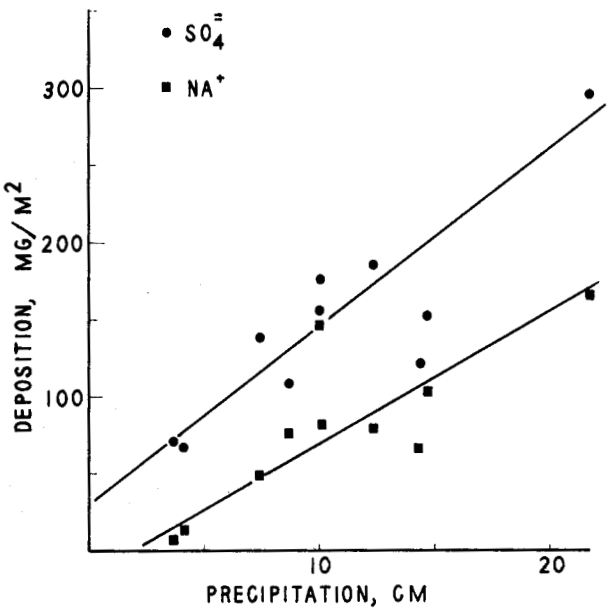

Figure 4. Deposition of sulphate and sodium versus precipitation amount for the period of 18 June to 31 July, 1974.

fallout should be deposited in amounts independent of the amount of rainfall, whereas those substances dissolved in precipitation should have loads that vary with precipitation amount. The data used in the plots are drawn from Table II. The data for Rangeley was not considered in drawing any of the least square lines. In addition, the Boothbay Harbor data, representing a marine source, and the Farmington data, greatly influenced by a local source, were not taken into account for the sodium correlation. The results for nitrate, sulfate and sodium suggest that these ions are mainly incorporated through precipitation processes. Low yields of these three ions in the Rangeley samples reflects the "unpolluted" rural atmosphere of this area. Excess sodium in the Boothbay Harbor precipitation very likely arises from dry deposition of sea salt aerosols. Calcium varies somewhat irregularly with precipitation amount, suggesting that soil dust and particulate matter entering as dry deposition may be important sources.

A great deal of the acidity and sulfate found in precipitation has been found to arise from the oxidation of sulfur dioxide and, perhaps, nitrogen oxides. In the absence of alkaline materials, the simple model projected by Scott and Hobbs (1967) predicts a decrease in pH with increasing quantities of sulfate ion. This relationship was observed in many of the bulk precipitation samples. In contrast, however, the Farmington and Belgrade samples were relatively alkaline (pH between 5.7 and 7.1). Corresponding increases in sulfate, nitrate, sodium, and calcium were also observed. Two factors appear to reduce the predicted acidity. The first involves the presence of large amounts of basic substances, as reflected by the sodium and calcium levels. Second, the large depositions of sulfate may not arise from the oxidation of sulfur dioxide, but rather from the presences of sulfate salts emmitted form a local source.

Rainout, or removal by cloud processes, has a high overall efficiency for the removal of gaseous pollutants such as sulfur dioxide, which become widely dispersed in the atmosphere during long range transport. Sulfate and nitrate contained in bulk precipitation was shown to arise primarily from rainout/washout. Because emissions from a point source must travel a great distance before intersecting the cloud layer, washout is expected to dominate as the primary mechanism in the vicinity of the source. This assumption serves as the basis for comparisons of the composition of particulate matter and precipitation.

Results of the chemical analyses of the rain and snow samples collected in the vicinity of the Jay mill are reported in Table III. The concentrations of the 15 November samples are significantly greater than those collected during the other precipitation events. Comparatively small amounts of precipitation (the network average was 0.3 cm) were deposited by a series of brief showers. This is in sharp contrast to samples collected from a twenty-four hour continuous rainfall on 13 November which deposited an average of 2.9 cm of rain. Gambell and Fisher (1964) report that small amounts of rainfall are subject to large changes in constituent concentration due to evaporation and other

TABLE III. Ion Concentrations in Rain and Snow Samples (mg ℓ^{-1})

Sample	Date	$[Na^+]$	$[Ca^{2+}]$	$[SO_4^{2-}]$	$[NO_3^-]$	pH
Farmington	11/13	0.32	0.17	1.24	1.12	4.99
	11/15	3.96	1.20	--	12.80	4.02
	1/13	4.24	0.40	0.52	1.70	4.72
	2/5	0.88	0.10	0.16	0.80	--
North Jay	11/13	0.55	0.10	0.80	0.58	5.38
	11/15	2.08	1.55	--	11.50	4.77
	1/13	0.12	0.15	0.20	1.60	4.89
	2/5	0.25	0.18	0.18	1.00	--
Jay	11/13	0.34	0.15	0.40	0.75	5.41
	11/15	1.92	4.55	--	11.20	6.61
	1/13	1.00	0.85	3.84	1.40	5.95
	2/5	1.09	0.90	3.76	0.90	--
Livermore Falls	11/13	0.12	<0.05	0.36	0.83	5.01
	11/15	1.64	1.20	--	9.50	3.97
	1/13	0.10	0.15	0.14	1.30	4.71
	2/5	0.59	0.35	1.80	0.75	--
North Fayette	11/13	0.15	<0.05	0.57	1.42	5.16
	11/15	1.04	0.45	--	9.30	4.00
	1/13	0.11	0.15	0.26	1.15	4.82
	2/5	0.23	0.10	0.79	0.85	--
Livermore	11/13	0.36	<0.05	0.67	0.80	5.93
	11/15	1.00	0.40	--	9.50	4.04
	1/13	0.12	0.12	0.29	0.90	4.78
	2/5	0.20	<0.05	0.26	0.97	--
North Turner	11/13	0.11	<0.05	0.56	0.20	4.96
	11/15	0.95	0.60	--	3.50	3.96
	1/13	0.11	0.15	0.56	1.30	4.75
	2/5	0.22	0.05	0.38	0.35	--
North Livermore	11/13	1.52	0.20	2.82	1.05	5.62
	11/15	0.98	0.85	--	9.00	4.06
	1/13	2.06	0.85	7.50	1.65	4.91
	2/5	0.81	0.42	2.92	0.77	--
Dixfield	11/13	0.32	0.17	1.24	1.12	6.36
	11/15	4.12	1.50	--	10.30	4.29
	1/13	0.27	0.10	0.44	1.70	4.70
	2/5	1.92	0.20	0.32	1.15	--
Canton	2/5	0.88	0.10	0.16	0.80	--

processes.

The concentrations of all ions vary considerably from site to site in the vicinity of the Jay mill. With a prevailing northeasterly wind, the North Livermore and Dixfield sites are downwind from the source and had sulphate concentrations of 300% and 90% above the network background. Increases of a similar magnitude are seen in snow collected downwind from the source on 13 January and 5 February. Similar variations are seen in the sodium concentration. The concentration of 1.52 mg ℓ^{-1} sodium collected downwind from the source on 13 November is more than five times the background concentration for that date. The pH of samples ranged from 3.97 to 6.36. Higher pH values were characteristic of rain and snow collected downwind from the mill.

In the particulate matter, sodium and sulfate comprise the major constituents of the ions analyzed. The correlation between wind direction and the chemical composition of particulate matter and precipitation permits a qualitative observation on the effects of the Jay mill.

CONCLUSIONS

While the results of this brief regional bulk precipitation study are tentative, two factors make the results from the individual precipitation events particularly interesting. Firstly, the kraft mill appears to contribute a buffering influence on rain and snow, balancing the acidic character of the regional precipitation. Most previous studies have been concerned with the increased acidity produced by point sources of sulfur dioxide and other pollutants. Secondly, the results show that this effect can be observed at considerable distances downwind from the source. While the magnitude of the increases in deposition of ions from these sources may not be significant for large scale regional considerations, the influence of an individual facility may extend to greater distances from the source than would be observed in an urban background. With the large number of pulp mills in Maine, the data stresses the importance of considering their influence on precipitation chemistry in establishing a regional precipitation network.

ACKNOWLEDGMENT

The authors would like to thank the staff of the Bureau of Air Quality Control of the Maine Department of Environmental Protection for their assistance in obtaining particulate matter samples and meteorological data.

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THE CHEMICAL COMPOSITION OF ATMOSPHERIC PRECIPITATION FROM SELECTED STATIONS IN MICHIGAN

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ACKNOWLEDGEMENTS

Financial support for this study was provided by the Michigan State University Department of Agricultural Engineering and an NSF-RANN (project GI-34898) to The University of Michigan. We wish to thank M. Quade, Y. Wang, and J. Kruse for precipitation chemistry. D. Kiel and W. B. Rockwell were invaluable in the areas of computer management and statistical analyses. Cooperation of the Michigan Department of Health, The Michigan State Climatologists, The University of Michigan's Biological Station and School of Public Health, and the many wastewater treatment plant operators without whose help this report would not be possible, is gratefully acknowledged.

ABSTRACT

The pH and amount of rainfall from over 60 selected stations throughout northern and lower Michigan was determined from September 1972 to December 1974. Precipitation pH was determined for each station by calibrated electrode meters.

The seasonal weighted average and median pH from all stations in the study was 5.0 and 6.3, respectively. Daily readings from stations throughout Michigan indicate that pH is dependent on the amount of rainfall and that variations in it are often locally controlled. Collectively the pH values suggest carbonic acid control for most of the state.

Annual median pH varied from a high of 8.45 at Dimondale, a

station located 1.5 km from a concrete tile plant in central Michigan to 4.65 at Vassar, a small town located east of several industrial centers in the thumb region of the state.

A comparison of annual nutrient loading for NO_3^-, $SO_4^=$, Cl^-, $PO_4^=$, Ca^{++}, Mg^{++}, Na^+, K^+, and pH of rainwater from selected stations revealed that the eastern U.S. stations reporting pH's < 4.02 have similar loadings for NO_3 but twice the SO_4 input found for rural areas of Michigan.

INTRODUCTION

Air pollution, a product of our highly industrial and mechanized world, is one of the serious environmental problems in the biosphere today. The release of large quantities of sulfur and nitrogen oxides to the atmosphere along with large amounts of contaminants and nutrients have created environmental problems at both the local and global scale.

Scientists in northwestern Europe (Barrett and Brodin 1955, Mrose 1966, Odén 1968, Brosset 1973, and Forland 1973) and the United States (Junge 1958, Junge and Werby 1958, Gambell and Fisher 1964, Fisher et al. 1968, Pearson and Fisher 1971, Likens et al. 1972, and Likens and Bormann 1974) have reported a trend toward increased acidity, NO_x and SO_4 loadings in rainfall due to human activities. Recent work by these scientists indicate a marked decrease in pH during the past two decades. The ecological effects of altering atmospheric chemistry is well documented. Almer et al. (1974) reported a reduction in phytoplankton and zooplankton species and the complete removal of roach, arctic char, trout and perch from many lakes in Sweden as a result of acidification. Johansson et al. (1973) have also noted that frequency of fish hatching in lakes and rivers in northwestern Europe decreased from about 50% at pH 7 to about 4% at pH 4. Jensen and Snekrik (1972) document that acid precipitation due to industrial effects has eliminated brown trout from many lakes and streams in southern Norway. In Ontario, Canada, Beamish and Harvey (1972) and Beamish (1974) traced the loss of lake trout, lake herring, white suckers and other fish to increasing levels of acidity caused mainly by SO_2 emitted by metal smelters in Sudbury.

The effects of increased air pollutants and acidity on increased soil leaching, reduced net primary productivity of coniferous forest species, foliar tissue damage and reduced growth in birch were shown by Overrein (1972), Westman (1974), and Wood and Bormann (1974), respectively. An understanding, documentation and reduction of man's influence on atmospheric chemistry and in turn on species diversity and ecosystem function is thus critical to the future survival of the

biosphere as we know it.

The purpose of this investigation has focused primarily on establishing to what extent acidification of precipitation is taking place throughout Michigan. This information coupled with a preliminary estimate of nutrient loadings for key constitutents should aid in determining the present influence of atmospheric inputs to various ecosystems in Michigan. The importance of urban and rural input differences and local influence versus regional effects are also discussed.

SAMPLING PROCEDURE AND METHODS

In 1972, a cooperative project was developed between the Department of Agricultural Engineering at Michigan State University, the Michigan Weather Service and the Department of Natural Resources of the state of Michigan utilizing the facilities of over 100 waste water treatment plants throughout Michigan to determine potential areas of air pollution damage to agricultural vegetation. Data in this report are from 60 stations which have reported at least 12 months. Since the type of pollutants being considered are transported through the atmosphere, it was hypothesized that the removal of pollutants by precipitation could be detected by examining the pH of rainfall.

Each station took daily pH readings and rainfall amounts from samples of rainwater collected during the previous 24 hours in a standardized rainfall collector located one meter above ground level. Precipitation pH was determined by calibrated electrode meters. Selected stations also recorded pH for rainfalls of less than 2.5 mm (0.1 in), 2.5 to 13 mm (0.1 to 0.5 in) and rainfalls of greater than 13 mm (0.5 in). For further discussion of methods see Merva (1974). In 1973 and 1974 fifteen selected stations were established by the School of Natural Resources and the School of Public Health, University of Michigan to determine nutrient loading for rural and industrially influenced areas, respectively. Ten of the stations were located in rural areas of northern lower Michigan and five were located around Saginaw Bay. Additional data from stations in Michigan were supplied by U.S. E.P.A. and the Canadian Government.

Immediately after each precipitation the samples were filtered through cheese cloth and frozen for analysis. Cation analyses (Ca^{++}, Mg^{++}, K^{+}, and Na^{+}) were completed following standard procedures of atomic absorption spectrophotometry (Perkin-Elmer 1973). An autoanalyzer (Technicon) was used to analyze for NO_3^-, NH_4^+, $PO_4^{\equiv}$, and Cl^-. Nitrate was analyzed for by the Greis-Ilsovary reaction and is reported as NO_3-N (E.P.A. 1974). The Berphelot reaction was used to analyze for NH_4-N (E.P.A. 1974). After manual digestion phosphorous was analyzed using molybdate reaction (E.P.A. 1974). All statistical analyses follow Sokal and Rohlf (1969). Acidity was calculated on

free hydrogen ion concentrations weighted proportionally to the amount of water and pH during each rainfall. Data are reported by the weighted mean and the median (M) statistic (1972-74). The weighted mean reflects the amount of rainfall while the median statistic reports only directly read pH units. The values for regions are compared by relative frequency in .1 pH units.

RESULTS AND DISCUSSION

An examination of pH values for rainfall from 60 stations in Michigan reveals that wide extremes are found throughout the state (figure 1). The median acidity for the entire state is 6.3. The

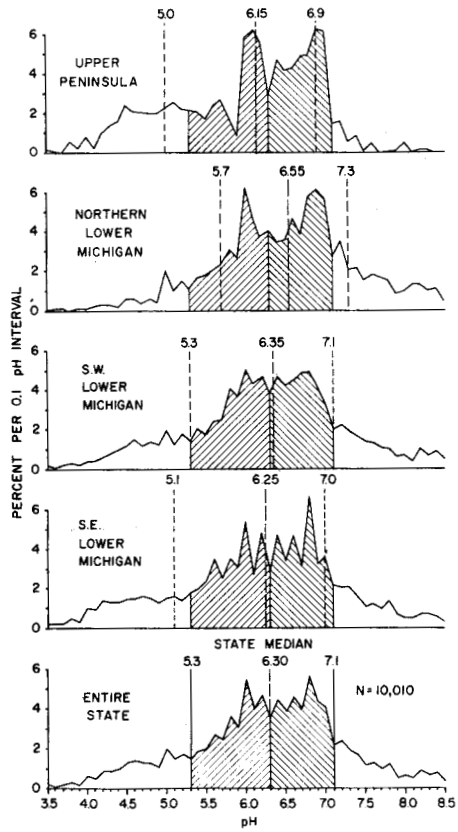

Figure 1. Frequency distribution by region for pH values collected in Michigan (1972-74) from 60 selected stations. The median pH value (±33%) is shown for the entire state by solid lines and hatching. Dashed lines indicate regional pH median values (- - -) and 83.3 and 16.7 percentile (---), respectively. (Note median = 50 percentile, 50 + 33.3 = 83.3, 50 - 33.3 = 16.7).

weighted annual pH is 5.03. This is considerably above the weighted pH values of 4.03, 3.91 and 3.98 reported by Likens et al. (1972) for selected stations in northeastern United States but is less than the average pH of six reported for Iowa (1971-73) by Tabatabai and Laflen (1975). The range of values (pH 3.5-8.5) do compare with those reported for other parts of the country by Whitehead and Feth (1974), Brezonik et al. (1968), and Klein (1974).

On a regional basis northern lower Michigan, an area of low population density and industry, has the highest annual median pH (figure 1). This trend was also found by Klein (1974). The heavily populated and industrialized southern portions of the state closely followed the entire state's frequency distribution and median pH value (figure 1). The Upper Peninsula had only six stations reporting and was heavily influenced by low pH values reported by stations located near pulp and mining industries in the western half of the peninsula.

Collectively the pH values suggest carbonic acid control for most of the state. However, analyses by individual stations reveal the importance of point source inputs and ground loading effects.

The importance of local influence on rainfall acidity is demonstrated by comparing four stations (Reed City, Vassar, Dimondale, and Deerfield) considered representative of locations influenced by forested land, heavy metal industry, a concrete tile plant, and a town adjacent to large population centers, respectively.

Reed City (population 2,296) is located in Oseola County in central Michigan and is bordered by federal and state forest on the west and east sides respectively. The seasonal variation in rainfall pH shows no consistent pattern over the three year period (figure 2). The weighted mean and range of pH's for this station indicate carbonic acid control (figures 2, 3).

The highest median pH (8.45) for the entire state occurred at Dimondale, a small village southwest of Lansing in central Michigan (figure 3). A seasonal trend is lacking through the time period measured (figure 2). The exceptionally high alkaline pH in rainwater is the result of a concrete tile plant located approximately 1.5 km from the collection site. The ecological effects of highly alkaline rainfall on entire systems are not well known, but potentially they add stress to the ecosystem. The tolerances of most species of flora and fauna (including man) to long term extremes in pH are in general low. Thus any variation from normal pH either acid or alkaline should be used as an indication of potential pollution problems.

Vassar (population 2,802) located in Tuscola County in the thumb region of Michigan is due east of several metal industries. There appears to be no seasonal pattern (figure 2) but the weighted annual acidity of 4.2 and the median pH (figure 3) of less than five

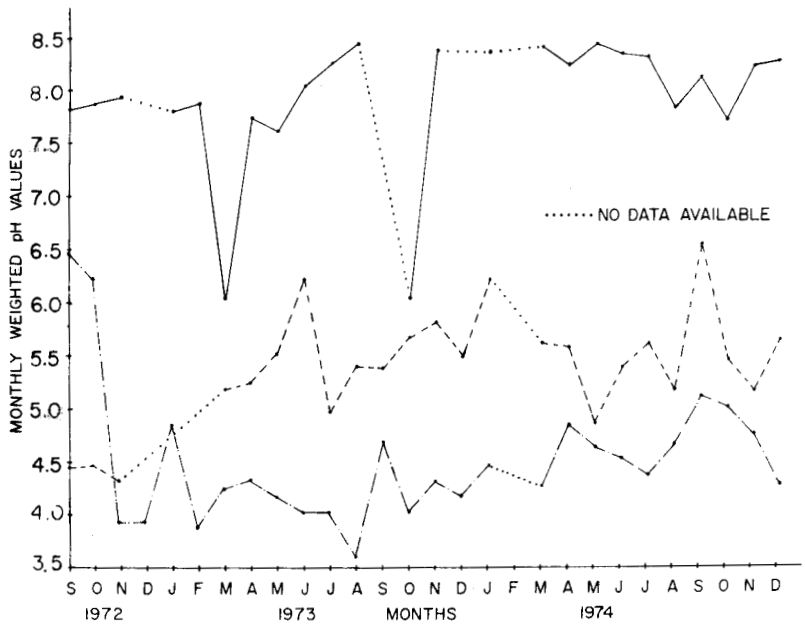

Figure 2. Seasonal trends (1972-74) in weighted monthly pH values for three stations in Michigan (Reed City ---, Dimondale ---, and Vassar -·-·).

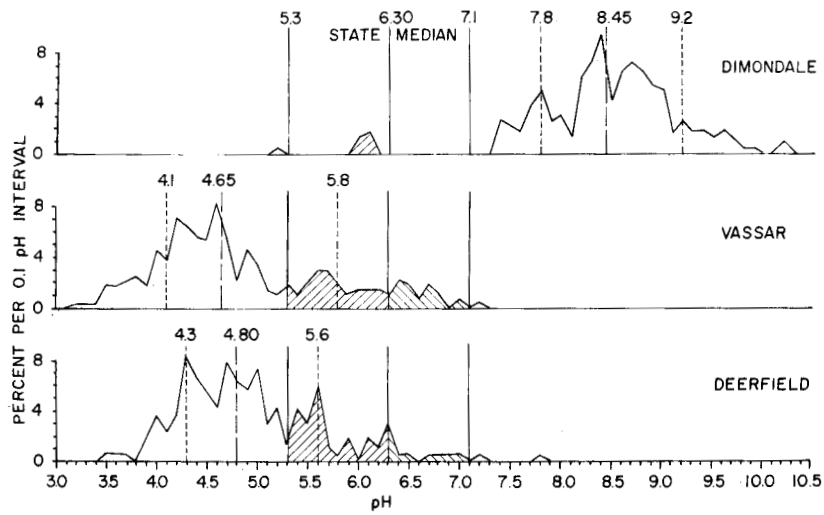

Figure 3. Frequency distribution of pH values for selected stations in Michigan. The median pH value ±33% is shown for the entire state by solid lines and hatching. Dashed lines indicate median station pH values (- - -) and the 83.3 and 16.7 percentile (---), respectively. (Note median = 50 percentile, 50 + 33.3 = 83.3, 50 - 33.3 = 16.7.)

indicates unusually strong acids in the rain (Likens and Bormann 1974).

Deerfield (population 834) reported the second lowest median pH for the state (figure 3). It is located in Lenawee County in the southeastern part of the state between Detroit, Michigan and Toledo, Ohio. Large metropolitan centers which have high emission levels of SO_x and NO_x can produce strong acid rainfalls (Likens et al. 1972). The levels in Detroit and Toledo for NO_x and SO_x emission (thousand tons per year) is estimated to be 1566 and 544, and 200 and 336, respectively (Acres 1975). This is considerably higher than the state's average of 101 and 103 for NO_x and SO_x, respectively (Acres 1975). Further research in meteorology and atmospheric chemistry is needed to help locate sources of nutrient loadings for specific elemental species and determine their role in rainfall acidity for this station and a number of key areas in the state.

Other stations reporting pH values below the "normal" of 5.7 (pH of pure rainwater which is saturated with CO_2 at normal pressure, Barrett and Brodin 1955) are found scattered through the state. At this time, it appears that local influences and ground loading [Michigan glacial soils are high in calcareous material as noted by basic pH values (>7.5) for many unpolluted lakes, streams, groundwater, and soil leachate (Richardson 1975)] are more important than regional influences on precipitation acidity as measured several meters above the ground by our study.

The median pH is dependent on the amount of rainfall (figure 4). A pairwise comparison (t-statistic) between the amount of rainfall ($\leq$ 2.5 mm, 2.5 to 13 mm and > 13 mm) and acidity (weighted hydrogen ion concentration) indicates that a statistically significant difference ($p<0.01$) does exist between light (<2.5 mm) and heavy (>13 mm) precipitation. Light rainfall is more basic (M pH: 6.36) than heavy rainfall (M pH: 6.15). The ecological significance of these differences seems minimal.

Mean annual nutrient inputs and pH for selected stations in Michigan and New York state are given in table I. The nutrient levels in general follow the values reported for the midwest by Junge (1958), Junge and Werby (1958), Lodge et al. (1968) Hoeft et al. (1972), and Wolaver and Lieth (1972). Because of a lack of long term data from comparable stations a definitive answer on temporal trends is not possible.

A comparison of values from the eastern U.S. (table I) indicates that the loading for most cations is similar except for higher Ca input in Michigan's rural locations and higher Na levels in the Pellston area.

Loading values for NO_3 and NH_4 are similar in both regions, but

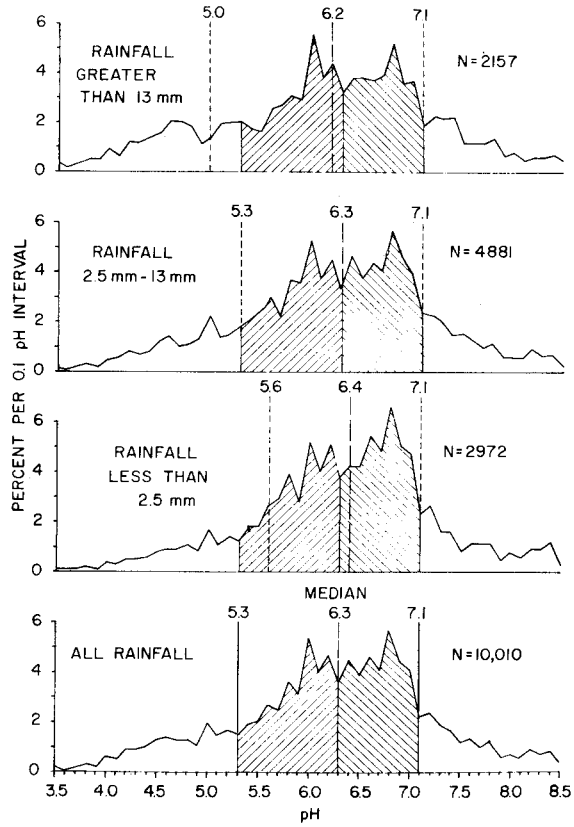

Figure 4. Frequency distribution of pH values for three depths of rainfall. The median pH value ±33% is shown for the entire state by solid lines and hatching. Dashed lines indicate median station pH values (- - -) and the 83.3 and 16.7 percentile (---), respectively. (Note median = 50 percentile, 50 + 33.3 = 83.3,
50 - 33.3 = 16.7.)

Table I. Preliminary estimate of nutrient loading (Kg/ha/yr) for bulk precipitation in selected stations in Michigan and New York.

LOCATION	CONSTITUENT Kg/ha/yr														
	NO_3-N	NH_4-N	NO_2	Total PO_4-P	Soluble P	Ca	Mg	K	Na	Cl	SO_4	Fe	Si	Rainfall[2] Cm	pH
Michigan															
Rural															
Pellston[3] (Northern Lower Mi.)	4.03	3.09	----	0.25	0.20	10.52	1.66	2.66	6.30	9.41	18.25	----	5.80	79.4	5.35[4]
Houghton Lake (Central Mi.)	3.20	2.09	0.01	0.31	0.29	9.46	----	3.20	----	----	----	0.36	----	72.8	5.27
Urban-Industry															
Saginaw Bay[5]	4.40	----	0.33	1.21	1.12	----	----	----	----	----	68.75[6]	----	----	68.9	4.90
New York[7] (1970-71)															
Ithaca	4.22	3.17	----	0.05	----	6.48	1.54	5.64	1.35	9.77	39.49	----	----	96.1	3.98
Aurora	4.28	3.26	----	0.06	----	4.77	0.75	1.09	0.95	12.69	49.65	----	----	98.4	3.91
Geneva	4.77	3.52	----	0.05	----	3.31	0.57	0.41	0.77	7.10	34.86	----	----	95.8	4.02

[1]Nutrient concentrations are weighted averages for bulk samples (rain and [illegible] fall).

[2]Twenty-five year average.

[3]Average loading from ten stations (1973-74).

[4]Average of northern lower Michigan region (station pH 4.8).

[5]Average loading from five stations (six months 1974). Michigan School of Public Health Data.

[6]Sulfate measured on three rainfalls in August 1973 (E.P.A., 1974).

[7]Data from Likens (1972).

the levels of phosphorous are considerably lower in New York (table I). Annual SO_4 inputs in central New York are about double those found in the northern rural areas of Michigan. Likens et al. (1972) reported that higher levels of SO_4 produce strong acid in rainfalls. This coupled with the stronger buffering capacity of Michigan precipitation (table I) may account for the generally higher pH values found in our study.

However, a few samples taken from one region in Michigan (Saginaw Bay, an area downwind of heavy industry and high population centers) indicate that seasonal inputs of SO_4 may be double those of central New York. The mean weighted pH (4.9) for the area is probably the result of strong acid precipitation. Vassar, the station with the state's median low pH (4.65), is also found in this area.

This study although preliminary does indicate potential problems

for some locations in Michigan. They seem to be local in origin at the present time but a final answer is not possible until long term regional meterorological and atmospheric chemistry studies are undertaken. The need to establish a statewide sampling network is paramount to our goal in understanding man's long term effects on the ecosystem.

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COOLING TOWER INFLUENCE ON THE RAINWATER pH NEAR A MAJOR POWER PLANT

TA-YUNG LI, University of Maryland.

ABSTRACT

The dense network of 12 rainguages, covering an area of 6 km in diameter, was reinstalled near PEPCO's 710 MW Chalk Point power plant in southern Maryland. The rainwater samples were collected from July to December 1974. This second season's collection of rainwater samples were analyzed and results showed a general shifting of pH toward higher values since the operation of a cooling tower. The pH values changed from a range of 3.4 to 4.6 to a range of 4.0 to 4.8. Graphs of mean pH distribution over our dense network show the influence of the cooling tower. Several selected cases of hydrogen ion concentration distribution will be presented to further illustrate this fact.

Analyses of our data confirmed the conclusions we had drawn previously. Chemical analyses show that sulfate and nitrite are the main ingredients of acidity. Hence, the main sources of low pH values were indeed attributable to SO_2 and NO_x from the combustion of coal.

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MONITORING PRECIPITATION CHEMISTRY ON THE MONONGAHELA NATIONAL FOREST

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ABSTRACT

Personnel from the Monongahela National Forest and the Northeastern Forest Experiment Station are collaborating in forest-wide monitoring of precipitation chemistry. Present monitoring facilities consist of one continuous precipitation collector/pH recorder and 12 precipitation collectors. Samples collected in these facilities are picked up and analyzed bi-weekly for specific conductance, pH, acidity , alkalinity, calcium, magnesium, sodium, potassium, nitrate-nitrogen, sulfate, and iron. Precipitation monitored at six (6) ranger districts is analyzed for pH and specific conductivity only. Results to date indicate substantial spatial and temporal variation, among as well as within storms. Precipitation throughout the Forest is decidedly acid; its chemical composition depends largely on the relative location of industrial centers. Our paper will describe the monitoring network and methods used, the automatic collector/pH recorder, the need and usefulness of the data, the data collected to date, and plans to expand the monitoring program.

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SATELLITE DETECTION OF SMOKE PLUMES AND INADVERTANT WEATHER MODIFICATION

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ABSTRACT

Satellite imagery provides a convenient and inexpensive means for monitoring smoke plumes and evaluating inadvertant weather modification. Visual examination of LANDSAT-1 imagery for two sites in east-central Ohio indicates that, at times, a plume may extend nearly 48 km downwind and reach a width of six km. Density slicing techniques provide clues as to the particulate loading in a plume.

The areal extent of plumes can be mapped and could be studied for adequate siting of ground stations in order to monitor the chemical quality of precipitation and evaluate the effects on the ecosystem.

Several satellite images show unusual cloud structures that occur in the vicinity of industrial sites. It is suspected that particulates and gases from the many stacks are related to the origin of the unusual cloud formations. A dense water vapor cloud originating at a large cooling tower is clearly visible on one image. About 20 km downwind, the snow belts spread out forming a snow field about 20 km long and 20 km wide. It is suspected that the water vapor released at the cooling tower is responsible for the large downwind snowfall.

INTRODUCTION

From the ground or even aircraft it is difficult to visualize or map the areal extent of smoke plumes or detect areas of possible inadvertant weather modification. Without an accurate mapping capability it frequently proves difficult to determine the average or maximum areal extent of smoke or vapor plumes thus adding to the problem of adequately locating ground stations to evaluate the effect of atmospheric pollutants on the forest or some other ecosystem.

Preliminary studies indicate that satellite data can be useful for the regional study of smoke plume dispersion, inadvertant weather modification detection, and provide several other potentially important bits of information. Satellite data are available on a repetitive basis (minimum of 9 days), require no sophisticated instrumentation for many types of analysis, and are very inexpensive. The imagery used in this study was obtained from the first Earth Resources Technology Satellite (ERTS-1), which is now known as LANDSAT-1*.

LANDSAT-1 was launched on 23 July 1972 and stabilized in a near polar orbit about 900 km above the earth. The satellite contains two remote sensors, a multi-spectral scanner (MSS), which records reflected visible and near infrared radiation in four spectral bands (4,5,6, and 7), and a return beam vidicon camera (RBV). The satellite's synchronous orbit allows fourteen orbits each day and coverage of the same area every eighteen days at the same local solar time, which is approximately 0942 hours at the equator.

The RBV system became inoperable shortly after launch therefore most of the satellite investigations have been based on the MSS. The MSS scans an area 185 km wide providing continuous coverage along each orbital track. Pictoral images are framed at Goddard Space Flight Center, Maryland with 10% forward and at least 14% sidelap between images. Each frame covers about 34,200 km^2; spatial resolution for the images averages about 80 meters.

Previous work with LANDSAT-1 and air pollution or weather modification includes recent studies by: 1) Lyons and Pease (1973), and Lyons (1974) to detect smoke plumes over Lake Michigan, 2) Griggs (1974) to measure atmospheric aerosol content over San Diego and the Salton Sea, 3) Kahan (1974) to use the satellite data collection system to monitor weather conditions for cloud seeding operations in the Colorado River basin, and 4) Murtha (1974) to study SO_2 damage to a forest in Ottawa.

SMOKE PLUME DETECTION

In view of the recent emphasis on air pollution control by the Ohio Environmental Protection Agency, a cursory examination of several LANDSAT-1 scenes was carried out in an attempt to evaluate their usefulness for monitoring smoke plumes. Enlarged prints (20 × 20 cm) were made from several 70 mm negatives representing different intervals of time. Originally no sophisticated techniques, such as density slicing, or color enhancement, were used; the images were evaluated only by a

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*Imagery is available to the public; write: United Sates Department of Interior, EROS Data Center, Sioux Fall, S. Dak., 57198.

magnifying glass or by the unaided eye. Photographic prints were enlarged to a convenient scale (approximately 1:500,000). The areal extent of visible smoke plumes, as best seen on the green and red bands (4 and 5, respectively) was recorded on a base map.

The major areas of interest included two sites on the Muskingum River in southeastern Ohio, and an industrial complex along the Mahoning River in the vicinity of Youngstown, in northeastern Ohio.

The areas examined along the Muskingum River lie in the vicinity of Philo and Beverly. In the Philo area are at least two major smoke producing industries. These include a ferro-alloy plant and an adjacent coal-burning electric generating plant. Satellite data clearly indicate that the ferro-alloy plant produces, by far, the greatest amount of smoke (Figure 1).

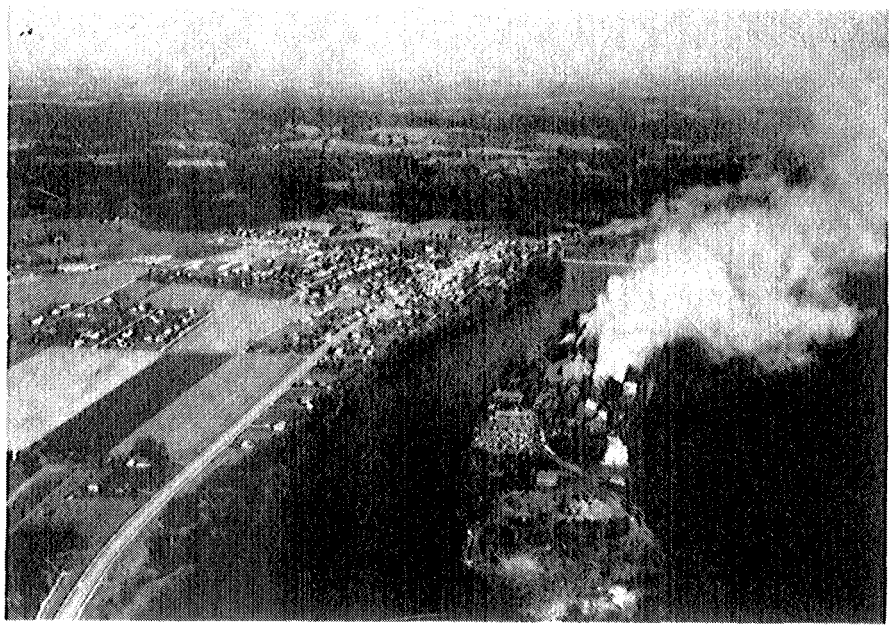

Figure 1. Ferro-alloy plant near Philo, Ohio (Site A).

The generating plant in the vicinity of Beverly (Site B) has a capacity of about 1530 megawatts and consumed 4192.4 thousand tons of coal in 1971. The coal had an average sulphur content of 4.9% and averaged 20% ash. The plant also consumed 46.7 thousand barrels of oil. During the same year the power plant at Philo (Site A), which has a capacity of 500 megawatts, consumed nearly 959 thousand tons of coal with an average sulphur and ash contents of 3.9% and 16.8% respectively. This plant required 12.5 thousand barrels of oil. These data indicate that the plant at Beverly consumed more than 4.5 times as much coal and

and 3.7 times as much oil as the Philo plant (Figure 2). Unfortunately recent fuel consumption records are not available.

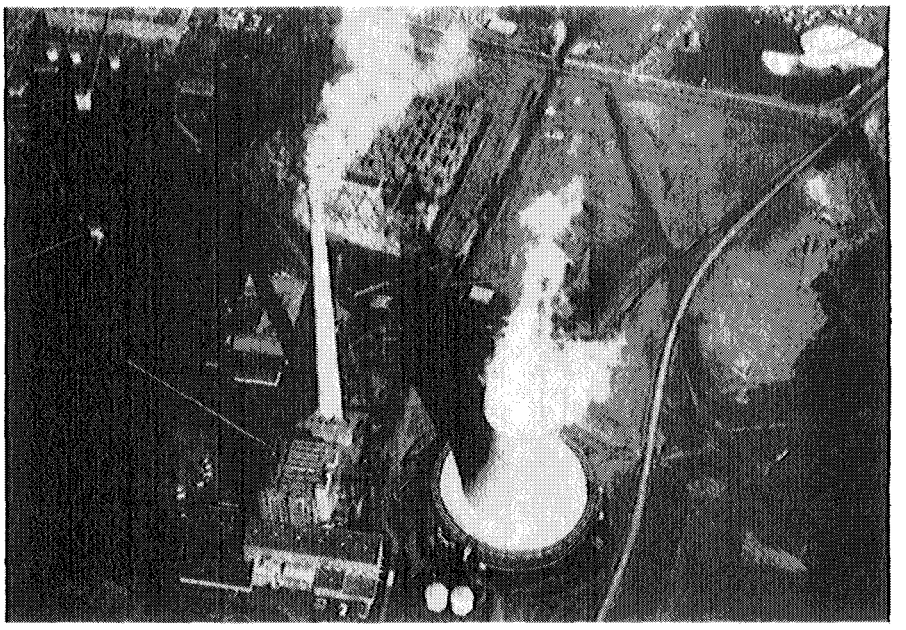

Figure 2. Coal-burning electric generating plant near Beverly, Ohio (Site B).

A partial satellite scene of the two smoke producing areas is shown in Figure 3. At Philo (Site A) and near Beverly (Site B), smoke was evident on seven LANDSAT-1 scenes, not evident on four scenes, and obscured by clouds on the other four scenes examined (Table I). The density and directional trend of the plumes are controlled by local atmospheric conditions. Wind direction, velocity and atmospheric mixing play dominant roles. As indicated in Figure 4, the plumes range from short, high-density to large, low-density features. The plume originating at the Beverly plant is most often the largest and may exceed 32 km in length. On 30 July, 1973, however, the Philo plume extended northward about 48 km nearly to Coshocton and reached a width of 6 km. Although severely limited in number, available imagery seems to indicate that the major direction of plume movement from both sites is generally southward, ranging laterally from 90^{o} to 270^{o}. Circles with centers at Philo and Beverly with a radius of 40 km would most likely enclose the major region of plume influence. The plumes commonly flow a few hundred meters above the ground.

If the images were examined by more sophisticated techniques, in particular density slicing, it is quite certain that the areal extent of

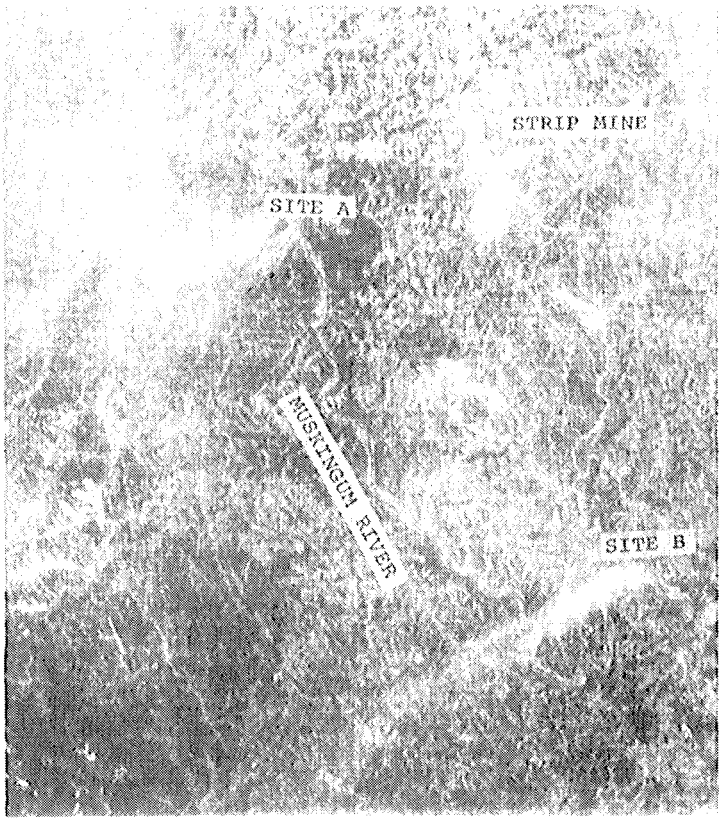

Figure 3. Partial LANDSAT-1 scene showing smoke plumes, trending southwest, originating at Philo (Site A) and Beverly (Site B) (Scene No. 1408-15410 04Sep73, band 5). Bottom edge of photograph is approximately 50 km.

the plumes could be more accurately mapped. Although it is a relatively simple process to map smoke plumes directly from LANDSAT-1 imagery, we do not know exactly what concentrations of particulate or gaseous matter the visible plumes represent. In order to be a truly viable monitoring technique, it would be necessary to determine, directly from the imagery, the total suspended particulate mass loadings and size concentrations in the plumes. Very likely this can be accomplished by aircraft, instrumentad with sensitive air pollution and meteorological sensors, flying through the plumes during LANDSAT-1 overpasses. The measured concentrations could then be compared with differences in spectral response evident on the imagery.

Figure 5 shows computer processed, density sliced, imagery of the smoke plumes at Philo and Beverly. The different shades of gray indicate differences in particulate loading of the smoke plumes. The

TABLE I

Visability of smoke at Philo (Site A) and Beverly (Site B), Ohio, satellite scene number and date of overpass.

LANDSAT-1 Scene Number	Date	SMOKE PLUME Evident	SMOKE PLUME Not Evident	Site cloud Covered
1029-15361	21 Aug. 72	x		
1048-15414	09 Sep. 72	x		
1173-15362	12 Jan. 73	x	1	
1192-15422	31 Jan. 73			x
1210-15423	18 Feb. 73		x	
1228-15424	08 Mar. 73	x		
1264-15425	13 Apr. 73			x
1299-15365	18 May 73		x, 2	
1299-15363	05 Jun. 73		x, 2	
1372-15414	30 Jul. 73	x		
1407-15352	03 Sep. 73	x, 3	2	
1408-15410	04 Sep. 73	x		
1425-15350	21 Sep. 73		2	x
1444-15401	10 Oct. 73			x
1461-15340	27 Oct. 73		x, 2	

1. Site A not on image
2. Site B not on image
3. Extent of plume too small to be shown in Figure 4.

illustration merely shows what might be done by means of density slicing techniques.

Smoke plumes, per se, are not evident on any of the imagery examined of the Youngstown area. There is visible on the 12 January and 21 September, 1973, imagery, however, what appears to be a very interesting, seldom recognized, phenomenon. Long narrow clouds originate at several sites just south of the Mahoning River but downwind of the Youngstown industrial complex (Figure 6). As these clouds are traced northeastward (downwind) they become significantly larger while the clouds on either side of them remain about the same size. It is strongly suspected that this is caused by particulate matter originating upwind at 10 or 12 individual stacks. Similar features have been described for the Gary-Chicago area by Lyons and Pease (1973).

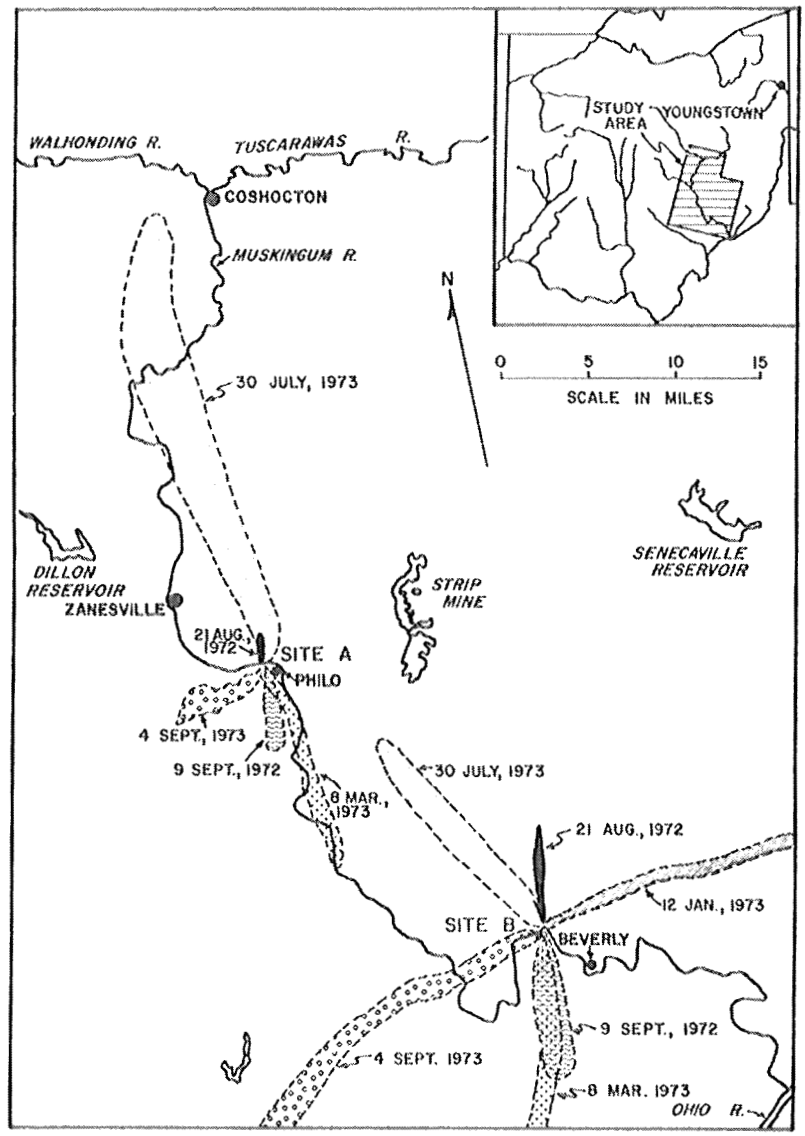

Figure 4. Map based on LANDSAT-1 data showing areal extent of smoke plumes originating at Philo and Beverly.

INADVERTANT WEATHER MODIFICATION

Several interesting phenomena are shown on a partial LANDSAT-1 scene acquired on 12 January 1973 (Figure 7). The area covered by this image includes a part of east-central Ohio and adjacent parts and western West Virginia. The Ohio River nearly bisects the scene; an abundance of clouds appear in the eastern part of the image with their long

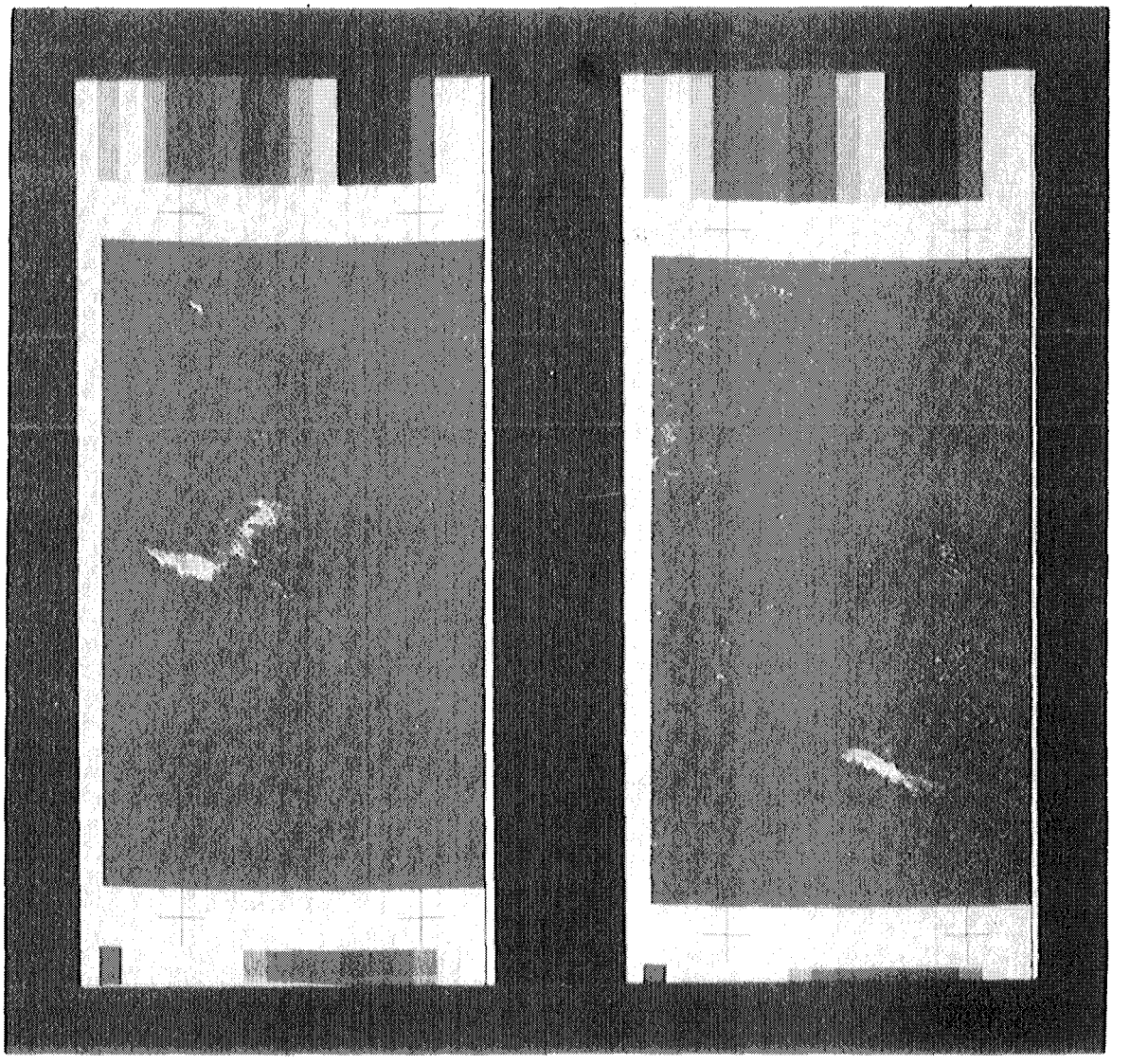

Figure 5. Density sliced smoke plumes at Philo (left) and Beverly (right) produced from satellite imagery. This is a contact print of a color transparency; the darker tones indicate the densest smoke. Bottom edge is approximately 48 km.

axis trending northeast-southwest. The light area in the northwest part of the image represents a thin cover of snow on the ground. The light bands extending diagonally represent trails of snow, which fell probably only a few hours before the image was taken. The snow clouds were moving southeast; the wind direction at the time of satellite overpass was blowing to the east as indicated by the plumes at Sites A, C and D, as well as several other plumes which are not marked. Site A is the location of a large cooling tower at an electric generating plant. The large white cloud that originates at Site A is caused by condensing water vapor discharged from the cooling tower. Notice that about 20 km

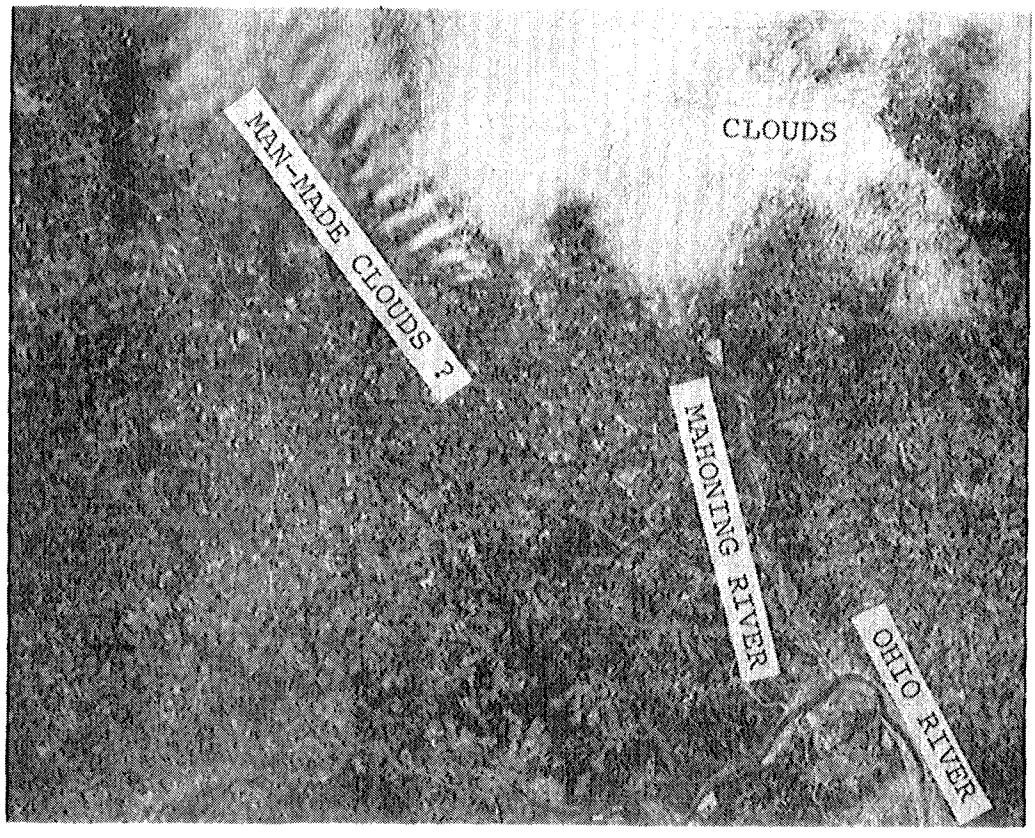

Figure 6. Partial LANDSAT-1 scene of the Warren-Youngstown, Ohio area showing man-modified clouds (?) originating in the vicinity of major industrial sites along the Mahoning River (Scene No. 1425-15350, 21Sep73, band 5). Bottom edge of the photograph represents approximately 80 km.

east of Site A is a large area where snow covers the ground (Site B). It is assumed that this larger area of snowfall reflects inadvertant weather modification caused by the high concentration of water vapor generated at the cooling tower.

The clouds in the vicinity of Site C appear to be less dense and larger than those in surrounding areas. This is also the location of a cooling tower, which is evident because of the condensation of the water vapor. It is suspected that the large quantity of water vapor and heat released at the cooling tower is directly related to the differences in the apparent density of the clouds. Similar features of different locations are evident on other satellite scenes.

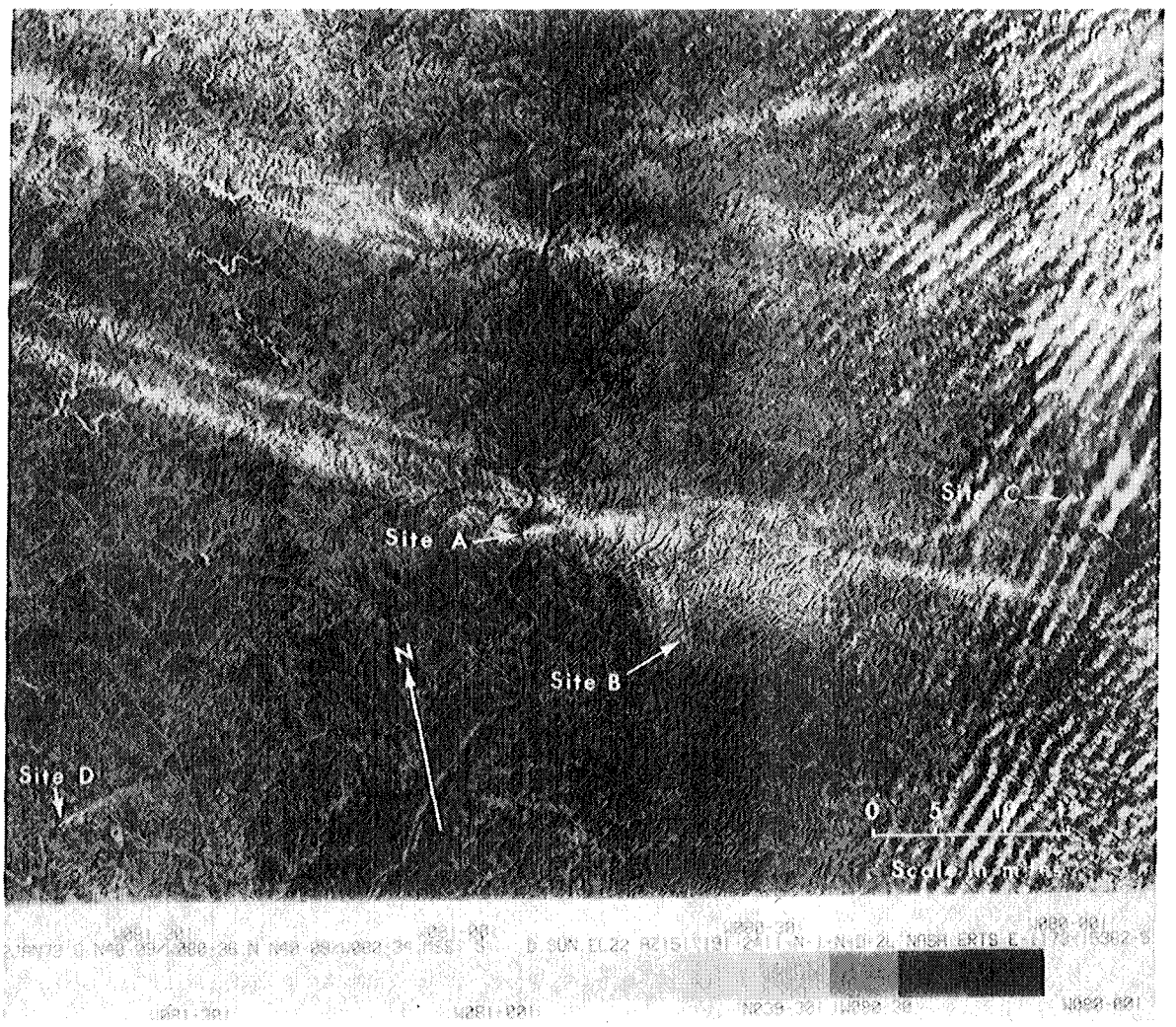

Figure 7. Partial LANDSAT-1 scene of eastern Ohio and western West Virginia showing snow belts, cooling towers and large area of snow caused by cooling tower vapor (Scene No. 1173-15362, 12Jan73, band 5).

SUMMARY

It is a well known fact that air pollution not only decreases visability but that it may also have a profound effect on the quality of rainfall thus increasing ecologic stress. This is exemplified by the decreasing pH rain that is related to the increasing concentration of atmospheric gaseous contaminants, such as sulfur and nitrogen oxides, released by the burning of high sulfur fuels. Although acid rainfall is not of immediate danger to humans, it does considerable damage to man-made structures and has serious implications for ecologic systems.

It is quite evident that satellite imagery can be used to examine and map the areal extent of smoke plumes and indicate areas of inadvertant weather modification. They can also be used to determine areas where ground surveys could be conducted in order to evaluate the effects of air pollution on vegetation.

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THE VARIABILITY OF pH IN CONVECTIVE STORMS

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ABSTRACT

The rainwater pH was measured in a total of 22 storms which occurred in 1972 and 1974 in the METROMEX (METROpolitan Meteorological EXperiment) rainwater sampling network. The network consists of 81 collectors in an area of 1800 km^2 over and east of St. Louis, Missouri.

The data set is composed of dry fallout samples as well as precipitation samples which have been analyzed independently. An analysis of the frequency distribution of these data show the rainfall samples form a bimodal distribution of pH with relative frequency maxima at pH 7.0 and 4.0 while the dry samples are unimodal with the maximum frequency at pH 7.0.

The areal distribution of precipitation weighted mean pH indicates a variability unrelated to total precipitation. However, the derived deposition of H^+ is more similar to the areal rainfall pattern than to the pH. The dH is defined which incorporates both the rainfall and pH which is useful for climatological trend studies of acid rainfall.

Examples of two individual storm events illustrate an inexplicable area-wide variation from nearly an all acid rain ($pH \leq 4.5$) to an all alkaline rain ($pH \geq 5.5$). These case studies indicate some of the meteorological as well as chemical problems which must be considered when attempting to characterize convective storm rainfall pH.

INTRODUCTION

A five-year research program on inadvertent weather modification was initiated in St. Louis, Missouri in the summer of 1971 under the acronym of METROMEX (METROpolitan Meteorological EXperiment) to examine the effects of human activity on local climate (Changnon et al., 1971). The research program represents the most comprehensive study of its

kind undertaken anywhere in the world incorporating diverse research groups possessing expertise in several areas of atmospheric science. A summary of the results after 3 years of field measurement efforts were published in the Bulletin of the American Meteorological Society (1974) with nearly all of the participants included as authors of various sections.

The major emphasis of METROMEX field effort is on the quantification, location, and causes of a summer season precipitation anomaly previously defined by climatological research (Huff and Changnon, 1972). In addition, the most important result anticipated from this large research effort is the identification of the *impacts* of the anomaly on various segments of society.

One of the obvious impacts involves the wet and dry deposition of atmospheric aerosol over both urban and rural areas in the downwind region of the St. Louis metropolitan area. The potential problem is analogous to the radioactive "hotspots" which periodically arose during the atmospheric testing of nuclear devices. In essence, the argument for concern with inadvertent precipitation modification rests upon the concept that convective storms result from the confluence of water substance in a localized atmospheric volume. Subsequent change-of-state initiates cloudiness with attendant microphysical processes forming precipitation.

All of these processes are active as transport and sink mechanisms for natural and anthropogenic aerosols. Consequently, either increased frequency of precipitation initiation or enhancement of precipitation processes can lead to localized enrichment of chemical deposition posing various topics for further research including impacts dealing with water quality, soil chemistry, agriculture, and structural damage.

Much of the air and precipitation chemistry research in METROMEX is directed toward assessing the magnitude of the alteration of rainwater quality in the region of the precipitation anomaly using a case study approach. As a part of this chemistry research effort, the pH of storm event wet and dry deposition samples is examined to assess its variation in proximity to an urban-industrial complex and to elucidate the sampling problem with regard to monitoring future trends.

SAMPLE ACQUISITION AND PROCESSING

The major goals (Changnon et al., 1971) of the METROMEX research program necessitated the installation and operation of the world's largest raingage network of 250 gages concentrated in an area of 8000 km^2. A subsection of this network shown in Figure 1 comprised a precipitation sampling network of 81 collectors in an area of 1800 km^2. The collectors were colocated with a recording raingage to aid interpretation of rainwater chemistry relationships to storm structure with regard to wet deposition of aerosols.

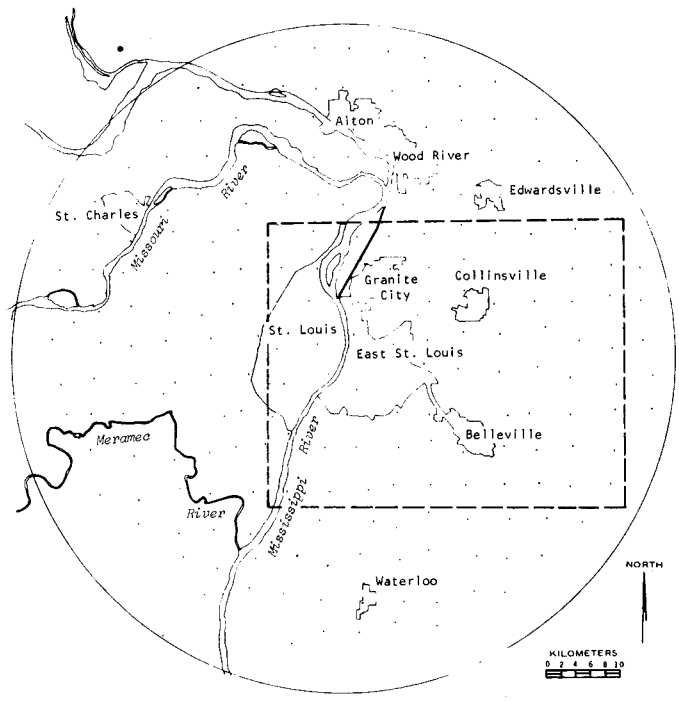

Figure 1. The research area encompassed by the St. Louis METROMEX field project. The recording raingage sites are indicated by the dots. The rectangle delineated east of the city is the precipitation chemistry network.

The collectors used in this program consisted of fence-post mounted polyethylene bottles installed approximately 1.5 m above ground level within clearly exposed areas. The bottle capacity was 2 liters with an opening of 60 cm^2. Typically the bottles were deployed in the field based on a weather forecast of precipitation during the immediate 24 hour period. During 1972 the samples were collected within one or two hours after the cessation of precipitation whereas those acquired in 1974 were collected on a 24 hour schedule.

Since the entire data collection was dependent upon the accuracy of the meteorological forecast of precipitation, it was inevitable that some data on completely dry samples occurred.

Each of the predicted precipitation events was assigned an experiment number to ease the later identification of samples for further processing and the chemical analyses for trace metals by flame emission and atomic absorption spectrophotometry. All of the collected samples were transferred from the field location to the analytical facility within 48 hours of the storm event. Within 24 hours of receipt of an experiment, the pH was determined and the rain sample was then

processed for subsequent elemental analysis. The samples obtained in the absence of precipitation were treated in exactly the same way after the addition of 50 ml of double-distilled, deionized water and allowed to equilibrate for 24 hours.

A commercial pH meter was used for the measurement. In a few instances, the meter was used in the field to determine the pH in near real time, at the field headquarters as samples were prepared for shipment to Champaign, and at the laboratory facility in Champaign. A comparison between these measurements did not indicate any significant variance in the values and all subsequent pH determinations were made in the laboratory.

pH FREQUENCY DISTRIBUTION

The field samples consisted of both wet and dry data since the area was sufficiently large that showers frequently did not cover the entire network and occasionally forecasted precipitation did not occur. A total of 941 determinations of pH were made with samples collected from 88 dry and 853 convective shower and thunderstorm events.

The frequency distribution of pH for the dry fallout samples is shown in Figure 2. This limited set of data shows a distinct trend

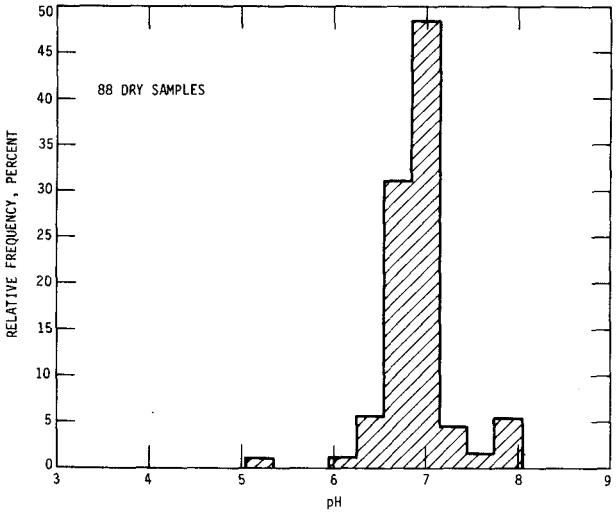

Figure 2. The relative frequency distribution of pH values derived by the addition of 50 ml of 6.5 pH laboratory water.

toward a normal distribution with a mean of pH 7. The deionized laboratory water has pH 6.5 and the observed distribution is not unexpected. However, it is worth noting that the dry deposition of potentially acid aerosol and the subsequent dissolution was not detected in these samples. In fact, it can be concluded that these observations indicate the presence of water soluble, alkaline materials in the dry samples.

The rainwater pH frequency data are shown in Figure 3. In contrast

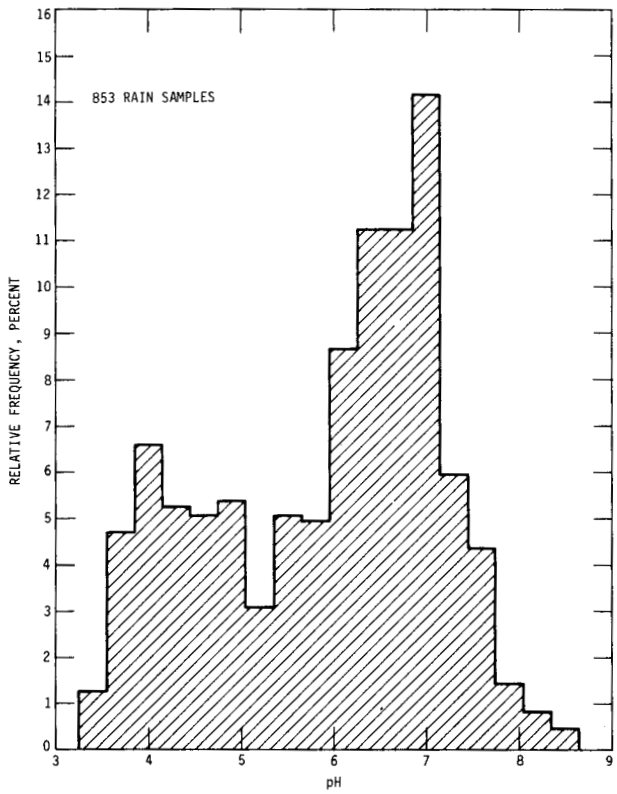

Figure 3. The rainwater pH relative frequency distribution obtained from 853 samples during 22 strom events in 1972 and 1974.

to the dry samples, the precipitation exhibits a bimodal distribution with only 12.6% of the data equal to or less than pH 4 and 27.2% equal to or greater than pH 7. It is interesting to note that the minimum between the two modes occurs at a value corresponding to equilibrium between air containing CO_2 and pure water of approximately 5.7.

The cumulative relative frequency distribution obtained from these data indicated that 50% of the values exceed pH 6.0 which is still more alkaline than CO_2 saturation. These data are not unlike those reported by Merva (1974) for various stations in Michigan. Merva showed separate distributions for maximum and minimum values with average values of 7.7 and 4.7 respectively. The overall average for the state of Michigan was reported as 6.17.

AREAL DISTRIBUTION OF pH

The precipitation weighted mean pH values at each of the sampling sites within the raingage network (Figure 1) are shown in Figure 4 for the 22 rain events. The weighted mean pH value for the entire 1800 km^2 area is 4.9. The corresponding mean rainfall is shown in Figure 5. It

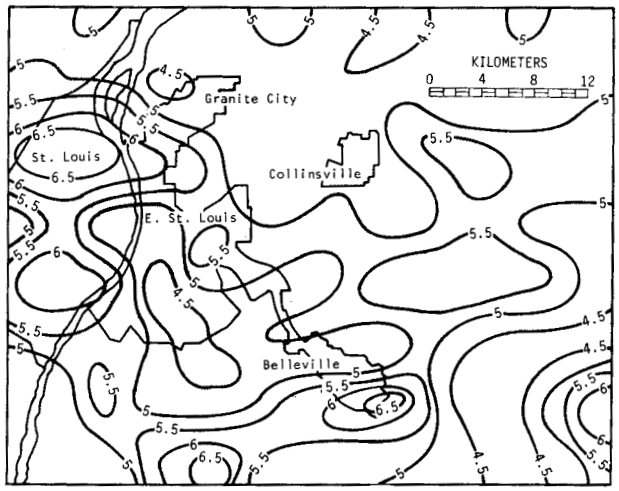

Figure 4. The rainfall-weighted mean pH pattern resulting from data acquired at 81 sites in the 1800 km^2 area. The areal mean of these data is pH 4.9 with a range of values from 4.3 to 6.8.

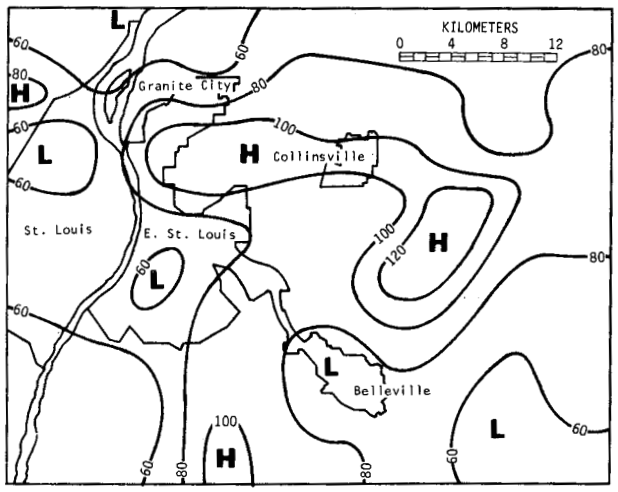

Figure 5. The mean rainfall in ml associated with the pH data in Figure 4 from 22 storms in 1972 and 1974.

is obvious that there is little correspondence between these data. The low pH values near E. St. Louis extending SE correspond to a gradient in rainfall from a low of < 60 ml to a high of > 100 ml. It should be noted that the maximum rainfall area in Figure 5 is in the same region as the climatically defined rainfall anomaly associated with St. Louis (Huff and Changnon, 1972). It is within this area that 20% to 30% increases in rainfall occur during the summer season amplifying the seriousness of understanding the local alteration of rainwater quality.

The relatively large areas of pH > 6 in the W-central, S-central and SE portions of the network appear perplexing in view of the distribution of SO_2 point sources shown in Figure 6. Equally difficult to relate to industrial activity is the area of pH < 4.5 in the SE part of the network which is an active agricultural area removed from any point SO_2 sources.

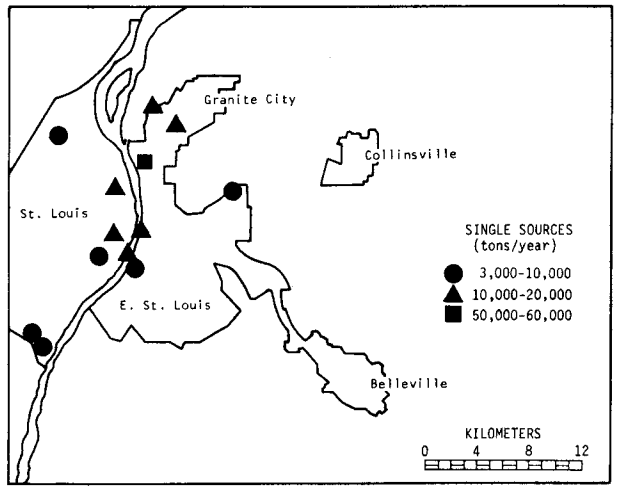

Figure 6. The location and extimated source strength of sulfur oxide in proximity to the chemistry network. These data were obtained from an emission inventory conducted during 1963-1964 as part of the St. Louis - East St. Louis Interstate Air Pollution Study and is contained in their report.

On the other hand, Kemmerer and Jackson (1973) demonstrated the balance between calcium aerosol and oxidized SO_2 as an explanation of neutral pH precipitation. Departures from this balance were shown to relate to acid or alkaline rains depending upon the proximity of the sample site to particulate sources. The pH data of Kemmerer and Jackson in Syracuse, New York relate quite well to these data for St. Louis. The absolute range of the data from the 4 Syracuse sites extended from 4.05 to 9.20 and the average values from 4.26 to 7.8. The range of the St. Louis data in Figure 4 extended from 4.3 to 6.8.

In addition to the SO_2 point sources shown in Figure 6, there are several point and areal sources in proximity to the chemistry network ascribed to the cement manufacturing industry. Several active quarries align the Mississippi and Missouri River valleys which are abundant sources of aerosol containing calcium carbonate and other basic anhydrides. In addition there are 2 cement processing plants providing additional sources of aerosol capable of neutralizing otherwise acidic rainfall. It has been shown by Semonin (1972) that surface released materials are transported by convective air motions to clouds and returned to the surface by precipitation relatively near the source. These experiments with unique chemical tracers suggest the possible rapid response of precipitation formation processes to scavenging of either water soluble alkaline or acid aerosol resulting in the observed pH.

In a review of rainwater as a chemical agent in geologic processes, Carroll (1962) indicated the potential importance of the H^+ to the weathering of soil minerals. As a first approximation, we may assume the pH as representative of the H^+ concentration and calculate the deposition by precipitation. The mean H^+ deposition in μg is shown in Figure 7. There is a reasonable correlation between the mean precipitation shown in Figure 5 and the deposition illustrating the dominating influence of rainfall on the spatial variability.

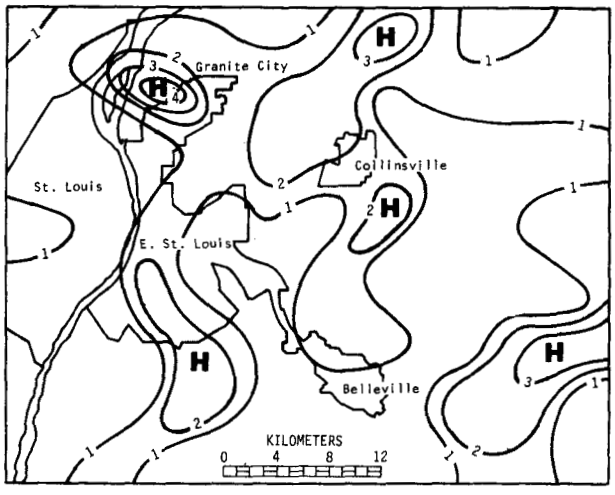

Figure 7. The mean H^+ deposition in μg calculated from the pH and rainfall of the 22 individual storm occurrences in 1972 and 1974.

For applications in the geophysical sciences, it seems apparent that rainfall pH alone is not sufficient to describe its potential impact. As with other chemical properties of rainfall, the quantity of material deposited at the surface is not specified by the concentration, but must be calculated from simultaneous measurement of the total rainfall. The environmental response may vary considerably between high concentrations with light rainfall and relatively low concentrations with heavy rainfall. A number can be defined, analogous to pH, which also includes the weighting factor of precipitation,

$$dH = -\log_{10} [P \cdot 10^{-(pH+3)}]$$

where P is the total sample precipitation.

The use of dH is an attempt to introduce a single number for investigations involving rainfall pH. The antilog of the negative dH is a direct indication of the H^+ deposition accounting for not only the acidity of the rainfall, but also the water volume involved. To illustrate the dH concept, the numbers were calculated for the mean pH and precipitation data discussed previously. The results are shown in Figure 8. The dH values range from 5.37 to 7.93 and these extremes are both found in the NW quadrant of the chemsitry network. The corresponding mean values of pH and precipitation at these sites were 4.3 and 6.6, and 78.4 and 45.5 ml, respectively. None of these individual site measurements were extreme values for either pH or rainfall.

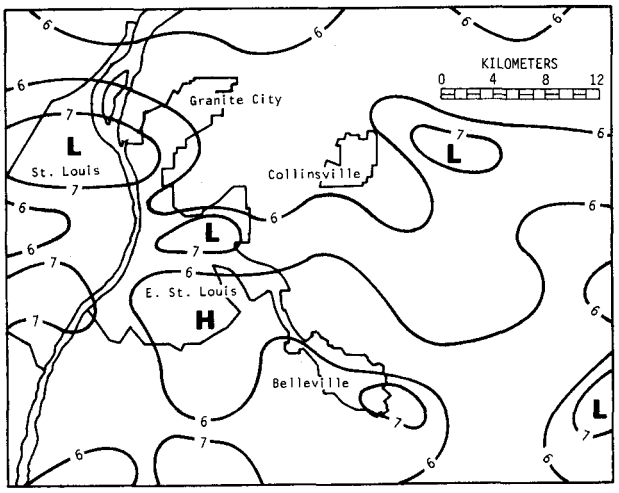

Figure 8. The pattern of the mean dH, a number incorporating both pH and rainfall.

CASE STUDIES OF INDIVIDUAL STORMS

28 July 1972

The St. Louis area was under the influence of circulation around a low pressure center in central Kentucky with a stationary front extending WSW through SE Missouri to W Texas. The winds throughout the lower 2 km were from the NE at 2 to 5 mps. The slow advection of the entire storm system to the E carried showers with it moving through the sampling network from the NW. Due to the complex relationship between the sub-cloud airflow, the movement of individual storms, and the advection of the cyclonic system, it is difficult to relate the measured pH to known industrial sources of gaseous and particulate materials.

The pH pattern observed from this storm system is shown in Figure 9. The corresponding rainfall (Figure 10) illustrates the variability of the convective shower activity. The high pH shown in the NW corner can be associated with cement plant operations in that area, but no comparable explanation is offered for the N - S band of high pH at the E edge of the network. The relatively low values S of E. St. Louis and extending SE can be related to the dense industry in the area, but, again, the low values in the N-central and NE are unrelated to known sources in the immediate area.

The weighted mean pH for this event was 4.8 with a standard deviation of 1.3. The range of values observed was from 3.4 to 8.2. This type of pattern is not unlike many others and would be classed as an acid rain for this area.

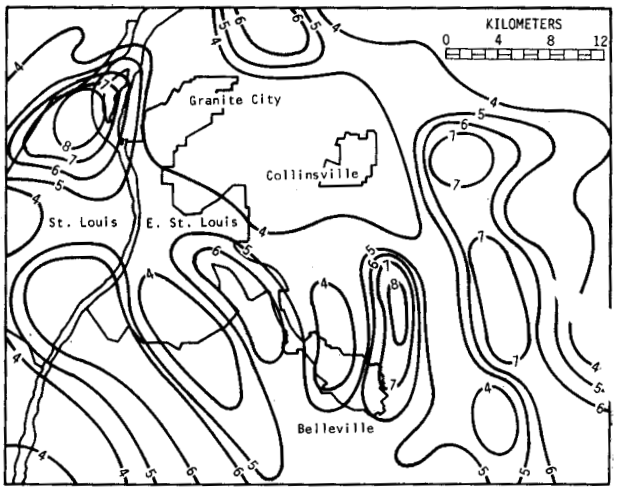

Figure 9. An example of the pH variability from a convective storm on 28 July 1972 with areal mean pH 4.8 and a range extending from 3.4 to 8.2.

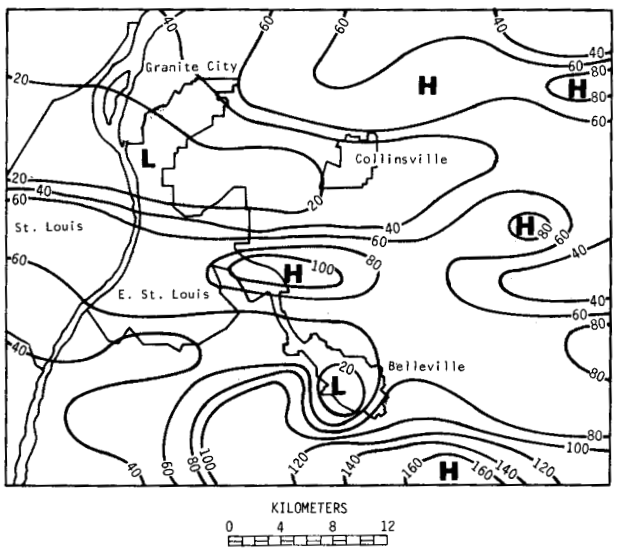

Figure 10. The precipitation in ml associated with pH shown in Figure 9.

6 August 1972

A cold front passed through the research area during the evening of 6 August with showers and thunderstorms preceding it during the day. The surface winds in advance of the approaching front were from the S at 3 mps becoming stronger from the NW after the frontal passage.

The pH distribution from this event is shown in Figure 11. The thunderstorm rainfall (Figure 12) was obviously more alkaline than the case of 28 July and with the low-level transport wind from the S, which is an agricultural flood-plain, the source of neutralizing aerosol remains a subject for future research.

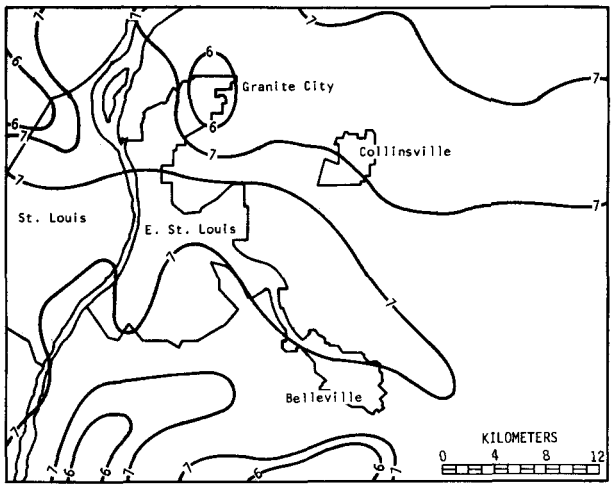

Figure 11. The pH pattern which occurred with a convective storm system prior to a cold frontal passage on 6 August 1972. The areal mean pH was 6.4 with values between 5.2 and 7.9. This case shows the alkalinity of many observed precipitation events.

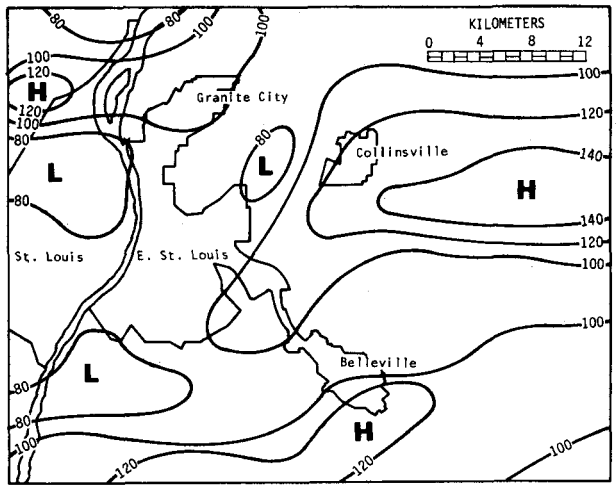

Figure 12. The rainfall in ml which produced the pH pattern shown in Figure 11.

The areal mean pH was 6.4 with a standard deviation of 0.7. The pH values ranged from 5.2 to 7.9. As in the case of the acid rain of 28 July, this pattern of pH occurs frequently, but is classed as an alkaline rain.

SUMMARY AND DISCUSSION

The two case study events illustrate the difficulties in sampling precipitation for chemical analyses. Even possessing knowledge of the locations and general character of industrial effluents, the causes of acid or alkaline rainfall will not be uniquely determined. The complex chemical matrix of rainfall in an urban area with numerous and diverse sources of gases and aerosols is certainly a contributing factor toward

the inability to clearly define the observed pH variability. In addition, many of the difficulties of interpretation arise from inadequate observational data with regard to meteorological measurements in conjunction with a poor understanding of the interaction between cloud and precipitation processes and the atmospheric aerosol.

These studies also indicate the difficulties encountered when siting sampling stations. The purpose of an individual study must be made clear to ensure adequate sampling. For the investigation of storm variability, identification of individual sources, and attempting to clarify mechanisms, a network *at least* as dense as the one used in METROMEX (1/22 km^2) is necessary.

The deposition of the H^+ is, of course, directly related to both the acidity and the quantity of precipitation. For climatological studies of long term trends of pH, a term, dH, is defined which is analogous to the pH, but also incorporates the precipitation. Since the impact of pH on much of the environment is related to both the acidity and the amount of rainfall, it is recommended that studies of dH be undertaken which will automatically include the climatic change of precipitation.

The METROMEX research has established the existence of an anomaly of 20% to 30% increase of precipitation downwind of the St. Louis area within 20 to 60 km. The increase of precipitation occurs in a locale favorable for the ingestion of the urban aerosol and, consequently, the quality of the water is subject to alteration. The impacts of such alterations in rainwater quality on the agricultural production, soil chemistry, and many other facets of economy in such a localized region have not been fully assessed. With the likely increase in fossil fuel usage in the coming years, it is time to seriously address these problems.

Finally, the frequency distribution presented indicate a distinct bimodality and together with the variations in the summer mean pH serve to further emphasize the caution which should be exercised in establishing and operating monitoring stations. Benchmark stations should be inaugurated in remote areas with several sites in and surrounding urban areas. While it would be economically beneficial to collect samples on a random, synoptic basis, the frequency data suggest that a biased selection of storm data might be acquired in a short duration project. The proposed network of stations should be operated continuously for many years to fully understand the incremental change in rainwater quality attributable to the increased rate of fossil fuel consumption in the United States.

ACKNOWLEDGEMENTS

The author is deeply grateful to A. Rattonetti and M. Peden for their extreme diligence in sample handling and analysis. The discussions with M. Peden and D. Gatz on portions of the paper were very helpful. This research was sponsored by the U.S. Energy Research and Development Administration under contract AT(11-1)-1199.

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THE HISTORY AND CHARACTER OF ACID PRECIPTATION IN EASTERN NORTH AMERICA[1]

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ABSTRACT

The history and present distribution of precipitation acidity in eastern North America is reviewed. Precipitation chemistry from the 1920's indicates heavy ionic deposition, but low acidity (calculated) in Tennessee (pH 7.4) and New York (pH 6.15). However, high acidity was apparently widespread over northeast North America by 1955-56 and measured pH's below 4.5 were observed earlier. The geographic distribution of acid precipitation has spread through the present. Yearly average pH values for 1972-73 are not significantly different in New York and New Hampshire, indicating a regional consistency in acid (pH 4.10) deposition. Summer acidity is currently lower in Tennessee than in the Northeast. Precipitation chemistry of individual storms reveals some local variation even within a 3 km range, but a storm in central New York is generally homogenous over 70 km.

INTRODUCTION

While the history of precipitation acidity in Europe is well documented (Oden 1968), little is known about its geographic spread or time trends in North America. Only two synoptic surveys of precipitation chemistry have been carried out (Junge 1958, Junge and Werby 1958, Lodge et al. 1968) and annual surveys are available for only a few locations (Herman and Gorham 1957, Gambell and Fisher 1966, Pearson and Fisher 1971, Likens 1972, Likens and Bormann 1974). Significantly, all recent surveys show a wide area of low pH over the northeastern United

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[1]This study was supported with funds from the Office of Water Resources Research, the National Science Foundation, and the E.I. DuPont de Nemours and Co.

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States. This paper summarizes the history and describes the geographic distribution of the acidity of precipitation in North America. This information can be used to assess historical acidity values, dates of changes, and the approximate magnitude of recent perturbations. Such information is essential for gauging possible effects of this phenomenon.

Early reports on precipitation chemistry frequently lack data on pH. Where missing, other chemical determinations were used to predict pH using the method of Cogbill and Likens (1974). Briefly, a stoichiometric relationship is derived using the chemical components found in precipitation, and an exact ionic balance predicts the acidity. This approach allows the history of precipitation acidity to be expanded and is combined with actual measurements of alkalinity and pH. Additionally, detailed sampling within the eastern United States is used to elucidate the spacial variability of present-day acidity and to establish statistical procedures for analysis of acid precipitation data.

HISTORY OF ACIDITY

The earliest data for which pH determination is possible are from Tennessee (MacIntire and Young 1923). All parameters needed for pH prediction, except Na^+, were measured periodically from 1917 to 1922. Employing either the MacIntire and Young's (1923) subtraction-derived Na^+ concentration or the sea-salt (Cl^-) equivalent Na^+ concentration produces a predicted pH of approximately 7.3. Endpoint titrations performed on these Knoxville, Tennessee, samples yield an estimated pH of 7.0 using Granat's (1972) theoretical alkalinity curve or 7.5 using his empirical alkalinity curve. Other titrations from stations across Tennessee during this same period show alkalinity-predicted pH determinations from 6.7 to 7.9.

Numerous other precipitation acidity values have been reported. In Blacksburg, Virginia, from 1923 to 1928 all rain samples tested showed a distinct "alkaline reaction" (Ellett and Hill 1929). Collison and Mensching (1932) determined HCO_3 concentrations of samples from Geneva, New York between 1919 and 1928. Using the carbonic acid-bicarbonate equilibrium equation, the average calculated pH is 6.15 with annual averages ranging from 5.46 to 6.36. Also, all the chemical data from the 1920's indicate heavy deposition of SO_4^{--} and particulates, but that the pH was at or above the expected normal value of 5.6 (the CO_2 equilibrium point).

Houghton (1955) found that cloud water pH at the top of Mt. Washington averaged 4.5 between 1937 and 1940. This survey also recorded the earliest known precipitation pH, a 5.9 reading in one rainstorm in Brooklin, Maine, on 22 August 1939 (H.G. Houghton, personal communication to G.E. Likens). Values of individual raindrop pH show that a 4.2 pH occurred in Washington, D. C. in 1949 and raindrop pH from

1952-53 outside Boston, Massachusetts, averaged 4 (Landsberg 1954).

Cogbill and Likens (1974) used the 1954-55 precipitation chemistry data from Junge's synoptic network to produce a map of predicted pH (Figure 1). This map shows a regional pattern of pH below 5.6 in

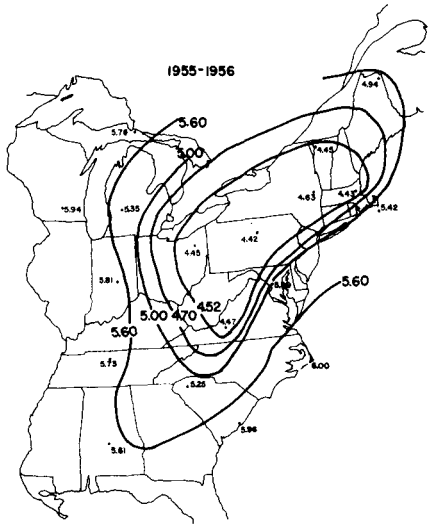

Figure 1. Distribution of predicted pH in 1955-56 (based on Junge 1958 and Junge and Werby 1958). Lines are placed at intervals of 10 μeq/l H^+, thus 5.6 is approximately neutral (=0 μeq/l), while each line lower indicates an increase of 10 μeq/l acidity.

eastern North America with the highest acidity (pH less than 4.52) centered over the New England and Middle Atlantic states. A second synoptic survey (Lodge et al. 1968, Pearson and Fisher 1971) formed the basis for predicting pH in 1965-66 (Cogbill and Likens 1974, see Figure 2). Also included on this map are acutal pH measurements from 1962-63 from the Southeast (Gambell and Fisher 1966). The same distribution of acidity seen 10 years earlier is found in 1965-66, but the acidity has spread south and west. The present pattern of pH acidity is obtained using measured pH values in eastern North America in 1972-73 (Kramer 1973, J. Miller personal communication, Cogbill and Likens 1974, see Figure 3). The region of high acidity (pH less than 5.6) has continued to spread and now covers all eastern North America

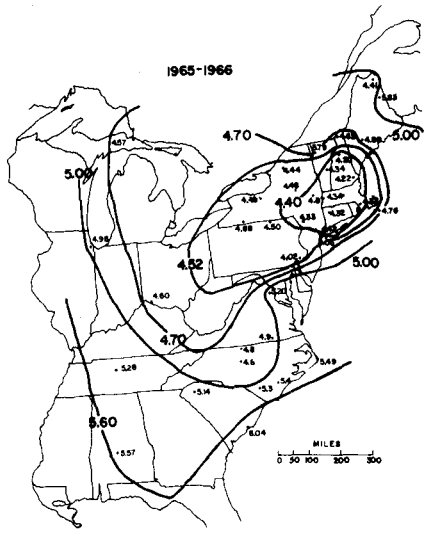

Figure 2. Distribution of predicted pH nominally for 1965-66 (based on Lodge et al. 1968, Gambell and Fisher 1966, and Pearson and Fisher 1971).

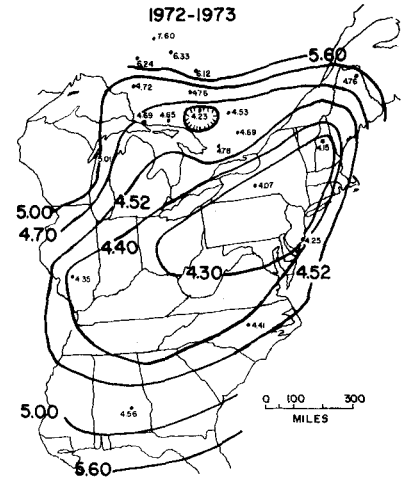

Figure 3. Distribution of observed pH during 1972-73 (based on Kramer 1973, J. Miller, personal communication (NOAA/EPA), and Cogbill and Likens 1974).

except the tip of Florida and northern Canada. Certain locations in the middle of the acid precipitation region display pH readings as low as 4.0.

Historically, highly acid precipitation has been prevalent over eastern North America since at least 1955. Low pH readings occurred in 1949 and probably earlier in some locations. While a source for acidity was present in the form of H_2SO_4 by 1939, indications are that there was no regional acid precipitation in 1928.

TIME TRENDS IN ACIDITY

The change of acidity is best illustrated by comparing predicted pH in 1955-56 to that measured 10 years later at the same locations. Nine stations at the periphery of the acid center occur in both surveys and permit an estimate of the spread of the acidity. Average increase in acidity at these sites was 12 μeq/l (about one isoline) over the 10 year period. This is about the accuracy of the prediction process. Two stations were included in all three synoptic surveys and they are located at the northern limit of the acid pattern. Caribou, Maine, had

an annual average pH of 4.94, 4.63, and 4.76 in 1955-56, 1965-66, and 1972-73 respectively. Concurrently, Sault Ste. Marie, Michigan, exhibited a change in pH from 5.76 to 4.76 to 4.69.

Two continuous series of precipitation chemistry data have been taken from 1966 to the present. The first is from the network of nine stations serviced by the United States Geologic Survey (USGS 1965-72) and the second is from Hubbard Brook, New Hampshire. Measured pH, averaged over the seven inland sites has remained between 4.30 and 4.66 in New York. In New Hampshire samples show a lower, but generally consistent pH between 4.04 and 4.19 (Likens and Bormann 1974). All these studies taken together indicate a definite spread of acidity over the past twenty years and a moderate, but irregular, decrease in pH in northeast North America.

GEOGRAPHIC VARIABILITY

I investigated the variability of precipitation acidity at locations within the extensive and consistent center of acid deposition. In 1972-73 56 individual storms were sampled at Ithaca, Aurora, and Geneva, New York (see Likens 1972, Cogbill and Likens 1974). Data for the same period from two locations in the Hubbard Brook Experimental Forest, New Hampshire was also collected (G.E. Likens, personal communication). In addition, weekly summer samples were taken at four locations in New Hampshire, including an altitudinal series up Mt. Moosilauke (from 215 m to 1370 m), and three locations in Great Smoky Mountains National Park, Tennessee (from Gatlinburg at 440 m to Newfound Gap at 1520 m). The pH of all samples was promptly measured with an Orion 401 pH meter standardized to 4.01 and 7.00. The Tennessee samples were from an area recently affected by acid precipitation and form a comparison for the Northeast samples.

All data were averaged using H^+ concentrations and compositing was accomplished by weighted averaging by precipitation amount. However, frequency distributions of the precipitation H^+ concentration in 82 storms throughout the year in New York and 40 weekly samples from New Hampshire show a log-normal distribution (X^2=8.99, d.f.=9, $p > .25$ and X^2 =5.24, d.f.=6, $p > .5$ respectively); that is, the pH is normally distributed. For this reason, all statistical tests are based on logarithmic transformations of the H^+ concentration, or equivalently the arithmetic mean and standard deviation of the pH values.

Local variation of pH over some 70 km was tested using the average seasonal pH values at the three central New York sites. A two-way factorial analysis of variance (ANOVA) (seasons by sites) demonstrates a significant difference ($p < .01$) between seasons, but no significant difference between sites. Winter had the highest pH (average 4.24)

while summer had the lowest (average 3.92). The pH at the three sites varied from 4.07 to 4.10. The logarithmic standard deviation per determination (s) was 0.06 pH units indicating that the overall variance over 70 km is very small. A two-way ANOVA (sites by storms) on 16 matched storms throughout the year at all three New York sites also failed to indicate significant differences as storms pass from one site to another, but a statistically significant difference ($p < .005$) between storms was found. The standard deviation per determination (s) is 0.16 pH units indicating that storms tend to add variation, but averaging over a year at a site reduces this variation (see s=0.06 above). In New Hampshire six summer storms were sampled at four sites less than 3 km apart. The two-way ANOVA (sites by storms) indicate a significant difference between both sites ($p < 005$) and storms ($p < .005$). Thus, under certain circumstances even over a short distance, there is considerable variability to precipitation pH in the same storm (in this case 3.83 to 4.02 site average). The standard deviation per determination (s=0.12) shows less variation than was seen between storms in central New York, but more variation over 3 km due to local sources than over 70 km in New York. Finally, ANOVA tests between sites spaced more than 1 km apart up mountainsides in New Hampshire (6 sites by 3 storms) and Tennessee (3 site one-way) show no significant differences between pH at sites on the same altitudinal series.

Differences between pH values at sites over 500 km apart indicate the magnitude of regional changes in precipitation acidity. A year of pH determinations at 5 sites, three in central New York and two at Hubbard Brook, New Hampshire were tested by one-way ANOVA. No significant difference between sites was found although the New Hampshire data show higher values (average pH 4.15 to 4.18) than New York values (4.04 to 4.11). However, the variation between the New York sites and the overall standard deviation per determination (s=0.27) show the tendency of local variation and small regional changes to obscure any differences over large distances. A one-way ANOVA using summer pH determinations in Tennessee, New York and New Hampshire yields a statistically significant difference between Gatlinburg (average pH= 4.18), Ithaca (average pH= 3.91), and Hubbard Brook (average pH= 3.96). By least significant differences, it is observed that the Tennessee pH is significantly higher in accord with its peripheral location, and the Northeast data is statistically indistinguishable. Significantly, the components of acidity (derived from the predictive pH relationship; Cogbill and Likens 1974) are about 62% H_2SO_4, 32% HNO_3, and 6% HCl at all three locations in the eastern United States. This indicates a quantitative difference over a distance of 1500 km, but little qualitative difference in precipitation chemistry across the regional pattern.

CONCLUSIONS

In summary, there is a regional pattern of acid precipitation covering almost all of eastern North America. This distribution is spreading to the south and west with some intensification at its center in the northeast United States. This concentric pattern existed in 1955-56, originating sometime after the 1920's. Highly acid precipitation (pH less than 4.52) was observed in 1949 and there is an indication that a source existed in 1939. Generally two historic types of precipitation chemistry in eastern North America emerge: sometime before 1950 precipitation was burdened with a heavy ionic load, but low acidity; since at least 1950 precipitation has had a lower ionic, but greater acidity load than before.

Individual storms and seasons differ significantly in acidity among themselves and sites even within 3 km show considerable local variation. However, acidity at sites over 500 km apart shows a regional (and annual) consistency in H^+ concentration. Peripheral areas indicate the spreading of acidity, but maintain higher pH values than central locations. The present distribution of acid precipitation (pH less than 5.6) seems well established. The bounded zone now covers a wide area, but it cannot yet be predicted how widespread and intense acid precipitation will become.

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EVIDENCE FOR MULTIPLE HYDROGEN-ION DONOR SYSTEMS IN RAIN[1]

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ABSTRACT

An integrated analytical system consisting of combined scanning electron microscopy and x-ray analysis, atomic absorption, colorimetry and coulometry was used to study rain water chemistry. The coulometry facilitated the determination in molarities of strong and non-volatile and volatile weak acids. The pH of individual rains in St. Paul - Minneapolis, Minnesota ranged from 4.0 to 5.65 during the summer of 1974. Samples of a given rain from different sites had different qualitative and quantitative bases for the measured pH. Increase in strong acid concentrations with a decrease in pH was not an exclusive phenomenon. Molarities of weak acids (volatile and/or non-volatile) also increased with an increase in the acidity. Studies conducted on Twin Cities rain samples indicated that the total salt content expressed from the electrical conductivity could not be accounted for by the total concentrations of individual metals quantified (Fe, Pb, Zn, Mn, Cu, Cr, Cd, Ca, Mg, Na, and K). In addition, no correlation could be shown between the contents of $SO_4^{=}$, NO_3^{-}, Cl_2^{-} & PO_4^{-} and the observed changes in pH.

INTRODUCTION

Fall out of acidic rain may be a threat to the regional environment. Rainfall with a pH as low as 2.8 and 2.1 has been reported from Sweden (Odén, 1968) and the United States (Likens and Bormann, 1974) respectively.

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[1]This investigation was supported by grants, in part from the National Park Service, U.S. Department of Interior and in part from the Northern States Power Company, Minneapolis, Minnesota. Paper No. 1570 of the University of Minnesota Agricultural Experiment Station.

Barrett and Brodin (1955) stated that since SO_2 is a major constituent of atmospheric pollution, H_2SO_4 is the most likely cause for the acidity of rain water. Since then, almost all of the published reports are based on correlations between total sulfate and pH (Pearson and Fisher, 1971). Measurements of total sulfates do not differentiate the levels and extent to which sulfate is present in the particulate fraction, soluble fraction, as salts and as acid *per se*. Similar considerations are also important in the case of nitrate (Pearson and Fisher, 1971) and chloride (ref. Junge, 1963) and their status as HNO_3 and HCl respectively. Furthermore, pH measurements do not indicate the parent species for the hydrogen ions. In general, our current knowledge of the chemistry of rain water is inadequate.

In this paper we report the results of some of our efforts to understand the chemistry of rain water in the St. Paul - Minneapolis, Minnesota area and the origin of its acidity, as a prelude to the study and interpretation of acidic rain effects on Minnesota vegetation.

MATERIALS AND METHODS

Approximately 250 ml of rain water were sampled from individual rainfalls at several locations in the St. Paul-Minneapolis area in the U.S.A. Sampling was performed manually at approximately 5-6 ft. from the ground, away from trees, buildings, etc. Sampling was started from the time the first rain droplets fell on the ground and was terminated after approximately 30 minutes. Samples were collected in FEP-TEP teflon (DuPont Co. U.S.A.) trays and were immediately transferred to screw cap bottles made of TEP teflon. Precaution was taken to prevent any dead space between the sample and the cap of the bottle. Samples were frozen as quickly as possible in a conventional freezer. At the time of analysis, samples were allowed to thaw and equilibrate to the room temperature (20 C) without opening the bottle.

The analytical techniques used, along with their application, are summarized in Table I. For determining the morphology and gross composition of the inorganic particulate matter in each sample, 10 ml of the rain water were filtered through 0.22μ Millipore (Millipore Corp. U.S.A.) or Nuclepore (Sargent Welch & Co., U.S.A.) filter. After drying the filter in a vacuum, discs were punched at random, mounted on scanning electron microscope (SEM) stubs, carbon coated and viewed under a Cambridge SEM at different magnifications. Whenever the gross inorganic composition was to be determined, the particle was bombarded for approximately 2 min with an energy beam from the internal electron source and the qualitative, relative composition was identified by a precalibrated x-ray analyzer.

TABLE 1

Some Techniques and Their Application in

Rainwater Analysis

Technique	Description of its use
Coulometry	Quantification in molarities (M) of: 1) non-volatile strong acid, 2) non-volatile weak acid, and 3) volatile weak acid.
Scanning E.M. + x-ray analysis	Morphology and gross qualitative inorganic composition of particulate matter.
Atomic Absorption	Quantification of metallic components Eg: Ca, Mg, Na, K, Fe, Zn, Cu, Mn, Pb, Cd etc.
Colorimetry + Specific ion electrode	Quantification of SO_4, Cl, NO_3, NO_2, NH_4, PO_4, F, etc.

Concentrations in molarities of different acids in the rain samples were determined by coulometry. The coulometric unit consists of a constant current source, a measuring cell located on a magnetic stirrer and a potentiometer (modified pH meter) with a four digit visual read out. Based on the relationship between Ψ (a function of the electromotive force) and time in seconds (t) in two portions of the same rain sample, with and without volatiles, the molarities of non-volatile strong, and non-volatile and volatile weak acids were calculated (Krupa et al. 1974). When a sample was to be freed of volatiles, the solution was bubbled vigorously with N_2 for 30 minutes with simultaneous stirring and kept under a blanket of N_2 throughout the analysis.

Quantification of the cations and NH_4^+ & anions were performed according to the conventional procedures using a Perkin-Elmer (U.S.A.) Model 330 atomic absorption unit and Technicon (U.S.A.) model II Autoanalyzer respectively.

RESULTS AND DISCUSSION

The pH of individual rains varied from 4.00 to 5.65 during the summer of 1974. Inorganic and organic particulate matter ranged in the samples at approximate ratios of 8 : 2 to 5 : 5. In the analysis of

randomly selected inorganic particles from various samples, the following elements were found, based on the order of frequency of their occurrence:

Al, Si > Fe > K > Ca > Ti > S > P > F > Cl

Gross morphology and elemental composition of some representative inorganic particles are shown in Figure 1. Based on frequency of

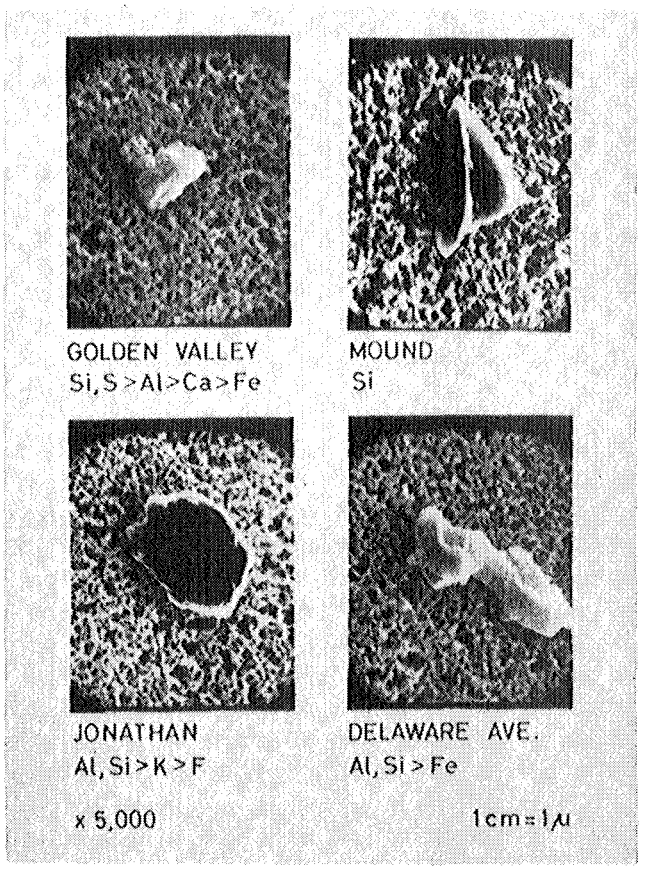

Figure 1. Scanning electron micrographs of inorganic particulate matter collected at different sampling sites during an individual rain event. Golden Valley, Mound, etc. are locations of sampling.

occurrence X relative amount (comparative peak height), elemental composition of these particles in the rain samples was as follows:

Si > Al > Fe > K > S,Ca > Ti > P > Cl,F

Coulometric data on samples collected at five different sites during a representative rain event are shown in Figure 2. Strong acid(s)

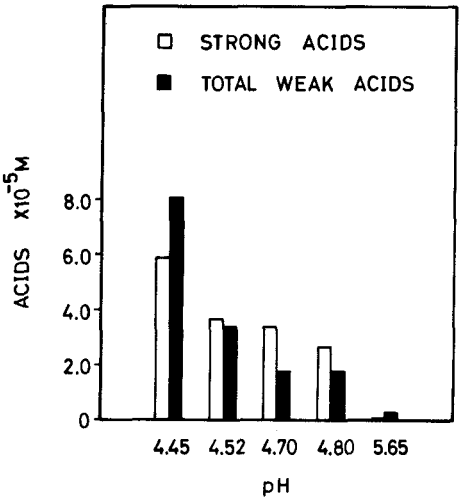

Figure 2. Relationships between pH and strong and weak acids in rain. Acid concentrations expressed as molarities.

concentration in the rain samples ranged from 0.0 to 5.89 × 10^{-5}M. There was an increase in the concentration of the strong acid component with a decrease in pH. However, this was not an exclusive phenomenon. Molarities of weak acids (volatile and/or non-volatile) also increased (0.22 to 8.01 × 10^{-5}M) with an increase in the acidity.

The strong acid component may consist of different combinations of H_2SO_4, HNO_3, HCl and possibly dithionate. Figures 3, 4, and 5 illustrate the relationships between pH and SO_4-S, NO_3 and Cl when they exist as their corresponding acids and when each acts as the sole hydrogen ion donor. These values are based on known dissociation rates in aqueous systems. Barium chloride precipitable sulfur content (expressed as sulfate units) ranged in the rain samples from 1.2 mg/l to 2.4 mg/l. There was no correlation between the changes in the strong acid concentration and $SO_4^=$ levels (Figure 6). Patterns of change in NO_3^- concentration paralleled the $SO_4^=$ change in relation to pH. One of the most effective methods of SO_2 oxidation and neutralization is considered to be the "SO_2-NH_3-H_2O" system (Scott and Hobbs, 1967; ref. Krupa and Wood, 1974). NH_4-N content in our samples ranged from 0.7 mg/l to 0.82 mg/l. No definite correlations could be found when ratios between ($SO_4^=$ + NO_3^- + Cl^-) and NH_4^+ or ratios between $SO_4^=$ and NH_4^+ were plotted against pH (Figure 7). pH of rain samples varied irrespective of the calculated levels of NH_3 neutralization. Inorganic acid forming groups other than $SO_4^=$ varied in their concentration as

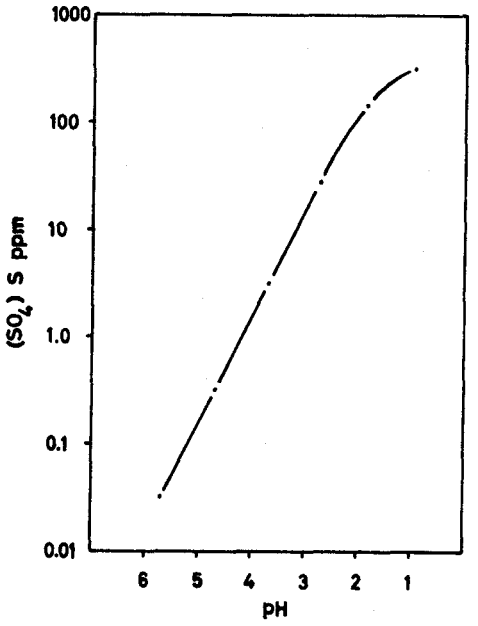

Figure 3. Relationship between pH and SO_4-S based on the values for the two step dissociation of H_2SO_4. SO_4-S should be multiplied by 3 to obtain SO_4 values.

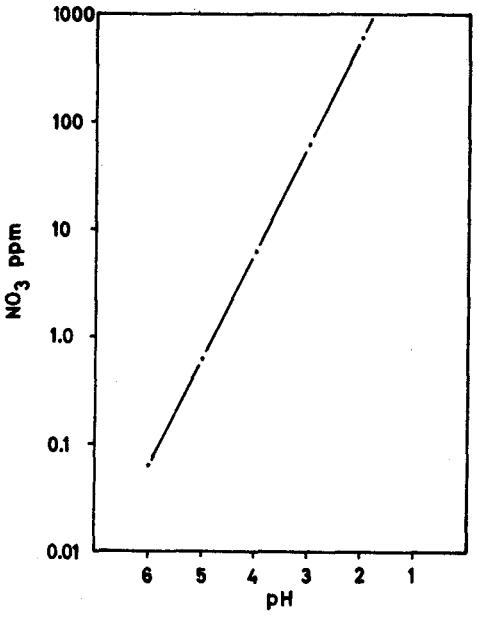

Figure 4. Relationship between pH and NO_3 based on the single step dissociation of HNO_3.

follows: NO_3-N - 0.063 mg/l to 0.450 mg/l; Cl - 0.10 mg/l to 0.60 mg/l; and PO_4-P - 0.002 mg/l to 0.009 mg/l.

Approximate total salt concentration expressed from electrical conductivity measurements (3.47 mg/l to 11.10 mg/l) could not be accounted by the total concentration of the individual cations quantified by atomic absorption (Table 2).

As mentioned previously the weak acid component also increased with a decrease in pH. Figure 8 illustrates the relationship between non-volatile and volatile weak acids and pH of our rain samples. It is not clear at this time as to what extent the volatile acid component is constituted by CO_2-H_2O-H_2CO_3-HCO_3 system. The CO_2-H_2O system can be influenced by the SO_2 dissolved species, HSO_3^-.

The aforementioned results demonstrate a multiple hydrogen-ion donor system in rain. These includes: 1) a strong acid component (H_2SO_4, HNO_3, HCl, and possibly dithionate); 2, a non-volatile weak acid component (HF, organic acids, hydrolysable salts etc.); and 3) a

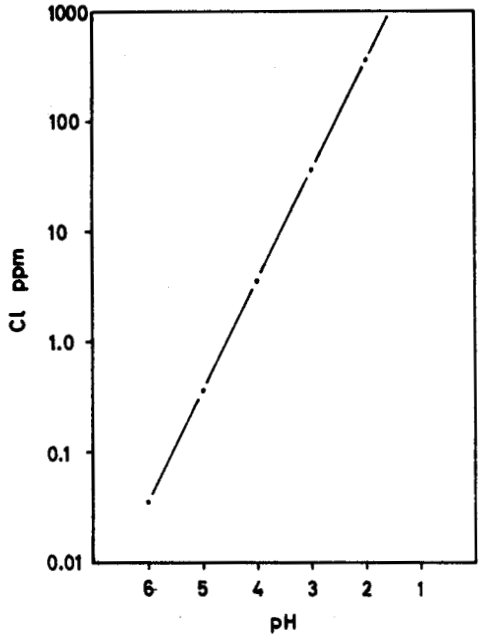

Figure 5. Relationship between pH and Cl based on the single step dissociation of HCl.

volatile weak acid component (CO_2-H_2O system and unknowns). Sulfur in the atmosphere may exist in several different forms: SO_2, SO_3, SO_4,

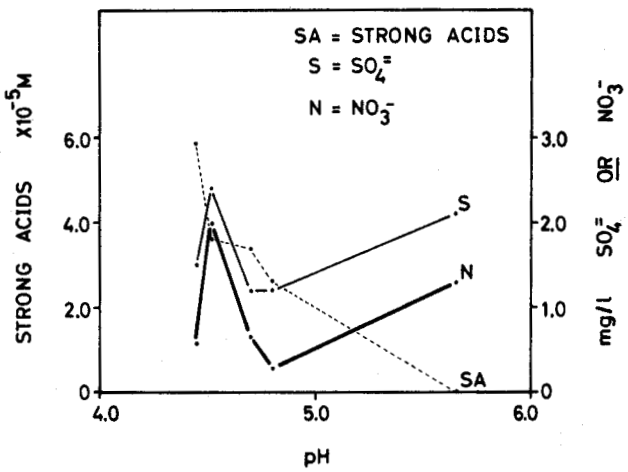

Figure 6. Relationship between pH and 1) molarities of strong acids, 2) $SO_4^{=}$ concentrations, and 3) NO_3^{-} concentrations in rain samples.

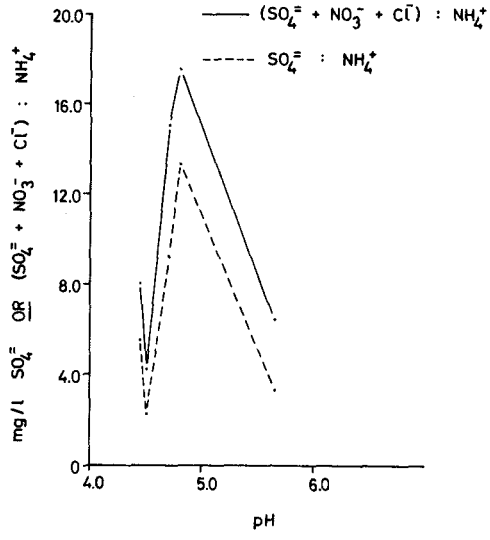

Figure 7. Relationship between pH and ratios of ($SO_4^=$ + NO_3^- + Cl^-) and NH_4^+ or ratios of $SO_4^=$ and NH_4^+. Ratios calculated on the basis of mg/l of different components in rain.

TABLE 2

Metallic components in the same rain collected at different locations in the Twin Cities area

Date of collection: June 6, 1974

Sampling Locaion	Concentration in ppm										
	Cu	Fe	MN	Zn	Cd	Cr	Pb	Mg	Ca	Na	K
Golden Valley	<0.01	<0.1	<0.01	0.02	<0.02	<0.02	<0.2	0.016	0.055	0.03	0.03
Mound	<0.01	<0.1	<0.01	<0.02	<0.02	<0.02	<0.2	0.053	0.529	0.04	0.11
Delaware Ave.	<0.01	<0.1	<0.01	0.02	<0.02	<0.02	<0.2	0.011	0.115	0.10	0.06
N.E. University Ave.	<0.01	<0.1	<0.01	<0.02	<0.02	<0.02	<0.2	0.012	0.020	0.05	0.07
Jonathan	<0.01	<0.1	<0.01	<0.02	<0.02	<0.02	<0.2	0.203	1.23	0.38	0.23

S_2O_5, S_2O_6, H_2S, dithionates, mercaptans, thionyls, $(NH_4)_2\ SO_4$, metallic salts, H_2SO_4 etc. Components such as organic acids form weak acids and may be part of the non-volatile weak acid component. Our results also show that samples of a given rain from different sites have different qualitative and quantitative bases for the measured pH. Semonin (1973) was unable to find correlations between point sources and pH of rain in the St. Louis, Missouri area and found that pH varied widely during the same rain at different sampling sites.

These considerations are important with reference to any direct vegetational effects. Shriner (1974) was able to demonstrate adverse effects on terrestrial vegetation by subjecting plants to pH 3.2 H_2SO_4 simulated to fall as rain. While acidity can have influence on plants through nutrient leaching etc., more recent evidence by Wood and

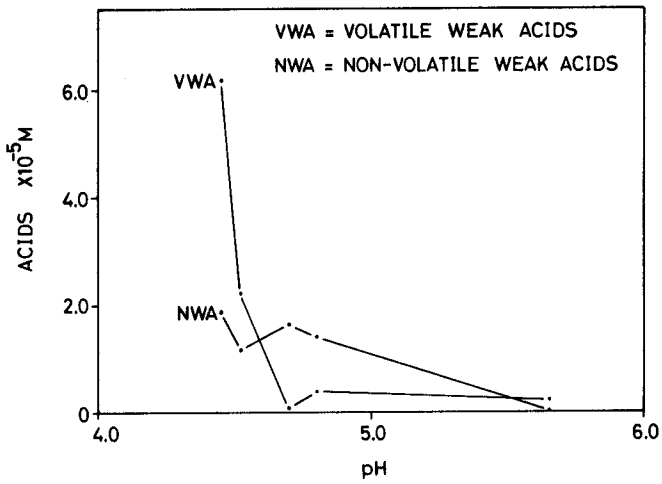

Figure 8. Relationship between pH and molarities of non-volatile and volatile weak acids in rain.

Pennypacker (1975) indicates that anions may play an important role in direct effects on foliage. The chemistry of rain in a given geographic region should be evaluated on per rain basis as a prelude to vegetational studies.

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THE WEAK ACID NATURE OF PRECIPITATION

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ABSTRACT

Recent measurements of the pH of precipitation leave no doubt that rainfall is acidic. Evidence will be presented that precipitation is a weak acid system. The results of this research indicate the need to establish standard sampling procedures to provide uniform sampling of precipitation

Samples were collected from twenty-six separate precipitation events and analyzed for free hydrogen ion concentration and total hydrogen concentration. The free hydrogen ion concentration ranged from 7.5×10^{-5} to 1.7×10^{-6} while the total hydrogen ion concentration ranged from 4.4×10^{-4} to 7.27×10^{-5}. These results cast doubt on the two basic assumptions concerning acid rain which are that the pH of "geologically pure" rain should have a pH of around 5.7 and that any decrease from that value is due to strong acids such as sulfuric acid.

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HYDROGEN ION SPECIATION IN THE ACID PRECIPITATION OF THE NORTHEASTERN UNITED STATES[1]

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ABSTRACT

The acidity of precipitation in rural, forested areas of the northeastern United States is dominated by the strong mineral acids, sulfuric and nitric. Weak acids have a negligible effect on the measured acidity (pH) of precipitation. These conclusions are based on total acidity titrations and detailed analysis of organic and inorganic components in precipitation.

INTRODUCTION

Precipitation in the northeastern U.S. has a mean pH of about 4 (Likens and Bormann 1974, Cogbill and Likens 1974). This phenomenon of high acidity is not unique to the U.S.; large areas of Scandinavia downwind of dense industrial complexes receive precipitation with a pH of 4 or lower (Odén 1968, Granat 1972). Atmospheric CO_2 in equilibrium with precipitation would not be expected to produce a pH < 5.6 (Barrett and Brodin 1955). Thus it has been hypothesized that SO_2 and NO_x from the combustion of fossil fuels are precursors to strong acids in precipitation (Likens and Bormann 1974, Cogbill and Likens 1974, Odén 1968, Granat 1972). This investigation, using detailed chemical analysis, describes the relative contribution of strong, weak and Brønsted acids to the acidity of precipitation.

Acids are ions or molecules that can donate protons to a water system. The strength of their donating power determines the strength of the acid. A strong acid, such as HNO_3, donates all of its protons to

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[1]A contribution to the Hubbard Brook Ecosystem Study. Financial support was provided by the National Oceanic and Atmospheric Administration and by the National Science Foundation. The Hubbard Brook Experimental Forest is operated by the U.S.D.A., Forest Service, Upper Darby, Pennsylvania.

solution. Therefore, when HNO_3 is added to water, it completely dissociates and there are only H^+ and NO_3^- ions present. The dissociation constant (K_a) of strong acids is much greater than one.

$$HNO_3 \rightleftharpoons H^+ + NO_3^- \qquad K_a = \frac{[H^+][NO_3^-]}{[HNO_3]} >> 1$$

At a pH value less than 5, many weak acids, such as H_2CO_3, do not donate all of their protons to a water system. Instead of dissociating completely, as strong acids do, weak acids may only partially dissociate. Thus, in addition to dissociation products, weak acids also may have appreciable quantities of the undissociated acid in solution. As an example, the reactions for carbonic acid are as follows.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 10^{-6.4}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^= \qquad K_2 = \frac{[H^+][CO_3^=]}{[HCO_3^-]} = 10^{-10.3}$$

Note that the equilibrium constants are < 1, indicating that a large proportion of undissociated acid is present in solution.

A listing of some strong and weak acids that could be present in precipitation is presented in Table 1.

Table 1. Possible Acids in Precipitation.

Strong Acids		Weak Acids	
Acid	K_a	Acid	K_a
H_2SO_4	>1	HSO_4^-	$10^{-1.9}$
HNO_3	>1	H_3PO_4	$10^{-2.1}$
HCl	>1	RCOOH	10^{-3} to 10^{-6}
		HF	$10^{-3.2}$
		$Fe(H_2O)_6^{3+}$	$\sim 10^{-3}$
		$Al(H_2O)_6^{3+}$	$\sim 10^{-5}$
		phenols	10^{-4} to 10^{-9}
		NH_4^+	$10^{-9.3}$

In any water sample there are two types of acidity that can be measured, free and total. Free acidity (H_F) is a measure of the concentration of protons in solution, regardless of source. They could have originated from the dissociation of a strong or weak acid. Free acidity is determined by an electrode; the negative log of the proton concentration is termed pH. Total acidity is a measure of the total concentration of protons, both those in solution and those still undissociated. Total acidity (H_T) is determined by titration, which is the quantitative addition of a strong base to a water system. The strong base is neutralized in direct proportion to the total amount of free and undissociated protons in the system. In a solution that has only strong acids in it, $H_F = H_T$. But in a system with strong and weak acids or just weak acids, $H_F < H_T$. A concept crucial to the understanding of the sources of free acidity in precipitation is that if $H_F < H_T$, it does not mean that the pH of precipitation is dominated by weak acids (Likens et al. 1976). The dissociation of weak acids is pH dependent, i.e. at lower pH's less of the weak acid dissociates (donates protons to a solution). As will be illustrated in this report, acid precipitation (pH < 5.6) is a mixture of strong and weak acids, but 1) because all the weak acids are in low concentration, 2) because all their dissociation constants are much less than unity (very weak acids) and 3) because most are only slightly dissociated at pH < 5.6, they contribute primarily to the total acidity and negligibly to the free acidity.

ANALYTICAL METHODS

The analyses for Ca^{++}, Mg^{++}, K^{+} and Na^{+} were performed on a Perkin-Elmer Model 403 atomic absorption spectrophotometer. Appropriate amounts of lanthanum and HCl were added to subsamples to avoid interferences with the Ca^{++} and Mg^{++} determinations. Standard procedures adapted and automated for use with a Technicon Autoanalyzer were used for analysis of NH_4^+, NO_3^-, $SO_4^{=}$, $PO_4^{\equiv}$, Cl^- and dissolved silica. Ammonium was determined by an alkaline phenolhypochlorite method (Solorzano 1969), nitrate by hydrazine reduction (Kamphake et al. 1967), sulfate by colormetric measurement of a barium-thymol blue complex (Lazrus et al. 1968), chloride by the liberation of thiocyonate ion from mercuric thiocyonate in the presence of ferric iron (O'Brien 1962) and dissolved silica by reduction of silicomolybdate to heteropoly blue with aminonaphtholsulfonic acid (Amer. Public Health Assoc. 1965). Phosphate was determined from a molybdenum blue complex after reduction with ascorbic acid in the presence of a small amount of antimony (Murphy and Riley 1962). Iron, aluminum and manganese were determined with a Perkin-Elmer 403 atomic absorption spectrophotometer, equipped with a HGA 2100 graphite furnace.

A modified method of Bulen et al. (1952) was used to assay organic acids in precipitation. The samples were heat concentrated to 1.0 ml, fixed onto 2 g of silicic acid, added to a column of 5.0 g silicic acid

and then eluted (in 5.0 ml fractions) according to the following chloroform-butanol schedule:

50 ml: 100% $CHCl_3$
75 ml: 98% $CHCl_3$
50 ml: 95% $CHCl_3$
75 ml: 85% $CHCl_3$
80 ml: 65% $CHCl_3$
60 ml: 55% $CHCl_3$

A standard chromatogram was generated with successive runs of known amounts of acids; the recoveries were quantitative, and the peak fractions between different runs varied by no more than ± 1 fraction. One liter double-distilled water blanks were run identically to determine any laboratory background; no acids were found. Some of the acids that may be determined by this procedure are given in Table 2.

Table 2. Organic Acid Standards.

Monoprotic	Diprotic	Triprotic
butyric	oxalic	aconitic
propionic	malonic	citric
acetic	succinic	iso-citric
formic	glutaric	trimesic
glycolic	adipic	
lactic	sebacic	
glyceric	malic	
crotonic	tartaric	
trichloroacetic	citraconic	
chloroacetic	fumaric	
cyanoacetic	maleic	
p,m-hydroxy benzoic	itaconic	
benzoic	phthalic	
salicylic		
mandelic		
gallic		

COLLECTION PROCEDURES FOR PRECIPITATION

Precipitation samples were collected in acid-washed containers, plastic for inorganic analysis and glass for organic analysis. Both bulk precipitation (wet and dry) and wet only precipitation were collected to determine the effect of dry deposition on the free and total acidity of precipitation. Samples were stored at 4 C until analyzed, usually less than one week for the inorganic constituents. Organic acids were analyzed immediately after individual storms. As shown by Galloway and Likens (1976) there is no significant change in the inorganic composition of precipitation samples when stored at 4 C if the pH of the sample is about 4.

Determination of free acidity (ambient pH) and total acidity (titrations to pH 9.0) were performed on a Sargent Welch PBL pH meter, equipped with a combination electrode. The measurement of pH with this system is accurate to ±0.03 pH units, which introduces a 6-7% error in the determination of hydrogen ion concentration. Therefore, at pH 4.00 the hydrogen ion concentration would be 100 ± 7 μeq/ℓ.

A three-port round bottom flask was used for the titrations. One port held the pH electrode, one held an aerator through which nitrogen flowed and the other was left open to add the titrant (NaOH). At all times a positive pressure of nitrogen in the flask excluded carbonic acid (H_2CO_3) from the sample. This was done because all the precipitation samples that we have collected in the northeastern United States have been below pH 5.0. Since H_2CO_3 does not contribute to the free acidity below pH 5, we excluded it so as not to mask other possible contributors. In addition, at pH's < 5.0, the dissolved H_2CO_3 concentration is only 20 μeq/ℓ, but at the higher pH values encountered during a titration the total concentration of H_2CO_3 increases by several orders of magnitude if the sample is in equilibrium with the atmosphere. These relationships are illustrated in Figure 1, which shows the result of a titration of two aliquots of the same sample. The first aliquot (solid dots) was titrated without removing H_2CO_3 from the system; the second aliquot (open circles) was titrated identically, but with all of the H_2CO_3 removed by bubbling nitrogen through the sample prior to and during the titration. Thus the influence of H_2CO_3 on the sample is removed, and the effect on the free acidity can be determined. The numerical values on Figure 1 give free acidity (H_F, measured acidity) and total acidity (H_T, titratable acidity) for the aliquots. The results of this experiment are summarized below:

1) Carbonic acid has no influence on the measured pH of this sample, and indeed has no effect on the measured pH of any aqueous sample below pH 5 that is in equilibrium with the atmosphere (Stumm and Morgan 1970).

2) The removal of H_2CO_3 from the system, while having no effect on the free acidity, has a potentially large effect on the total titratable acidity when titrated to pH's > 5.0. This effect is variable due to the

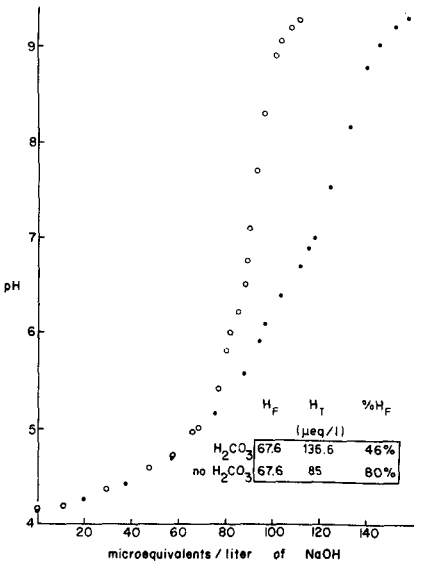

Figure 1. The effect of carbonic acid on the free, bound and total acidity of precipitation. The open circles represent an aliquot from a sample that has had the carbonic acid removed by N_2 purging. The solid dots represent an aliquot of the same sample with the carbonic acid present.

increasing solubility of CO_2 as the pH increases. In fact, if the solution were kept in equilibrium with the atmosphere throughout the course of the titration from pH 4 to 9, the total acidity due to carbonic acid would be about 5000 μeq/ℓ. Such titrations would reflect exchange rates of CO_2 between the atmosphere and the water sample as influenced by stirring, etc. and would be totally misleading with regard to the proton chemistry of the initial sample.

RESULTS AND DISCUSSION

Free acidity and total acidity were determined for precipitation samples from Ithaca, New York (a semi-urban community), Hubbard Brook Experimental Forest, New Hampshire (forested area in the White Mountains) and Paul Smith, New York, a forested area in the Adirondack Mountains (Schofield 1975). The samples were collected from February to

May, 1975. From the results presented in Table 2, the following points are evident:

1) While the range of free acidities is similar in the rural areas and the semi-urban area, the amount of weak acids is significantly higher in the urban samples. Low pH's in both urban and rural areas characterize the regional phenomenon of acid precipitation, but the urban areas have additional amounts of materials (Fe, Al, particulates, organics) in their atmospheres that contribute to the total acidity, but not significantly to the free acidity. This is substantiated when the total and free acidities of bulk precipitation versus wet precipitation are compared from the same precipitation event. Dry precipitation contributes substantially to the weak acid concentration and therefore to the total acidity in four sets of bulk samples from the Ithaca area (Table 2). Moreover, in two of the cases, the dry precipitation neutralizes the free acidity that is found in wet precipitation.

2) It appears that once the influence of the urban atmosphere is removed, the concentration of weak acids in precipitation decreases significantly as shown in the Hubbard Brook and the Adirondack Mountain samples where the free acidity can be approximately equal to the total acidity.

3) Even with the carbonic acid removed, the semi-urban Ithaca samples have appreciable amounts of weak acids. It is important to determine whether these weak acids are contributing to the pH, or if they are completely undissociated at the pH of ambient precipitation and thus influence only the total acidity and not the free acidity. For this reason, we have analyzed for a series of weak acids in our precipitation samples (Table 3).

CARBONIC ACID

As shown in Table 3, this weak acid contributes to the total acidity but it has no influence on the free acidity of precipitation if the pH is below 5, as is the case in most of the precipitation events in the northeastern United States, especially in rural areas.

PARTICULATES

The influence of particulates on the acidity of precipitation is variable due to the large number of minerals that could be present. The particles that would have the greatest effect would be the clays because of their large cation exchange capacity.

Table 3. Hydrogen Ion Distribution in Acid Precipitation from the Northeastern United States (μeq/ℓ).

Collection Date and Location		pH	H_F*	H_T†	$\frac{H_F \times 100}{H_T}$
Ithaca, New York					
27 Feb. - 21 March 1975	(wet)‖	4.10	79.4	102.8	77%
	(bulk)	4.11	78.0	115.0	68%
21 March - 8 April 1975	(wet)	4.18	66.0	88.0	75%
	(bulk)	4.18	66.0	119.0	55%
7 May - 19 May 1975	(wet)	3.82	151.4	228.1	66%
	(bulk)	4.05	89.1	178.2	50%
19 May - 2 June 1975	(wet)	3.88	155.0	187.0	83%
	(bulk)	4.11	77.6	136.0	57%
Hubbard Brook Experimental Forest, New Hampshire					
18 Feb. - 25 Feb. 1975	(bulk)	4.03	93.3	105.3	89%
11 March - 18 March 1975	(bulk)	4.11	77.6	87.4	89%
1 April - 8 April 1975	(bulk)	4.39	40.7	39.9	102%
Adirondack Mountains, Paul Smith, New York					
10 October 1974	(wet)	4.31	49.0	60.0	80%
16 October 1974	(wet)	4.05	89.1	103.6	86%
27 January 1975	(wet)	4.45	35.5	44.4	80%
12 March 1975	(wet)	4.21	61.7	76.2	81%

*H_F - free acidity is determined by ambient pH measurement

†H_T - total acidity is determined by titration to pH 9.0

‖(wet) indicates the sample was either rain or snow with no dry deposition; (bulk) indicates that the sample collected dry deposition in addition to rain or snow

Assuming that the particulate matter in precipitation is all clay and that the clay is montmorillonite, and knowing that the exchange capacity is 10^5 μeq/100 g of montmorillonite (Garrels and Christ 1965), the expected contribution to the total acidity from 10 mg/ℓ of particulates in a precipitation sample (concentration arrived at by gravimetric analysis) would be 10 μeq/ℓ. There would be no contribution to the free acidity due to the fact that protons are not released from clays until pH > 7.

AMMONIUM (NH_4^+)

In a titration to pH 9 the following reaction will occur above pH 8:

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O.$$

Approximately 30 to 50 percent of the ammonium (NH_4^+) will become ammonia (NH_3) by pH 9. If the titration were performed with nitrogen purging, then the reaction may go to completion, depending on the rate of ammonia stripping by the nitrogen stream. Therefore, if the original concentration of ammonium in the sample is 30 μeq/ℓ, there will be a contribution of 10-30 μeq/ℓ to the total acidity. However, since ammonium does not begin to release protons until above pH 8, ammonium will have no effect on the free acidity.

ALUMINUM (Al)

The concentration of dissolved aluminum in precipitation can vary from 1-4 μmoles/ℓ. Because of the aquatic chemistry of aluminum, in a titration between pH 4-9, it has the capability to "consume" three times its molar concentrations of hydroxide ions. At pH 4 it exists primarily as Al^{+++}, and at pH 9 it exists as the $Al(OH)_3$ soluble complex. Therefore, if the initial concentration was 2 μmoles/ℓ, then the potential contribution to the total acidity is 6 μeq/ℓ. As in the case of ammonium, although there is an influence on the total acidity, there is no influence on the free acidity.

IRON (Fe)

The aqueous chemistry of iron in a titration is similar to that of aluminum with the exception that iron will "consume" two equivalent amounts of hydroxide because at pH 4 it exists as the $Fe(OH)^{++}$ complex, and at pH 9 it is present as the $Fe(OH)_3$ soluble complex. Therefore, since the concentration of iron is about 1 μmole/ℓ in precipitation, the possible contribution to the total acidity is only 2 μeq/ℓ, and there would be no contribution to the measured, free acidity.

MANGANESE (Mn)

Again, manganese is similar to the previous two metals in that it contributes a small amount to the total acidity and nothing to the free acidity. The concentration of manganese in precipitation is about 0.1 μeq/ℓ, and hence even its contribution to the total acidity is an order of magnitude less than that of iron.

SILICA (SiO_4)

As in the case of manganese the concentration of dissolved silica in precipitation (0.4 μeq/ℓ) is too low to have any noticeable effect on the total acidity and it will have none at all on the free acidity.

ORGANIC ACIDS (RCOOH)

We have investigated the influence of 45 organic acids (Table 2) on the free and total acidity of precipitation. On the samples analyzed to date (April 1975, winter and spring storms) we have found only organic acid (iso-citric) in precipitation and at a concentration so low as to contribute at most only 15% to the free acidity, depending on the concentrations of other compounds (NH_4, Al, etc.).

Using column chromatography, we have identified iso-citric acid in two precipitation samples. The concentration and identification of this acid was accomplished by comparing peak heights and retention times for known amounts of organic acids. Iso-citric acid is a triprotic acid with pK values estimated at 3.2, 4.7 and 5.5. Because pK values are not available in the literature, the above pK values were estimated from published values for citric acid, which differ from iso-citric acid in the placement of the hydroxy group, and tricarballylic acid which has the same number of carbons as citric and isocitric but has no hydroxy groups. These estimated K_a values are probably within a factor of two of the true values. Since we are only using the pK to determine which of the acid groups will be protonated below pH 5, the estimated values are adequate for that purpose.

Iso-citric acid was found in samples collected from 7 February to 27 February 1975 (17 μeq/ℓ was detected) and in the sample collected from 27 February to 10 March 1975 (37 μeq/ℓ).

The contribution to the free acidity of the sample by iso-citric acid (ICH_3) can be calculated by solving the following equations.

$$ICA_{Total} = (ICH_3) + (ICH_2^-) + (ICH^{-2}) + (IC^{-3}) = 5.7 \quad 10^{-6} \text{ M}$$

$$K_1 = \frac{(ICH_2^-)(H^+)}{(ICH_3)} = 6.3 \times 10^{-4}$$

$$K_2 = \frac{(ICH^{-2})(H^+)}{(ICH_2^-)} = 2.0 \times 10^{-5}$$

$$K_3 = \frac{(IC^{-3})(H^+)}{(ICH^{-2})} = 3.1 \times 10^{-6}$$

The calculated contribution to the free acidity for the two samples mentioned above is 7% and 15% respectively.

This paper was prepared in April 1975, since then our organic acid analytical system has been expanded to include analysis by gas chromatography with mass spectrographic verification. We now have analyses of organic acids in 20 additional precipitation samples representing 15 storm events in two locations--Ithaca and Hubbard Brook. Of these 20 samples, eight showed no detectable organic acids (<1 μeq/ℓ), while the remaining 12 had trace amounts. We identified acetic, butyric, formic, lactic, glycolic and propionic; the sum of the concentrations ranged from 1.1 to 15.6 μeq/ℓ (Galloway et al. 1976). Since these are all weak acids (with pK values of about 4) the total contribution to the free-acidity of a sample, at an ambient pH of 4.0 would be from 0-10%.

A summation of the contribution to the free and total acidities from the sample collected on 27 February 1975 is presented in Table 4.

SUMMARY

It is evident that the primary sources of hydrogen ions that cause the phenomenon of acid precipitation are the strong mineral acids, sulfuric acid and nitric acid. All of the other components, with the exception of a small and irregular contribution from an organic acid, contribute only to the total acidity (Table 4).

Although precipitation collected from rural, forested regions (Hubbard Brook, Adirondack Mountains) has less weak acids than that collected in semi-urban areas (Ithaca), the levels of free acidity are within the same range of pH 3.8-4.4 (Table 2). This indicates that the regional phenomena of acid precipitation is influenced by local urban effects.

Table 4. Sources of Acidity in Acid Precipitation* in the Northeastern United States

	Concentration in Precipitation (mg/ℓ)**	Contribution to Free Acidity at pH 4.19 (μeq/ℓ)	Contribution to Total Acidity in a Titration to pH 9.0 (μeq/ℓ)
H_2CO_3	0.62	0	--***
Clay	5	0	5†
NH_4	0.195	0	11††
Al	0.036	0	4
Fe	0.040	0	2
Mn	0.005	0	0.1
RCOOH	1.1	5	17
HNO_3††	2.26	23†††	23
H_2SO_4††	2.80	36†††	37ϕ
	TOTAL	64	99

*Sample collected 27 February 1975 at Ithaca, New York.

**The total chemical composition is as follows: H, 65 μeq/ℓ; Ca, 7.4 μeq/ℓ; Mg, 1.6 μeq/ℓ; K, 0.3 μeq/ℓ; Na, 2.1 μeq/ℓ; NH_4, 10.8 μeq/ℓ; Al, 4.0 μeq/ℓ; Fe, 2.6 μeq/ℓ; Mn, 0.1 μeq/ℓ; SO_4, 58.2 μeq/ℓ; NO_3, 36.4 μeq/ℓ; Cl, 5.6 μeq/ℓ; PO_4, 0.2 μeq/ℓ; and dissociated organic acid, 5 μeq/ℓ. The ion balance agrees within 10%, which is the equivalent of 0.04 pH units.

***H_2CO_3 was removed from system by N_2 purging. If the H_2CO_3 was not removed and the system was at equilibrium with the atmosphere, there would have been 5000 μeq/ℓ contribution to total acidity and no contribution to free acidity in a titration to pH 9.

†This assumes that all of the particulate is montmorillonite; most likely the contribution to total acidity is an order of magnitude less than 5 μeq/ℓ because of minerals other than montmorillonite with much lower exchange capacities.

††This assumes that all of the NH_4^+ is converted to NH_3 which is subsequently removed by the N_2 purge. The most likely value is between 4 and 11 μeq/ℓ.

†††The contribution to the free acidity is determined by a stoichiometric formation process in which a sea salt anionic component is subtracted from the total anions (Cogbill and Likens 1974).

ϕAt pH 4.0, 1.5% of the total sulfate is present as HSO_4^-; thus total acidity for sulfate is greater than the free acidity.

The inclusion of dry deposition in a precipitation sample can partially neutralize the free acidity and add substantial amounts of weak acids (Table 3).

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HYDROGEN ION INPUT TO THE HUBBARD BROOK EXPERIMENTAL FOREST, NEW HAMPSHIRE, DURING THE LAST DECADE[1]

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ABSTRACT

Being downwind of eastern and midwestern industrial centers, the Hubbard Brook Experimental Forest offers a prime location to monitor long-term trends in atmospheric chemistry. Continuous measurements of precipitation chemistry during the last 10 years provide a measure of recent changes in precipitation inputs of hydrogen ion. The weighted average pH of precipitation during 1964-65 to 1973-74 was 4.14, with a minimum annual value of 4.03 in 1970-71 and a maximum annual value of 4.21 in 1973-74. The sum of all cations except hydrogen ion decreased from 51 μeq/ℓ in 1964-65 to 23 μeq/ℓ in 1973-74 providing a significant drop in neutralizing capacity during this period. Based upon regression analysis, the input in equivalents of hydrogen ion and nitrate increased by 1.4-fold and 2.3-fold respectively, from 1964-65 to 1973-74. Input of all other ions either decreased or showed no trend. Based upon a stoichiometric formation process in which a sea-salt, anionic component is subtracted from the total anions in precipitation, $SO_4^{=}$ contribution to acidity dropped from 83% to 66%, whereas NO_3^{-} increased from 15% to 30% during 1964-65 to 1973-74. The increased annual input

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[1]A contribution to the Hubbard Brook Ecosystem Study. Financial support was provided by the National Science Foundation. We thank J. Galloway for critical comments and suggestions on the manuscript. The Hubbard Brook Experimental Forest is operated by the U.S.D.A., Forest Service, Upper Darby, Pennsylvania.

of hydrogen ion at Hubbard Brook during the past 10 years is highly correlated with the increased input of nitrate in precipitation.

INTRODUCTION

Precipitation chemistry has been monitored at the Hubbard Brook Experimental Forest in New Hampshire since 1963. To our knowledge this is the longest comprehensive record of precipitation chemistry in the United States. The Hubbard Brook Experimental Forest, within the White Mountain National Forest, is downwind of eastern and midwestern industrial centers and as such offers a prime location to monitor changes in regional precipitation chemistry. Bulk precipitation samples are collected on a storm or weekly basis rather than the more commonly used monthly interval. Considering the problems of contamination and biogeochemical transformations that may occur in the reservoir of a precipitation collector in the field, our experience has shown that sampling intervals of a week or less are highly desirable, if not necessary, to obtain accurate data on precipitation chemistry. In areas where dry deposition is more prevalent, sampling of individual precipitation events may be the only alternative to obtain reliable precipitation chemistry.

PRECIPITATION CHEMISTRY AT HUBBARD BROOK

Sulfate and hydrogen ions dominate the precipitation falling on the forested watersheds at Hubbard Brook (Likens et al. 1976). On an equivalent basis sulfate is 2.5 times more important than the next most abundant anion, NO_3, and hydrogen ion is 5.9 times more abundant than the next most abundant cation, NH_4^+. For an 11-year period the total negative equivalent value is 94.9% of the total positive value (Table 1). The determination of hydrogen ion is probably our principal analytical error in the equivalent balance. Hydrogen ion concentration was estimated from measurements of pH and errors on the order of ±0.05 pH unit would be sufficient to explain the discrepancy in the cation-anion balance. However, considering that these long-term averages include the various sampling and analytical errors over an 8- to 11-year span, the agreement is quite good.

One of the more significant findings from these studies of precipitation chemistry was that the rain and snow at Hubbard Brook was highly acid (Likens et al. 1972 , Likens and Bormann 1974). Essentially, the incident precipitation at Hubbard Brook may be characterized as a contaminated solution of sulfuric and nitric acids at a pH of about 4.

Table 1. Weighted annual mean concentration in bulk precipitation for the Hubbard Brook Experimental Forest during 1963-1974.

Substance	Precipitation (mg/ℓ)	Precipitation (μeq/ℓ)
Ca^{++}	0.16	7.98
Mg^{++}	0.04	3.29
K^{+}	0.07	1.79
Na^{+}	0.12	5.22
NH_4^{+}	0.22[a]	12.2
H^{+}	0.073[ab]	72.4
$SO_4^{=}$	2.9[a]	60.3
NO_3^{-}	1.47[a]	23.7
Cl^{-}	0.47[c]	13.3
$PO_4^{\equiv}$	0.008[d]	0.25
HCO_3^{-}	∿0.006[e]	0.1
TOTAL	5.54	(+) 102.9 (-) 97.7

[a] 1964-1974

[b] calculated from pH measurements on weekly samples

[c] 1965-1974

[d] 1972-1974

[e] calculated from H^{+}-HCO_3^{-} equilibrium

The average annual weighted pH during the period from 1964-65 to 1973-74 ranged between 4.03 and 4.21 (Figure 1). The lowest value reported for a storm at Hubbard Brook was pH 3.0. Such precipitation is decidedly abnormal chemically since the lowest pH value for pure water in equilibrium with CO_2 in a pollution-free atmosphere should be about 5.7 (Barrett and Brodin 1955). Furthermore much of the dissolved and particulate material normally present in precipitation would tend to increase the pH. In other words, the precipitation at Hubbard Brook has a hydrogen ion concentration 50 to 500 times greater than expected.

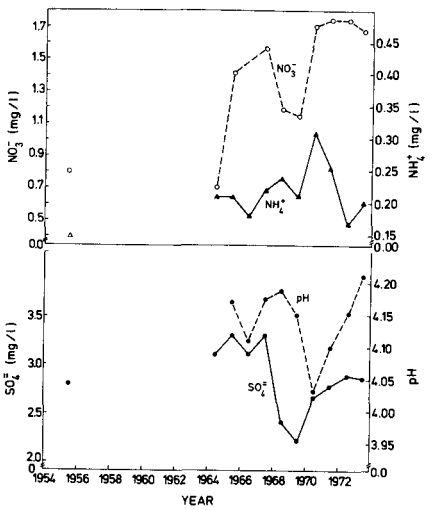

Figure 1. Annual weighted mean concentrations in precipitation for the Hubbard Brook Experimental Forest during 1955-1974. The values for 1955-56 were extrapolated from isopleth maps given by Junge (1958) and Junge and Werby (1958). Note that the ordinate has been compressed.

HYDROGEN ION INPUT

Acid precipitation apparently is a recent phenomenon (Likens 1972, Cogbill 1975, Likens and Bormann 1975), but has been falling on much of the eastern United States since at least the early 1950's (Cogbill and Likens 1974, Likens and Bormann 1974). The record at Hubbard Brook, although relatively short, provides some information on trends during the last 10 years. There was a downward trend in annual pH values between 1964-65 and 1970-71 followed by an upward trend until 1973-74, but no overall trend (1964-1974) is statistically significant (Figure 1). Likewise, concentrations for $SO_4^=$ and NH_4^+ vary from year to year, but there are no statistically significant trends for the period. In contrast, annual NO_3^- concentrations currently are about 2.3-fold greater than they were in 1955-56, or in 1964-65 (Figure 1). The sum of all cations except hydrogen ion ($\Sigma M^+ - H^+$) decreased from 51 μeq/ℓ in 1964-65 to 23 μeq/ℓ in 1973-74, which represented a 55% reduction in this $\Sigma M^+ - H^+$ component in precipitation during the period.

Even though the annual hydrogen ion concentrations are variable, the annual input (concentration times volume) in precipitation increased by 1.4-fold during the period 1964-65 to 1973-74 (Figure 2). In 1973-74

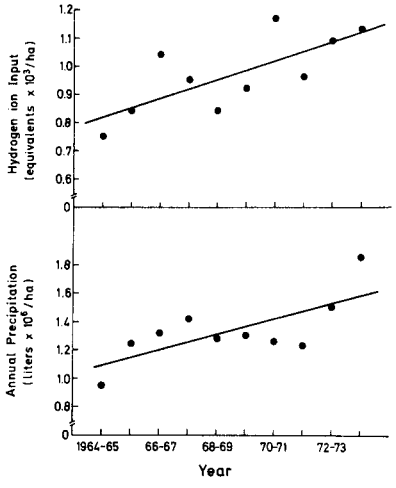

Figure 2. Annual hydrogen ion and precipitation input in precipitation for the Hubbard Brook Experimental Forest. The regression line for hydrogen ion is Y = 0.033X + 0.819 where Y is the H^+ input in equivalents X 10^3 per hectare and X is the year. The significant correlation coefficient is 0.74. Note that the ordinate has been compressed.

more than 1.1 equivalents X $10^3 H^+$/ha-yr were deposited on forested ecosystems at Hubbard Brook in precipitation. This increased input in hydrogen ion was in sharp contrast to the annual input of all other ions except nitrate (Table 2). Based upon a regression analysis, annual nitrate input increased by 2.3-fold during the decade, and it should be noted that there was no significant increase in annual sulfate input during the period.

The increased annual input of hydrogen ion is partially explained by the significant increase in amount of annual precipitation during the 10-yr period (Table 2), but data for individual years show that factors other than increased precipitation are important (Figure 2). In fact hydrogen ion input is only weakly related to annual precipitation input (Figure 3). Thus other factors are operative in regulating

Table 2. Regression analysis of annual precipitation input on year for the Hubbard Brook Experimental Forest.

Substance	Slope	Correlation Coefficient	Time Period
Ca^{++}	-0.174**	-0.83	1963-74
Mg^{++}	-0.046*	-0.66	1963-74
K^{+}	-0.126*	-0.66	1963-74
Na^{+}	-0.003	-0.02	1963-74
NH_4^{+}	0.110	0.57	1964-74
H^{+}	0.033*	0.74	1964-74
$SO_4^{=}$	0.279	0.32	1964-74
NO_3^{-}	0.388**	0.78	1964-74
Cl^{-}	0.300	0.22	1967-74
Water	4.96*	0.72	1963-74

*probability of a larger F-value < 0.05

**probability of a larger F-value < 0.01

the annual input of hydrogen ion, and consequently annual weighted concentrations (pH) alone do not accurately reflect trends in total annual input.

The input of nitrate and sulfate also are directly related to the amount of annual precipitation (Figure 4). There is more variability in the sulfate relationship to precipitation than for nitrate, and in fact without the very wet and very dry years the relationship would not be meaningful (Figure 4). We were fortunate to have rather extreme variation in the hydrologic data during the 10-yr period. This spread from dry to wet years provided a clearer view of the relationships involved. In contrast to hydrogen ion, sulfate and nitrate, the input of all cations (summed) except hydrogen ion is not related to amount of annual precipitation (Figure 3). A plot of the ratio of inputs of hydrogen ion to the sum of all other cations by year shows a highly significant correlation (Figure 5). This relationship compares the relative input of hydrogen ion to all other cations independently of amount of annual precipitation.

Surprisingly the input of hydrogen ion is not significantly related to sulfate input over the 10-yr period (Figure 6). Even though sulfuric acid is the dominant acid in precipitation at Hubbard Brook (Table I), the annual input of sulfate has not significantly increased during the period whereas the annual input of hydrogen ion has (Table 2).

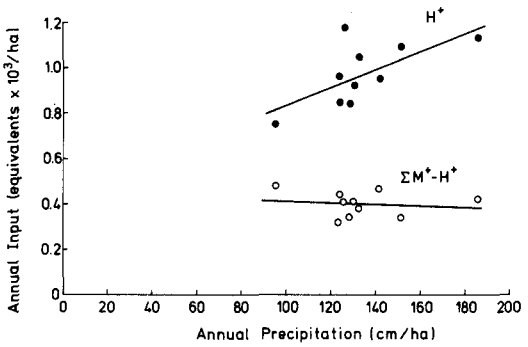

Figure 3. Relationship between annual input of hydrogen ion and all other cations except hydrogen ion (ΣM^+-H^+) and precipitation input for the Hubbard Brook Experimental Forest during 1964-1974. The H^+ regression line is Y = 0.004X + 0.437, where Y is the annual hydrogen ion input in equivalents X 10^3 per hectare and X is the annual precipitation in cm per hectare; the correlation coefficient is 0.67 and the probability of a larger F-value is < 0.05. The slope of the regression line for ΣM^+-H^+ is not significantly different from zero.

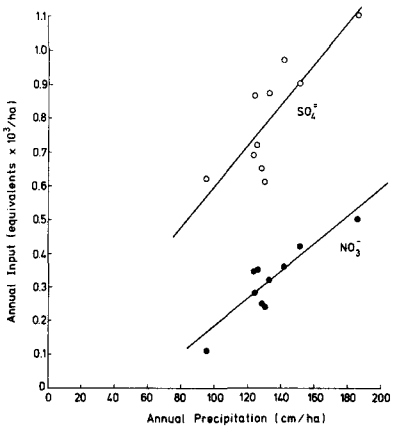

Figure 4. Relationship between annual input of sulfate or nitrate and annual input of precipitation. The sulfate regression line is highly significant (correlation coefficient, 0.81) and the nitrate regression line is very highly significant (correlation coefficient, 0.90).

In contrast, the annual hydrogen ion input is highly correlated with the annual nitrate input during the past decade at Hubbard Brook (Figure 7). The 1:1 relationship between annual inputs of hydrogen ion and nitrate is a powerful argument that nitric acid is the crucial variable in explaining the increased input of hydrogen ion during the past 10 years.

Precipitation chemistry has changed both qualitatively and quantitatively at Hubbard Brook during the past decade. Absolute concentrations have varied (Figure 1), and relative proportions of the component chemicals have changed (Figure 8). Based on a stoichiometric formation process in which the sea-salt, anionic component is subtracted from the total anions in precipitation (Cogbill and Likens 1974), the sulfate contribution to acidity dropped from 83% to 66% and nitrate increased from 15% to 30% from 1964-65 to 1973-74. Annual inputs reflect these changes in complex ways. In an attempt to resolve the relative importance of the various factors controlling the annual hydrogen ion inputs, a step-wise, multiple regression analysis was done to relate the annual hydrogen ion input to a variety of independent variables. An analysis of five independent variables indicated that

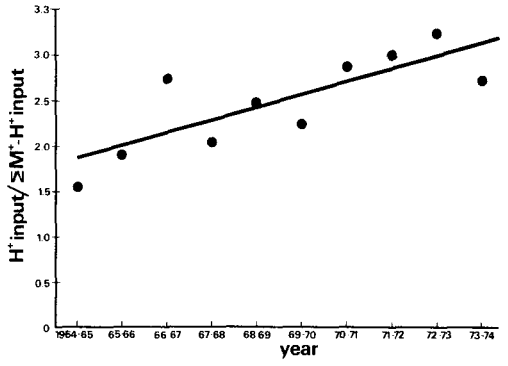

Figure 5. Relationship between cation inputs in precipitation and year. The regression line is highly significant (correlation coefficient, 0.80).

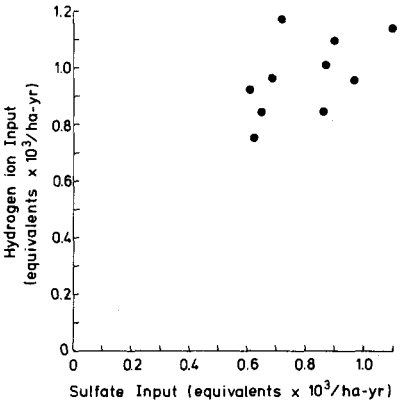

Figure 6. Relationship between the annual hydrogen ion input and the annual sulfate input during the period 1964-65 to 1973-74. The slope of a regression line fitted to these data was not significantly different from zero.

86% of the variability in annual hydrogen ion input during the decade was related to annual nitrate input. Six percent of the variability was due to annual sulfate input, 5% to the input of the sum of all cations minus hydrogen ion, 2% to year and < 0.01% to the annual amount of precipitation.

Thus although sulfuric acid dominates the precipitation at Hubbard Brook and has for a decade, the increased annual input of hydrogen ion during the past 10 years apparently has been due to an increase in the annual nitric acid input to this rural forested ecosystem.

An explanation for the increased concentration of nitrate in precipitation and the subsequent input of nitric acid for Hubbard Brook can only be surmised. Changes in nitrate concentrations in precipitation correlate well with increased emissions of nitrogen oxides (Figure 9) from combustion of fossil fuels, and to a regional spread of these materials (e.g. Likens 1972, Likens and Bormann 1974). However, there may be other factors operating to produce these changes. Data from the Hubbard Brook Experimental Forest suggest that acids in precipitation may result from a complex array of environmental factors, which affect both sulfuric and nitric acids and their proportions. This would seem to be a critical area for further research, since air quality standards and control measures relative to sulfur and nitrogen oxides often are considered independently.

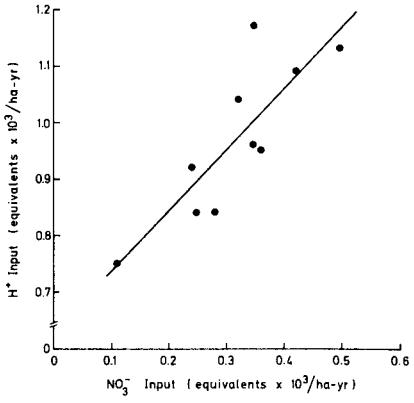

Figure 7. Relationship between the annual hydrogen ion input and the annual nitrate input during the period 1964-65 to 1973-74. The regression line: $Y = 1.07X + 0.631$, where Y is annual input of hydrogen ion in equivalents X 10^3/ha-yr and X is annual nitrate input in equivalents X 10^3/ha-yr, is highly significant (correlation coefficient of 0.84, and probability of a larger F-value is < 0.01).

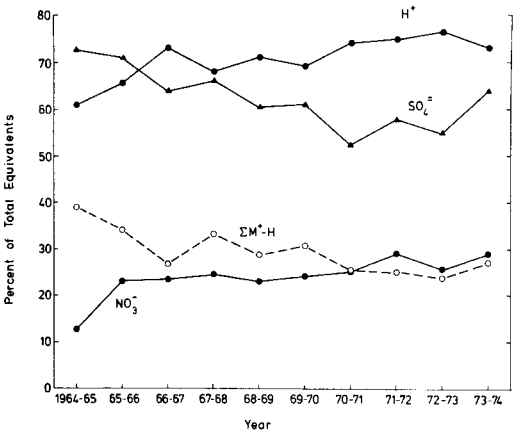

Figure 8. Variation in ionic composition of precipitation for the Hubbard Brook Experimental Forest during 1964-65 to 1973-74.

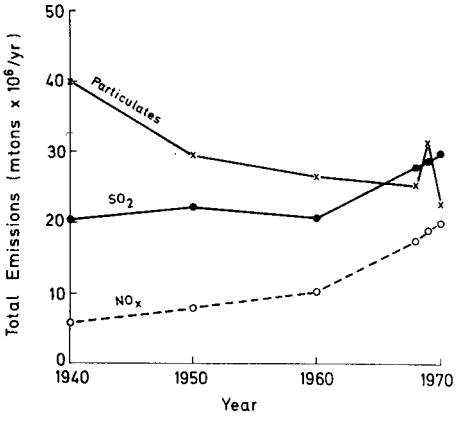

Figure 9. Total emissions of particulates, SO_2 and NO_X for the United States during 1940 to 1970 (from U. S. Environmental Protection Agency 1973).

ECOLOGICAL EFFECTS

The biogeochemical effects of excess acidity and its increased input during the past decade on forests, streams and the lake within the Hubbard Brook Valley are currently under study. The geochemical effects at present seem to be minimal (Johnson et al. 1972), but we do not know what the geochemical conditions were some 20-35 years ago when the precipitation first became more acid. The biological effects on forest dynamics are potentially significant (e.g. Whittaker et al. 1974), but data on forest dynamics are difficult to interpret and further analysis and study are required (Cogbill 1975).

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PRECIPITATION AS A CHEMICAL AND METEOROLOGICAL PHENOMENON

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ABSTRACT

Sequential rain and snow sampling has been performed at Burlington and Concord, Massachusetts. The samples have been collected during 1974 and 1975 in one-quarter inch and one inch rain equivalents and chemical analysis performed on the aliquotes. Meteorological data was documented at the time of collection.

The time variations of pH, conductivity, acidity, chloride, and sulfate have been measured for several storms. A chemical procedure for sampling and analyzing SO_2 dissolved in rain and snow has been developed. The method utilizes a swinging door rain collector, a chemical complexing solution, and a modified West-Gaeke SO_2 analysis procedure.

The analytical methodology utilizes a pararosaniline dye to measure the SO_2 colorimetrically and a complexing solution of sodium tetrachloromercurate to collect and preserve the rain samples. The sensitivity of the technique is 0.3 ppm. Data is presented for several storms in which both SO_2 and SO_4= results have been tabulated. The amount of sulfate ion present at the time of collection is 5 - 10 ppm whereas, the SO_2 concentrations measured in the same rain are generally less than 1 ppm.

The concentrations of ionic species in snow are significantly less than in rain. An explanation of this phencmenon is offered relative to precipitation formation theory, washout phenomenon, and chemical reaction rates.

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ACID PRECIPITATION IN CANADA

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ABSTRACT

The total annual emissions of sulfur oxides and nitrogen oxides in Canada are estimated to be 7.2×10^6 tons and 1.4×10^6 tons, respectively. These figures represent 5% and 2%, respectively, of the estimated worldwide anthropogenic emissions. Nearly two-thirds of the Canadian SO_2 emissions come from primary smelters located in low population areas. The remainder originate from natural gas processing, pulp mills, fuel combustion and transportation in the more heavily populated areas. Transportation is the major source of oxides of nitrogen.

No co-ordinated precipitation sampling has been carried out on a national basis prior to the establishment of the World Meteorological Organization regional stations in 1974, but several local projects in problem areas have been conducted over the last 20 years. These data are reviewed with respect to sulphate and nitrate content, and when available, the pH.

The geographical distribution of acid rain in Canada is discussed in relation to main source areas of pollutants, prevailing meteorological conditions and precipitation type.

Finally, the extent of current and potential problems associated with acid rain is discussed, and current and recommended future monitoring and research programs are outlined.

1. INTRODUCTION

Acid rain has been identified as contributing to serious ecological effects in some parts of the world downwind of regions with large SO_2 emissions. Since Canada, with only half of 1% of the world's population,contributes 5% of the worldwide anthropogenic emission of SO_2, and further, has the largest single source of SO_2, this would suggest that acid rain may already be occurring on a significant scale in parts of the country. An attempt has been made to collect

all the information available on precipitation chemistry projects in Canada and also data from locations within the United States close to the border. These data are reviewed with respect to sulphate and nitrate content and, when available, the pH. The occurrence of acid rain (and rain with high sulphate and/or nitrate content) is discussed on a geographical basis by breaking the country down into five regions, and is then related to the main source areas of emissions, the meteorological conditions and precipitation type. The effects on the ecosystem depend on the chemical and biological characteristics of the receptors, but since this topic will be dealt with in other papers it will not be considered here. This paper will concern itself only with the chemical characteristics of the precipitation as it reaches the earth's surface. However, those regions where acid rain is already falling or where the acidity of the rain is expected to increase in the future are indicated, since these are areas of potential ecological problems.

2. AIR POLLUTION SOURCES

The two most common pollutants that cause lowering of the pH of precipitation below its equilibrium value of 5.7 are sulphur (either as sulphate particles or absorbed SO_2 gas) and nitrogen (in the form of nitrate). Generally speaking, the greater the concentrations of these compounds in precipitation the lower the pH, although the actual acidity is dependent on the amounts present in the strong acid form, which in turn depend on the amounts of neutralizing constituents present.

An inventory of emissions for the five major air pollutants in Canada was carried out for year 1970 (Environment Canada, 1973). Both sulphur oxides and nitrogen oxides were included in this survey. The total annual emissions of SO_x were estimated to be 7.2×10^6 tons (6.5×10^6 metric tons) distributed as shown in Figure 1. The only known new large source of SO_2 emissions not included is from the oil extraction plant in the Oil Sands region of northeastern Alberta where current emissions are approximately 0.1×10^6 tons per year. A breakdown of these emissions by broad categories is shown in Table I. The total annual emissions of NO_x were estimated to be 1.4×10^6 tons (1.3×10^6 metric tons) and the breakdown by source category is shown in Table I.

The significant features of the distribution patterns are as follows.

(i) A few very large primary smelting operations account for nearly two-thirds of the SO_x emissions in Canada. Generally speaking these are located in remote areas and, except for the associated company town, are in regions of low population density. The world's

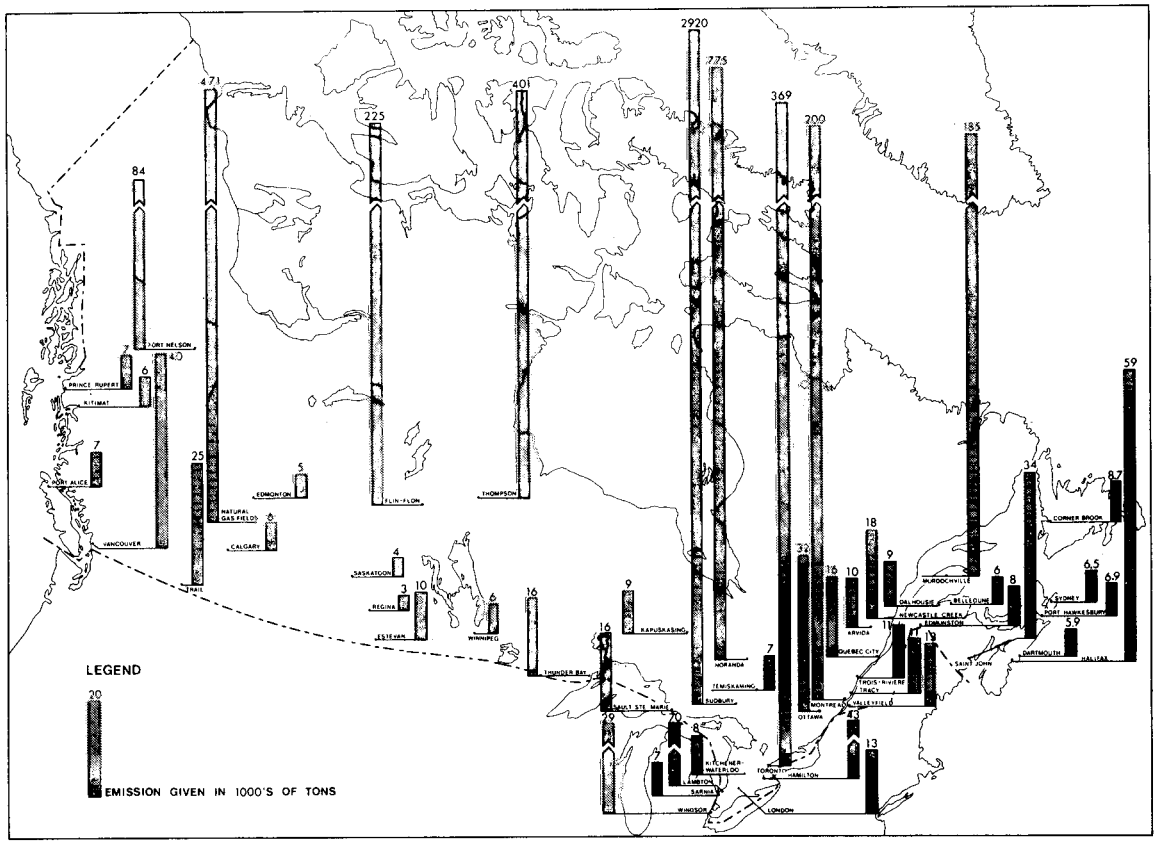

Figure 1. Distribution of major emissions of oxides of sulphur for 1970 (Environment Canada, 1973).

largest emissions of SO_2 (2.9×10^6 tons per year) occur in the Sudbury area of northern Ontario. Approximately 85% of this is emitted from a single 380 m high stack, the world's tallest.

(ii) Most of the remaining SO_x emissions occur in, or near, urban areas as a result of combustion of fossil fuels for power generation, commercial and industrial activities and home heating. The extensive use of natural gas for these purposes in western Canada results in far less SO_2 being generated in western urban areas than in the east.

(iii) In sharp contrast to SO_x, nearly all of the NO_x emissions occur in urban areas with transportation responsible for nearly two-thirds of these emissions.

(iv) Total SO_x emissions are five times as great as NO_x emissions, and in all source categories except transportation the SO_x emissions are dominant.

Table I. Nationwide Emissions of Sulphur Oxides and Nitrogen Oxides for Canada - 1970 (Environment Canada, 1973)

Source Category	SO_x tons ($\times 10^3$)	%	NO_x tons ($\times 10^3$)	%
Primary Smelters	4,560	63	-	-
Industrial, Commercial and Private (mainly urban)	1,106	15	256	18
Natural gas, petroleum and chemical industry	680	9	15	1
Utilities and Power generation	479	7	176	13
Transportation	171	2	837	62
Pulp and Paper mills	165	2	-	-
Miscellaneous	49	1	75	6
TOTAL	7,210		1,359	

3. PRECIPITATION CHEMISTRY DATA SOURCES

An attempt was made to collect all published papers and reports on precipitation chemistry projects in Canada and in several cases additional material was received by private communication. Although data from over 30 projects were obtained some may still have been omitted, but this is not expected to change the general conclusions which follow. Quite clearly the data from all of these projects cannot be presented here, and thus they will be summarized and interpreted by region. The regions and the locations of the specific projects are shown in Figure 2. The WMO Regional Stations operated by the Atmospheric Environment Service of Environment Canada are also shown. These stations are carefully sited with standardized collection and analysis procedures and are thus generating a good base of quality-controlled data from which meaningful comparisons can be made in the future. In the other projects a very wide variety of collection, storage and analysis techniques were used. Thus caution should be exercised in comparing the results, and not too much emphasis should be placed on the precise reported values of pH or ion concentrations. The purpose here will be to look at broad regional differences.

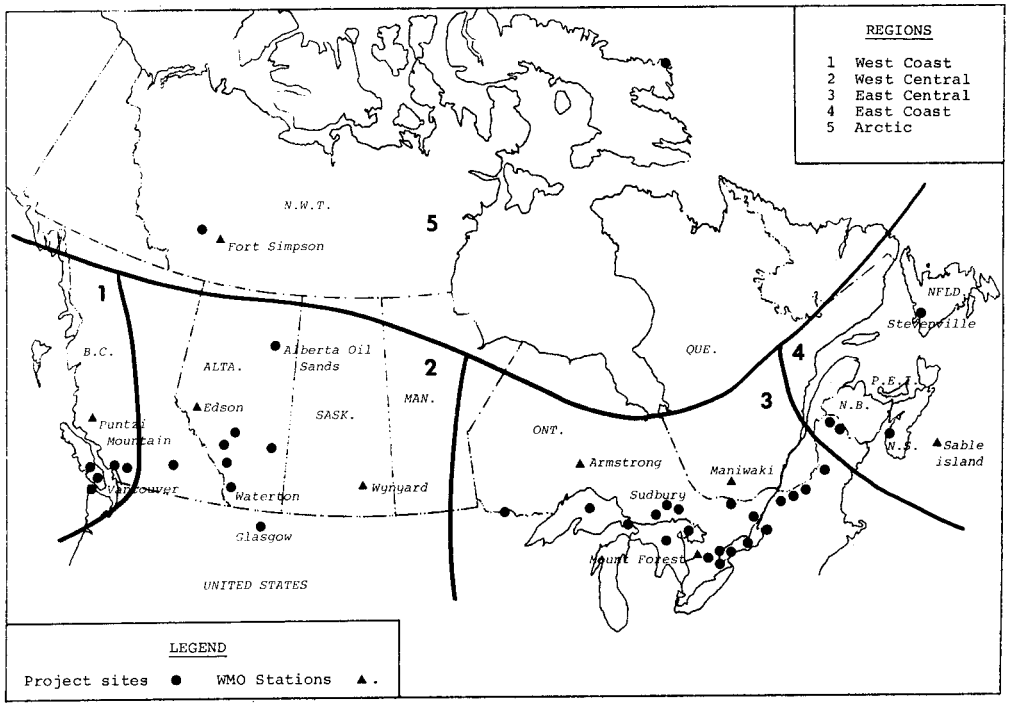

Figure 2. Geographical regions and project sites for acid precipitation study in Canada.

4. GEOGRAPHICAL DISTRIBUTION

4.1 WEST COAST

Concentrations are generally low for both sulphate (<2.0 ppm) and nitrate (<0.5 ppm), with pH values near neutral (5.0 - 6.5) except downwind of major sources in the Vancouver area, (e.g., Zeman and Nyborg, 1974).

4.2 WEST CENTRAL CANADA

The major source of SO_x in this region is the processing of natural gas in the foothills belt of Alberta between Waterton and Edson. In recent years concern about the possible effects on the soil in this important agricultural area has resulted in several studies. Downwind of this source concentrations of sulphate in event samples have been as high as 10 - 15 ppm with long term averages in rain running in the 2.0 - 3.0 ppm range, and the pH values slightly acid. In these same regions the concentrations in snow are very low (<0.5 ppm) even though the emissions remain essentially constant on a year round basis.

Sulphur budgets carried out on single sources (Summers and Hitchon, 1973; Nyborg et al., 1973) indicate that a large fraction of the emitted SO_2 is removed within 50 km of the source in summer by precipitation scavenging and direct up-take at the surface. Annual deposition rates of sulphur by precipitation have been estimated at between 2 and 10 lb/acre (2.2 and 11 kg/ha).

Elsewhere in this region concentrations of sulphate and nitrate are low and pH values are slightly basic, but no measurements are available near the two large smelters in northern Manitoba.

4.3 EAST CENTRAL CANADA

This region accounts for 60% of the Canadian emissions of SO_x and is the region where the most sampling has been carried out. Higher concentrations of sulphate occur at all sampling stations in southern Ontario and the Great Lakes basin -- even those well removed from known sources. Typical values in rain run between 2.0 and 7.0 ppm and near large sources run as high as 10 - 15 ppm. The general pH level is 4.0 to 5.0 and has been detected below 4.0.

The highest nitrate concentrations in Canada were measured in this region, ranging from 1.0 to 6.0 ppm, and could thus be a significant contributor to the acidity of the rain.

4.4 EAST COAST

Emissions of SO_x drop off again in this region with two urban areas and one smelter contributing the bulk. No recent precipitation chemistry data are available, but in the 1950's and 1960's sulphate concentrations of 2.0 to 4.0 ppm were reported with near neutral pH values. Concentrations of nitrate were between 0.25 and 1.00 ppm.

4.5 ARCTIC

No major pollution sources exist in this region of Canada and sulphate concentrations are generally <1.0 ppm with nitrates <0.7 ppm. The pH ranged from 5.0 to 7.0 in a very limited number of samples.

5. SECULAR TRENDS

The U.S. network operated by Junge (1958) in 1956 - 57 had several stations close to the Canadian border and one at a U.S. base (Stevenville, Nfld.) in Canada. Unfortunately no recent measurements have been made close to these same locations. However, the one year's data

from Wynyard, Sask. appear to be yielding an annual average close to that reported by Junge for Glasgow, Montana.

Sulphate concentrations measured in bulk samples at several rural stations in northern New York State and Vermont in the mid to late 1960's (Pearson and Fisher, 1971) were in the 3.5 to 5.5 ppm range with pH values between 4 and 5. Although these ranges are very close to those currently being recorded in monthly precipitation - only samples at Mount Forest in rural southern Ontario, the data are not directly comparable.

While the above cases indicate no dramatic change in the regional characteristics of the precipitation chemistry, the data available are obviously inadequate for establishing any meaningful trends. After several years of operation, the WMO Regional network should be able to indicate such trends if they exist.

6. EFFECTS OF PRECIPITATION TYPE

Data from Alberta (Walker, 1969; Summers and Hitchon, 1973; Nyborg et al., 1973) all indicate much lower sulphate concentrations in snow compared to rain. Earlier data from Nova Scotia (Herman and Gorham, 1957) showed the sulphate concentrations in rain to be about 2.5 times that in snow. Since emissions from industrial sources remain essentially constant round the year, and the use of fossil fuels for heating and electric power generation increase in the winter, the total emissions are higher in winter than in the summer. The lower sulphate concentrations in snow are therefore attributed to the less efficient precipitation scavenging mechanism (Summers, 1975).

7. DISCUSSION

Three major air mass types dominate the weather in the populated belt across southern Canada. Arctic air which moves in from the NW or N, most frequently in winter, is very clean and thus precipitation (mainly snow) falling in such an air-mass tends to have very low sulphate and nitrate content.

Pacific air contains very little man-made pollution, although some sulphate associated with chloride and originating from sea spray is detected in precipitation on the west coast. Most of this is removed by the time the air reaches the interior of British Columbia and Alberta. The air mass remains essentially clean, except near the Alberta gas fields, as it moves east across Canada until it reaches the major source region in southern Ontario.

The third, and perhaps most important, air mass is the warm moist tropical air which moves north from the Gulf of Mexico across the major source regions in the eastern United States and makes frequent incursions into southern Ontario and eastern Canada, especially in the summer. It is within this air mass that the greatest potential for long range transport of pollutants into Canada exists. A study of haziness in the Atlantic Provinces by Munn (1973) presents evidence for such transport. It is also within this air mass that much of the summer rainfall occurs, often in the form of convective storms, which appear to be the most efficient at scavenging pollutants (Summers,1975) and hence giving the highest sulphate and nitrate concentrations and lowest pH values.

The configuration of pollution sources in Canada and the United States, and the major air mass flows, thus combine to make southern Ontario the main known receptor of acid rain in Canada on a regional basis. Although we are not aware of any recent precipitation chemistry data in the area east of Ontario, pH measurements in northern New England (Likens, 1972) and Munn's study suggest that southern Quebec and the Atlantic Provinces are probably receptor regions for acid rain also. The new WMO regional stations currently being set up at Maniwaki, Que. and Sable Island, off Nova Scotia, will soon provide additional data on this matter. Additional precipitation sampling stations are also being established in southern New Brunswick and southern Nova Scotia.

In southern Ontario the regional acid rain effect is strongly enhanced downwind of some of the major sources. For example pH values as low as 3.6 have been detected in rain falling through the plume near Sudbury (Wiebe and Whelpdale, 1975).

The potential for transboundary flow of pollutants contributing to acid rain is greatest in the east. With winds from the NW sector, pollutants from the major source area in southern Ontario could be transported into New England, although with these winds, rainfalls are not frequent or heavy. Snow often occurs in winter with winds from this sector, but in view of the lower scavenging efficiency probably does not contribute much to acidity of precipitation on an annual basis.

On the other hand, winds from the SW sector transport pollutants from the major sources in the eastern United States into southern Ontario, southern Quebec and the Atlantic Provinces, and the concentrations are further increased by the intense local sources. Most of the summer rainfall occurs with this flow and hence probably makes a major contribution to the acidity of precipitation on an annual basis. Quite clearly a major study of air mass motions, polluted parcel trajectories and an extensive precipitation monitoring program in the eastern U.S. and eastern Canada would be required to quantitatively define the extent of acid rain and the pollutant sources responsible as a result of long-range transport in general and transboundary transport in particular.

8. SUMMARY AND RECOMMENDATIONS

Two regions of Canada have been identified as currently being receptors for precipitation containing high sulphate and nitrate concentrations and/or with low pH values.

The first region is in central Alberta downwind of the natural gas processing plants. Although sulphate and nitrate concentrations are moderately high, the rain is only slightly acid. A potential future problem exists in northeastern Alberta where development of the Alberta Oil Sands over the next ten years could cause a dramatic increase in the sulphur dioxide emissions. A large inter-disciplinary environmental study of this region is now being initiated and will monitor present levels of pollutants and attempt to establish the pathways for both air and water pollutants and their likely effects on the ecosystem. This information will be used to establish appropriate control and land-use strategy in the area in order to minimize environmental damage.

The second region is southern Ontario (probably extending into southern Quebec, and the Atlantic Provinces) where slight to moderately acid precipitation appears to be falling over a large area. In this region, in addition to sulphate, nitrate appears to be making a significant contribution to the acidity. In general the rain is more acid than the snow. The effect is enhanced downwind of some of the major sources where extremely acid (pH < 4.0) precipitation has been detected.

Because of the "energy crisis", consideration is being given to a much greater use of coal for electric power generation in North America. This will undoubtedly lead to a sharp increase in emissions of both SO_x and NO_x especially if tall stacks are used, rather than best practical control technology, to satisfy the ambient air quality standards. Since many of these emissions will occur in the heavily populated and industrialized regions of eastern North America which are already experiencing acid rain this may result in a further lowering of the pH and an increase in the geographical extent of the affected areas. It is therefore recommended that the current extent of acid rain be better delineated by setting up a suitable monitoring network in Canada on a finer scale than the WMO network. This should comprise of the order of 100 stations, with maximum density in the eastern half of southern Canada and a few stations in the arctic. Such a network would enable the regional distribution of acid precipitation to be determined using standardized collection and analysis techniques. The establishment of such a network would not preclude the necessity for continuing more intensive sampling around known large sources. In fact it will make interpretation of results from these studies more definitive if the regional background levels are known more accurately.

Along with the operation of a Canadian precipitation chemistry network, further research effort needs to be devoted to gaining a better understanding of the precipitation scavenging mechanisms. This is particularly important because of the wide range of precipitation amounts and types that can occur in Canada. The relative importance of the wet and dry deposition processes is also a very critical aspect of assessing the environmental impact of new industrial developments.

Finally it is recommended that any large-scale Canadian effort in precipitation sampling and research devoted to acid rain should be closely co-ordinated with any similar activities in the United States.

ACKNOWLEDGEMENTS

The authors wish to thank those working on precipitation chemistry in Canada who provided the information used as the basis for this review, particularly the following, F. C. Elder, J. P. Kimmins, J. C. Scrivener, and B. Webber, who provided data from projects currently underway.

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ACID PRECIPITATION AND AQUATIC ECOSYSTEMS

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ACID PRECIPITATION AND ITS INFLUENCE UPON AQUATIC ECOSYSTEMS--AN OVERVIEW[1]

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ABSTRACT

The impact of acid precipitation reflects a usually deleterious balance between good and bad effects which may lead to serious and sometimes extreme degradation of aquatic as well as terrestrial ecosystems, particularly around metal smelters. Addition of hydrogen ions as sulfuric, nitric, and hydrochloric acid can alter and impoverish the species composition of biotic communities, and lead to severe leaching of beneficial metal cations such as calcium from ecosystems. Heavy metals and other trace elements which accompany acid precipitation may reach toxic levels, particularly where acid fallout leaches additional amounts from the soil into streams and lakes. Complex and often toxic hydrocarbons also comprise a little known organic component of acid precipitation.

Alternatively, acid precipitation usually is enriched in plant nutrients such as nitrate-and ammonia-nitrogen, potassium, calcium, and sulfur; and at certain concentrations some of the associated trace elements may also be beneficial. Moreover the initial effect of soil leaching by acid fallout may be to enrich aquatic ecosystems in metal cations such as calcium.

Basic materials in air pollution, biogenic ammonia from the soil, dust fall from arid regions, and soils rich in adsorbed metal cations or in carbonates may neutralize some of the harmful effects of acid precipitation upon ecosystems. However, associated heavy metals, other trace elements, and toxic hydrocarbons may still constitute serious problems in many environments.

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[1]Contribution No. 152 from the Limnological Research Center, University of Minnesota.

1. INTRODUCTION

The broad dispersion of strong acid precipitation into country areas far removed from urban and industrial sources of air pollution was first shown by the work of Barrett and Brodin (1955) in Fenno-Scandia, by my own studies (Gorham, 1955, 1958a) in the English Lake District, and by those of Houghton (1955) on fog and cloud water in New England. At the same time the acidity of precipitation in many British cities was documented extensively by Parker (1955). In the late 1940's and through the 1950's a complete European network was set up to study the chemistry of air and precipitation (Emanuelsson et al., 1954; Rossby and Egnér, 1955), providentially it came into operation near the beginning of a trend toward rapidly increasing pollution and acidification following World War II (Air Pollution Across National Boundaries, 1971; see also recent issues of the journal AMBIO). Unfortunately, early data are lacking for Eastern North America, where extremely acid precipitation has been recorded in the past several years by Likens (1972, see also Likens et al., 1972; Likens and Bormann, 1974). However, by indirect methods Cogbill and Likens (1974) have calculated that an acidification process similar to that in Europe has occurred in recent decades. Many of the more recent studies of acid precipitation have been reviewed by Nisbet (1975). A general account of the way in which the chemistry of precipitation influences the chemistry of inland waters is included in an earlier review of mine (Gorham, 1961).

2. THE NATURE AND ORIGIN OF ACID PRECIPITATION

The reaction of precipitation is conditioned by a wide variety of acids and bases from diverse sources. Barrett and Brodin (1955) pointed out that pure water in equilibrium with atmospheric carbon dioxide would exhibit a pH of about 5.7, well below the neutral point of 7.0. Added to that primary solution of carbonic acid are three strong mineral acids. For example, at Hubbard Brook, New Hampshire (Likens and Bormann, 1974), where hydrogen ions account for 69% of cations in precipitation, the anion proportions are sulfate 62%, nitrate 23%, and chloride 14%.

Among these strong acids sulfuric acid predominates, with a strong correlation evident between hydrogen ions and sulfate ions (Gorham, 1955, 1958a), or between hydrogen ions and sulfate minus calcium ions (Fisher, 1968; Pearson and Fisher, 1971; cf. however Likens, 1972). The sulfuric acid originates chiefly from the oxidation of sulfur in fossil fuels (Table I), which is between 1 and 3% in 56% of U.S. coals, above 3% in more than 30% of cases, and may exceed 6% (Perry, 1975). Fuel oils may also be quite high in sulfur. Lesser and more local

TABLE I

Estimated rates of sulfur mobilization from biogenic sulfur emissions, fossil fuel combustion, industrial sources, and volcanoes

Source	Sulfur (10^6 metric tons/yr)	
	Friend (1973)	Kellogg et al. (1972)
Natural		
Sea spray*	44	43
Biogenic (sea)*	48	89
Biogenic (land)	58	
Volcanoes**	2	0.7
Total	152	133
Anthropogenic		
Fossil fuel combustion	51	50
Non-fuel sources	14	
Total	65	

Examples of individual anthropogenic sources

Sudbury metal smelters, 1972	> 1.8 (Hutchinson and Whitby, 1975)
Thirty-five gas processing plants, Alberta	0.17 (Summers and Hitchon, 1973)
Coal-fired power plant, 600 megawatts, burning coal with 3%S	0.14 (North and Merkhofer, 1975)

* Most marine emissions return directly to the sea

** Stoiber and Jepsen (1973) estimate 5 x 10^6 metric tons/yr

sulfur sources are sulfide-ore smelters and volcanoes. Locally, gas processing plants can emit sufficient sulfur to have an appreciable impact upon sulfur and acidity in precipitation (Summers and Hitchon, 1973; Summers and Whelpdale, 1975). Whether the catalytic converters designed to reduce auto emissions will increase concentrations of sulfuric acid near the ground in urban areas is currently a vexing question (Holden, 1975). Although natural biogenic emissions of sulfur are estimated to be very large (Table I) they do not seem to be a major factor in producing acid rain, and may be presumed mostly to have been in balance with natural sources of neutralizing bases.

Oxides of nitrogen (NO and NO_2) may also contribute significantly to the acidity of precipitation. They come from oxidation of organic nitrogen in fossil fuels. U.S. coals average 1.4% N, U.S. crude oils 0.15%, and residual oils 0.4%, (Anon., 1975, Chapter 15). Thermal fixation of gaseous molecular nitrogen also occurs, during the process of high-temperature combustion in air. Approximately 5-40% of the nitrogen in coal and 20-100% of the nitrogen in oil is oxidized by combustion, and becomes oxidized further to nitric acid in the presence of

water vapor (Anon., 1975, Chapter 14). World-wide urban emissions of nitrogen oxides owing to combustion are shown in Table II, which

TABLE II

Wide-world emissions of nitrogen oxides by combustion processes and natural sources (Anon.,1975)

Source	N_{ox} emissions as N (10^6 tons/yr)	
COAL COMBUSTION		8.2
Power generation	3.7	
Industrial	4.2	
Domestic/commercial	0.3	
PETROLEUM COMBUSTION		6.6
Residual oil	2.7	
Gasoline	2.3	
Fuel oil	1.1	
Other	0.5	
NATURAL GAS COMBUSTION		0.6
FOREST FIRES		< 0.2
NATURAL SOURCES		150

indicates coal and petroleum as the major sources. Although far less important than natural sources, their combustion in urban localities may lead to atmospheric concentrations of nitrogen oxides 1 to 2 orders of magnitude higher than in non-urban atmospheres (Anon., 1975, Chapter 14). Likens and Bormann (1974) have shown that at Hubbard Brook, on an equivalent basis, hydrogen ions exceed sulfate ions in precipitation, and more recently Likens et al., (1975) have demonstrated a high degree of correlation between the increase of hydrogen-ion input and the increase of nitrate input over the past ten years, with no correlation between inputs of hydrogen ions and sulfate.

Hydrochloric acid is the third component of the strong acids in precipitation. It has been noted particularly in urban locations in Britain (Gorham, 1958b), where the chlorine content of coal averages one-fifth the sulfur content (Meetham, 1950), and may reach 1% by weight as compared with an upper limit of 0.65% in U.S. coals (Abernethy and Gibson, 1963; Perry, 1975). In urban Britain during the decade 1944-1954 the deposit of chloride has been estimated as 400 mg/m^2 in summer and 670 mg/m^2 in winter, as compared with 290 and 370 mg/m^2 of sulfate-sulfur respectively (Parker, 1955). The summer and winter concentrations of chloride in precipitation were 6.7 and 10.3 mg/l, as compared with 4.8 and 5.6 mg/l of sulfate-sulfur. Such

high amounts of chloride are much greater than can be accounted for by marine sources, and indeed substantial amounts of chloride have been observed in smoke solids (Gorham, 1958b) as well as in coal. Moreover, 50-75 ppm of hydrochloric acid have been reported in flue gases from coals burned by the Tennessee Valley Authority (Anon., 1975). Small amounts of hydrochloric acid may also come from the interaction of atmospheric sodium chloride particles with droplets of sulfuric acid (Gorham, 1958a; Eriksson, 1958), and from volcanoes, near which Bottini (1939) has observed pH values of 2.8 to 7.0 in precipitation. There is an extremely strong correlation between chloride and hydrogen ions in Bottini's samples below pH 5.7, and no correlation with sulfate. Total solids average 44 mg/l in the samples below pH 5.7, and 76 mg/l in samples above pH 5.7. According to Cadle (1975), emissions of hydrogen chloride by volcanic eruption are about one order of magnitude less than emissions of sulfur dioxide.

In addition to strong acids, weak acids may also be found in precipitation (Krupa et al., 1975), but appear not to contribute appreciably to free hydrogen ions in rural precipitation (Galloway et al., 1975).

A point that arises here is how to refer free hydrogen ions to the various anions in precipitation. Cogbill and Likens (1974), after subtracting other sea-salt ions in proportion to sodium, have assumed a straightforward stoichiometry by which hydrogen ions are assigned to the remaining sulfate, nitrate, and chloride in proportion to their ratio in the precipitation sample. However, this procedure may not tell us what we wish to know about the sources of acidity, as shown by the situation in some British cities. There the deposit of hydrogen ions correlates to a highly significant degree with chloride deposit, and not at all (after partial correlation) with sulfate deposit, although the latter is substantially greater on a chemically equivalent basis (Gorham, 1958b). Such a statistical treatment is probably essential if a proper assignment is to be made, and the simultaneous calculation of partial regressions may also be very informative. For example, data for different locations in Sheffield, England, show that the proportion of chloride balanced by hydrogen ions increases from about 3.7 to 9.6 milli-equivalents % as the chloride deposit doubles from the least to the most polluted sites. The reason for hydrochloric acid prevailing in cities, whereas sulfuric acid predominates in rural Britain, is believed to be the greater solubility of gaseous hydrogen chloride as compared to sulfur dioxide, and its greater ability to lower the vapor pressure of water, leading to the rapid growth of droplets to a precipitable size (Gorham, 1958b). Presumably nitric acid ought also to fall out nearer to source than sulfuric acid, because nitric oxide is oxidized more rapidly than sulfur dioxide in the atmosphere (Wilson, 1975).

One might expect that the shift in recent years from coal combustion emitting large amounts of sulfur oxides to natural gas emitting

rather small amounts would greatly reduce not only sulfur emissions but also the acidity of precipitation. This does not seem to have been the case in New England, where sulfate deposition has been much reduced. Likens and Bormann (1974) speculate that the use of taller smokestacks, and particle precipitators capable of removing alkaline neutralizing substances such as the particles of fly ash in smoke (cf. Gorham, 1958a, b), has resulted in a broader dispersion of gaseous sulfur dioxide and its oxidation product sulfuric acid, despite a decreased total production by fuel combusion. Moreover, the emission of nitrogen oxides from the combustion of petroleum has increased greatly in recent decades (Likens, 1972). Although such emissions are small in proportion to natural emissions (Table II), they do seem to have produced an increase in the nitrate content of New England precipitation and a concomitant increase in its acidity (Likens et al., 1975).

3. MECHANISMS FOR THE CLEANSING OF ACIDS OR THEIR PRECURSORS FROM THE ATMOSPHERE

Most attention has been focused upon rainout and washout of acid precipitation as a probable cause for the deterioration of both terrestrial and aquatic ecosystems. In the case of sulfur dioxide, rainout within clouds is probably very important near to major centers of emission. Farther away, washout of sulfate particles below cloud base is likely to predominate in the sulfur-scavenging process (Nisbet, 1975). Other mechanisms of atmospheric cleansing which may have deleterious effects deserve greatly increased study. A good deal of the sulfur dioxide emitted into the air is absorbed directly upon the moist surfaces of plants, soils, etc., where it may subsequently be oxidized to sulfuric acid. According to Nisbet (1975; cf. Eriksson, 1960), deposition of sulfates in precipitation accounts for 40-80% of the sulfur deposited on land, with direct absorption of sulfur dioxide accounting for much of the rest, though most significantly in dry and relatively unpolluted air. Such direct absorption will be inhibited by tall smokestacks, which will increase the time available for conversion of sulfur dioxide to sulfates which are better removed by washout (Wilson, 1975).

Another factor, impaction upon surfaces, may be important in the fallout of acid aerosols and acid-forming soot particles, although its significance has not been clearly established (Kellogg et al., 1972; Knabe and Günther, 1975). One study (Nihlgård, 1970) suggested that tree canopies may impact substantial amounts of sodium, magnesium, calcium and chloride, and release from leaf cells appreciable amounts of manganese, potassium, and in the case of spruce forest, hydrogen ions. The effectiveness of impaction will vary greatly with the sizes of particles and the degree to which they are hygroscopic or

hydrophobic. Some of the problems involved have been discussed by Eriksson (1960), White and Turner (1970), and Hidy (1973).

A final point to be mentioned here is the difference between rain and snow in their capacity to cleanse the atmosphere. Herman and Gorham (1957) found that Nova Scotian snow samples contained only a quarter as much mineral ash as winter rains, two fifths as much sulfur, one-third as much ammonia, and one-half as much nitrate. Snow in central Alberta also contained much less sulfur and chloride than rain (Summers and Hitchon, 1973), and Beamish (1974) has reported a similar situation for sulfur in snow and rain in Ontario (see also Berlandi et al., 1975). How far the lower snow concentrations result from a lower scavenging capacity of snowflakes than of raindrops, and how far they are owing to differences in the ion content of air mass sources, remains to be determined. Summers and Hitchon (1973) suggest that very low liquid contents in winter snow-producing clouds may account for a lesser scavenging efficiency. In the case of SO_2 they also suggest low oxidation rates in the presence of freezing ice crystals as compared with warm cloud droplets. High chemical concentrations in snow can sometimes be observed where blizzards entrain large amounts of soil dust (Table V).

4. FACTORS TENDING TO NEUTRALIZE ACID RAIN

Among the bases entering the atmosphere and capable of neutralizing the acids in precipitation, those in fly ash are likely to be very important. Shannon and Fine (1974) record pH values above 9 in 100:1 water extracts of fly ash, and above 11 in 5:1 extracts. Calcium and sodium are the predominant cations, and sulfate is equivalent to about half of total soluble cations. Calcium predominates among the soluble metal cations in smoke solids (Gorham, 1958a), and it accounts for about 60 milli-equivalents % of sulfate in urban British precipitation and 35 milli-equivalents % of sulfate plus chloride (Parker, 1955). Ammonia is another such atmospheric base, supplied biogenically (see, e.g., Denmead et al., 1974) to a far greater degree (250:1) than by fuel combustion (Anon., 1975, Chapter 14). Ammonium sulfate is a major component of atmospheric aerosols (Junge, 1954) and soot particles (Brosset, 1973; 1975), and the two ions are correlated in acid Nova Scotian rain and snow (Herman and Gorham, 1957). They also show a strong correlation in precipitation over the British Isles (Figure 1) and in British air masses (Stevenson, 1968). Rain in Illinois exhibits a similar relationship (Figure 2, data of Larson and Hettick, 1956). The correlation does not, however, hold for U.S. data on a continent-wide basis (data of Junge and Werby, quoted by Carroll, 1962). Barrett and Brodin (1955) have suggested ammonia from dairy farms as a factor reducing the acidity of precipitation in Denmark and parts of south Sweden. Where ammonium sulfate is an important component of precipitation, it is

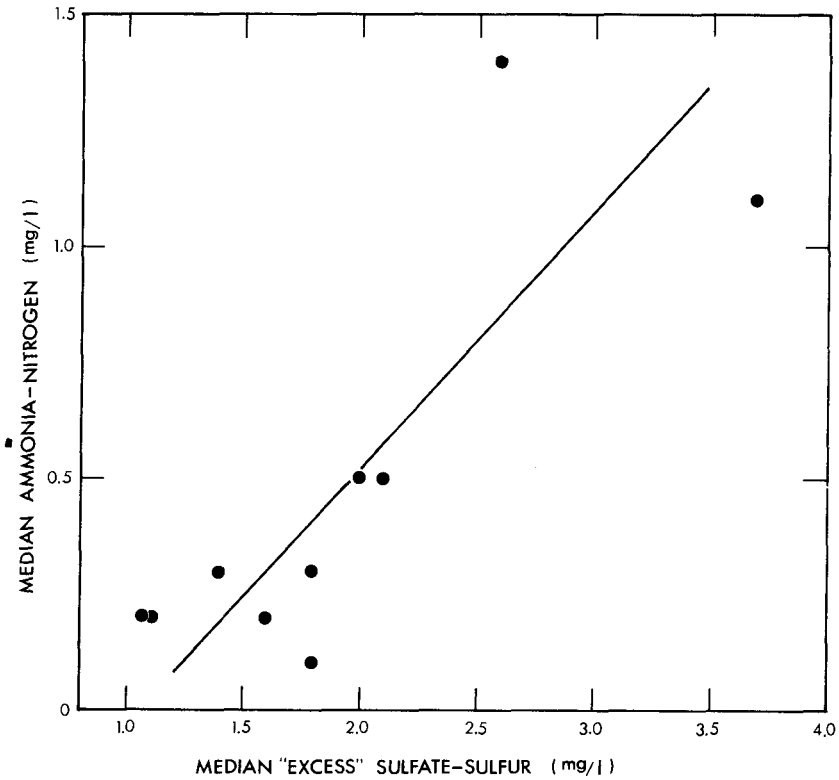

Figure 1. The relationship between ammonia-nitrogen and "excess sulfate-sulfur" (subtracting sulfur from sea salt) in British precipitation. Data of Stevenson (1968), fitted by reduced major axis (Imbrie, 1956) because neither variable is dependent.

likely to have a distinct acidifying influence upon the soil, as has long been known from fertilizer practice (Russell, 1950).

In maritime areas, sea spray is also a neutralizing factor. The pH of surface sea water, under control of a bicarbonate buffer system, is usually close to 8.2

Another cause of atmospheric neutralization is dustfall. Fisher (1968) noted a distinct correlation, in the precipitation of the southeastern U.S.A., between bicarbonate ions and calcium minus sulfate ions; and an equally distinct correlation between hydrogen ions and sulfate minus calcium ions. The clear inference is that in some cases acid, sulfur-bearing aerosols predominate, and in other cases alkaline calcareous dust.

Junge and Werby (1958) noted a pronounced maximum for calcium in precipitation (excluding dry fallout between rainfalls) in the

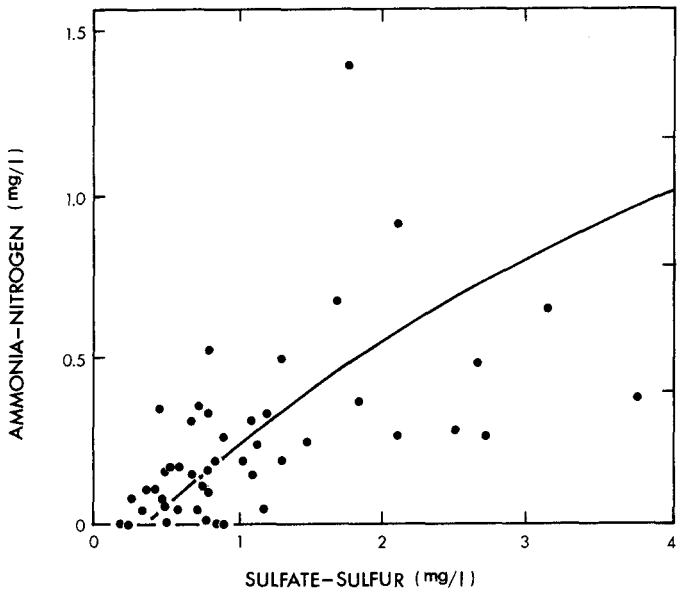

Figure 2. The relationship between ammonia-nitrogen and sulfate-sulfur in Illinois rainwater. Data of Larson and Hettick (1956), fitted by reduced major axis (Imbrie, 1956).

southwestern U.S., with a lesser maximum in the central plains where heavily cultivated prairie loess soils are very susceptible to wind erosion. In terms of absolute supply of calcium to the ground, Eriksson (1960) pointed out that the central plains actually exceed the arid southwest. In both the southwest and the central plains pH appears to be near or above 5.7, the value for pure water in equilibrium with atmospheric carbon dioxide (Nisbet, 1975). Smith et al. (1970) provide extensive data on dust deposition in the U.S. in relation to geography, climate, and cultivation(Table III). Their data indicate that the drier areas of the mid-U.S.A., with less than 85-90 cm of precipitation, are not only dustier than the wetter areas to the east (cf. Hagen and Woodruff, 1973), but also usually produce alkaline dusts (pH 7-8). The eastern dusts are usually faintly acid (pH 6-7), in line with known soil differences.

Long-distance transport of fine dust particles is well known, and Salmi (1969) has noted the utility of pollen analysis in identifying sources. In contrast, the very local effects of dustfall from an unpaved road have been shown by Tamm and Troedsson (1955). Industrial dust sources can also be important, for instance Barrett and Brodin (1955; see also Emanuelsson et al., 1954) implicated a large cement factory in southwest Sweden as the cause of an unusually high pH and calcium content of precipitation in that region. Table IV (Gorham,

TABLE III

Dustfall in the U.S.A. (data of Smith et al., 1970)

Location	Site*	State	Oxidized Dust (kg/ha/month)	Dust pH	Oxidation Lose (%)
North	Sidney	Montana	70	7.9	11
Central	Tribune	Kansas	460	8.0	3
	North Platte	Nebraska	76	7.1	10
	Hays	Kansas	57	7.2	8
	Manhattan	Kansas	50	7.1	12
	McCredie	Missouri	48	6.7	11
South	Water Valley	Texas	22	7.7	12
	Riesel	Texas	24	7.6	10
	Oxford	Mississippi	62	6.3	25
East	Coshocton	Ohio	17	6.0	18
	Marcellus	New York	49	6.3	26
	Marlboro	New Jersey	28	6.4	19

*Sites ordered from west to east within each group.

TABLE IV

Chemical composition of dust from Greenland ice

(data of Free, from Gorham, 1961)

Si	29.0%	Ca	3.6%
Al	7.9	Mg	1.8
Fe	4.1	Na	3.0
Mn	0.05	K	1.7
H_2O	0.34	P	0.05
Ignition loss	2.9	Cl	0.06

1961) provides an analysis of dust from Greenland ice, which may be representative of long-distance fallout.

The major source regions for alkaline atmospheric dust are usually

far from the chief areas of urban and industrial pollution which cause acid precipitation. Instead, these urban industrial areas are generally close to extensive areas of crystalline igneous rocks, whose soils lack reserves of basic minerals or adsorbed metal cations to neutralize readily the accessions of acid now falling upon them. Therefore, ecosystems in these areas are especially susceptible to degradation.

In the U.S., the state of Minnesota appears to lie in a tension zone between the two regions where alkaline dustfall and acid fallout predominate. In the moister northeast, mixed conifer/hardwood forests predominate on non-calcareous glacial drift, whereas in the drier south and west agriculture dominates the former prairie region. A dustfall gradient across the state may be inferred from several lines of evidence. First, precipitation-fed pools in Sphagnum bogs on deep peat near the northwestern forest border exhibit calcium concentrations averaging 4.4 mg/l and pH values of 4.0 in their waters (Hofstetter, 1969), whereas about 100 km to the east calcium concentrations are only 1.7 mg/l and pH values 3.5 (Heinselman, 1970). The slight difference in precipitation/evaporation balance at the two sites is not at all sufficient to account for such a difference. The presence of opal phytoliths assignable to prairie grasses in the surface peat of the western bogs (Finney and Farnham, 1968) suggests dustfall of calcareous wind-blown loess from the prairies as a likely source of their higher calcium. Another line of evidence comes from a study in Minnesota and elsewhere of the moss Sphagnum fuscum (E. Gorham and D. L. Tilton, 1972 and in prep.). This species grows in tall hummocks on open bogs, where deep peat isolates it from the mineral soil so that the mineral content of the moss is supplied wholly from the atmosphere. In those forested areas where agricultural disturbance is absent, Sphagnum fuscum has a mineral ash content of about 1.5% dry weight, which rises to about 5.5% where more than 40% of the nearby landscape is harvested cropland. The increase in ash content is very closely correlated with an increase in the content of aluminum and iron, both major components of soil dust. According to Winkler (1975), a dense forest cover yields almost no airborne dust, which accords well with the moss data.

That dustfall can greatly enrich precipitation in soluble materials is demonstrated by a comparison (Table V) of dirty and clean snows, sampled after a blizzard in North Dakota (Adomaitis et al., 1967), with snow from the Experimental Lakes Area deep in the forests of western Ontario (Barica and Armstrong, 1971). The melted Ontario snow is very dilute (specific conductivity 11 μmho/cm, 25° C), but distinctly acid. The dusty Dakota snows, in contrast, are much more concentrated, and distinctly alkaline under the influence of dustfall from arid regions (cf. Table III).

These very striking differences in snow chemistry, strongly supporting the likelihood of a dustfall gradient across Minnesota, have been followed up by another study of snow chemistry (E. Gorham and J. K. Underwood, unpubl.) shortly after one of the most severe

TABLE V

A comparison of the chemical composition of snow from North Dakota, sampled after a severe blizzard (Adomaitis et al., 1967), and snow from Western Ontario (Barica and Armstrong, 1971)

Location	Site	pH	Soluble				Total
			Ca	SiO_2	SO_4	NO_3-N	PO_4-P
			(mg/l)				(µg/l)
North Dakota	Wetlands in cultivated areas (n=12)	8.1	23	7.5	5.7	2.5	130
North Dakota	Wetlands in vegetated areas (n=17)	7.9	14	4.0	4.9	0.9	82
W. Ontario	Lake surfaces (n=10)	5.0	0.35	0*	1.2*	0.2	6

*in 4 samples from a single lake at different times

windstorms in the last several decades, which blew large amounts of dust into the state from the west. Table VI shows various aspects of

TABLE VI

Chemistry of snow sampled along a prairie/forest transect from eastern North Dakota to eastern Minnesota after a severe blizzard in 1975

Location	pH	Specific conductivity (µmhos, 25°C)	Filterable solids (mg/l)	Total PO_4-P (µg/l)
Western prairie, > 40% of harvested cropland (n=10)	8.0 (6.6-9.5)	29 (7-48)	274 (60-643)	69 (26-188)
Eastern forest, 1-10% of harvested cropland (n=9)	4.9 (4.5-5.6)	16 (11-20)	17 (3-61)	16 (5-68)

the chemical composition of the top 40 cm (approximately) of snow sampled along a transect from west of Grand Forks in North Dakota to east of Grand Rapids in northern Minnesota. Melted snow from the eastern forested part of the transect where there is little cultivation (east of Bemidji), resembles the snow from western Ontario a little to

the north, being dilute and acid, but distinctly richer than the Ontario snow in total soluble phosphorus. The snow from the western prairie part of the transect (west of Fosston) is sixteen times richer than that of the forested part in filterable solids, four times richer in total phosphorus, and has about twice the concentration of total dissolved salts (as measured by specific conductivity). This prairie snow resembles the clean North Dakota snows of Table V in pH and phosphorus content, the only two properties measured in both cases. In this particular case the influence of dustfall from the west declines sharply east of the prairie border. Nevertheless, local dustfall may be significant wherever there is open ground to supply it, as indicated by the studies of Sphagnum fuscum which grows only within the forested region of Minnesota. Although most soil dust falls out within about 250 km of the source (Winkler, 1975), some may travel long distances in the atmosphere, as shown by its occurrence in Greenland ice (Table IV).

From the above considerations it appears that Minnesota is indeed a tension zone under the influence of short-range dustfall from the west and pollution from local and eastern sources (Table VII). In this connection, Chicago is about 800 km and Sudbury about 1000 km from the westernmost extent of acid snow. Although Minneapolis and St. Paul are only about 250 km away, they seem unlikely to be major sources of acid precipitation. Only two of fourteen snows sampled along a transect from west to east of the Twin Cities, shortly after the northern transect was sampled, exhibited pH values (4.7, 5.4) appreciably below the pH (5.7) of pure water in contact with atmospheric carbon dioxide. Specific conductivity averaged 36 μmho at 25°C. Duluth is about 75 km from the eastern end of the transect, and may be an important source of acid, but we have no knowledge of precipitation chemistry there. The possibility that local pulp and paper operations could be an important source seems unlikely, in view of their low emissions of sulfur oxides in northern Minnesota and Wisconsin (Table VII). There are also such sources in Ontario, but they seem unlikely to match fuel combustion as a source of acid.

Further exposure to acid precipitation may come to Minnesota in the near future if major developments in power generation from coal take place in the western states. This exposure will be even greater if their coal is shipped to power plants in the middle west, where cooling water is more readily available. Exposure may also be enhanced if the copper/nickel ores of northeastern Minnesota are eventually smelted locally.

Once acid precipitation is removed from the atmosphere, further neutralizing mechanisms come into play. Forest canopies may bring about a reduction of as much as 90% in the acidity of precipitation leaching through them (Eaton et al., 1973), which may be owing to bases in impacted soil dust, or to bases in leaf cells. On the other hand, precipitation which is not already strongly acidified may become so by throughfall, and especially by stem flow (Nihlgård, 1970). Soils, of

TABLE VII

Emissions of sulfur oxides in Minnesota and neighboring states (from Anon., 1974)

State	Category	Sulfur oxide emissions, 1972 (10^3 tons/yr)
Minnesota	Grand total	432
	Minneapolis/St. Paul	208
	Duluth	120
	Fuel combustion	394
	Industry	27
	Wood products (all northern)	4
	Transportation	11
Wisconsin	Grand total	785
	Wood products (all north central)	15
Sudbury smelters*	Grand Total	> 3500
Michigan	Grand total	1617
	Detroit	815
Illinois	Grand total	2252
	Chicago	530
	St. Louis	720
Indiana	Grand total	2260
	Chicago	622
Iowa	Grand total	312
North Dakota	Grand total	86
South Dakota	Grand total	19

*From Hutchinson and Whitby, 1975

course, have a neutralizing capability which varies greatly with differences in their degree of saturation by metal cations such as calcium and magnesium, and for wholly base-saturated soils, their carbonate content. In general the capacity to neutralize acid precipitation is lowest in heavily leached, non-calcareous soils derived from hard crystalline rocks such as granites and quartzites, and high in soils derived from more easily weathered sedimentary rocks, especially where

carbonates are abundant (Gorham, 1958a). Deep, acid Sphagnum bog peats also lack the capacity to neutralize acid precipitation (Gorham, 1958c, 1967). Some soils rich in sulfides (e.g., drained peats and lake muds, soils in the vicinity of ore bodies and volcanoes, or soils recently raised above sea-level) may themselves exert an additional degree of acidification as the sulfides are oxidized to produce sulfuric acid (Chenery, 1953; Wiklander and Hallgren, 1949; Wiklander et al., 1950).

5. THE ECOLOGICAL EFFECTS OF ACID PRECIPITATION

Accounts of the ecological ill effects of air pollution are numerous, and have focused chiefly upon the gaseous pollutants such as sulfur dioxide, ozone, nitrogen oxides, and compounds such as PAN (peroxyacyl nitrate), etc., which affect terrestrial ecosystems (cf. papers reviewed by Webster, 1967; Hindawi, 1970; Tamm and Aronsson, 1972; Ferry et al., 1974; Anon., 1973; Smith, 1974; Missouri Botanical Garden, 1975). Other pollutants are of far greater significance for aquatic ecosystems, chief among them hydrogen ions from acid precipitation, and the trace elements from urban and industrial sources (e.g., Cu, Ni, Pb, Zn, As, and others) which usually accompany it. An example of the difference in trace element content between rural and urban atmospheres in Britain is given in Table VIII (cf. also Kramer, 1973, for a contrast between smelter-influenced and more normal precipitation in Ontario). Organic toxins also accompany acid precipitation. A factor

TABLE VIII

Annual averages for trace elements in British air (from Stocks et al., 1961)

Site		Cu	Ni	Pb	Zn	As	Mn	Sb	V	Cr	Mo	Co	Be
		µg/1000 m^3											
Rural (n=3)	Min.	7	1	80	48	5	5	1	1	1	0.3	0.3	0.06
	Max	38	75	470	205	27	13	5	2	3	1.3	0.9	0.15
Urban (n=12)	Min	44	2	260	130	31	12	4	1	2	1.3	1.0	0.19
	Max	252	205	1430	490	130	130	20	54	22	6.1	4.3	1.00

of particular importance to northern aquatic ecosystems is the suddenness with which toxins may be added during the spring thaw (Air Pollution Across National Boundaries, 1971). The earliest melt water is the

most contaminated (Overrein and Abrahamsen, 1975; Wright, 1975) because the intercrystalline brines containing the impurities in snow are the first to be washed out (cf. Gorham, 1958d).

The effects of acid pollution are most severe in the vicinity of metal smelters such as those at Sudbury, Ontario, where the pH of lake waters may fall as low as 3.2 (Gorham and Gordon, 1960) and rain may reach pH 2.85 (Hutchinson and Whitby, 1974). Such lakes carry a very restricted flora of aquatic macrophytes (Gorham and Gordon, 1963) as well as of phyto-plankton (Stokes et al., 1973). The fish fauna is also greatly reduced in diversity and abundance in acid lakes near Sudbury (Beamish and Harvey, 1972; Beamish, 1974). Similar effects of acid precipitation upon fish, zooplankton, benthos, phytoplankton, and aquatic macrophytes have been observed in Scandinavia, where the source of acidity is general air pollution from the urban/industrial areas of Europe (Almer et al., 1974; Grahn et al., 1974; Jensen and Snekvik, 1972; Wright, 1975). Natural analogs showing similar biotic depletion are found in the volcanic lakes of Japan, where pH may fall below 2 (Yoshimura, 1933, 1935).

In lakes subject to acid pollution it is difficult to separate the influence of acidity from that of accompanying pollution by heavy metals such as copper, nickel, lead, zinc, iron, manganese, etc. Table IX illustrates this point for the Sudbury smelter area, where extremely high metal concentrations in precipitation (see Ontario maximum) are matched by those in local lakes. Almer et al. (1974) observe that a similar but lesser problem exists in southern Scandinavia, where zinc, copper, and lead are in the order of several micrograms per liter of precipitation; and mosses dependent for their mineral supply largely upon atmospheric sources are known to be strongly contaminated with these elements and with cadmium, nickel, chromium, and mercury (Rühling and Tyler, 1973). Precipitation in southern Ontario (Table X) does not show a clear increase in trace elements, except for lead, as the environment becomes increasingly urban, but it is possible that the non-urban background is high owing to the proximity of the industrial northeastern U.S.A.

According to Peirson et al., (1974), from studies in widely separated non-urban regions of the British Isles, a fairly uniform airborne particulate material may be widespread in northern latitudes, varying considerably in concentration but rather little in elemental composition except very close to major industrial sources. For example, in 1972 the average concentration of lead in British air ranged from 29 to 330 ng/kg at seven sites, and scandium ranged from 0.014 to 0.180 ng/kg. However, if lead is normalized to scandium, an element largely derived from the soil, by calculating

$$\frac{\text{air concentration of lead}}{\text{air concentration of scandium}} \Big/ \frac{\text{average soil concentration of lead}}{\text{average soil concentration of scandium}},$$

TABLE IX

Minor metallic elements in precipitation and surface waters (μg/l)

	Precipitation					Surface Waters							
	Ontario [1,2]			Southern Ontario [3]	USA[4]	Sudbury 9 lakes[5]		Water Supplies USA [4]	Lake Erie [6]	Lake Superior [7]	Streams (est) [8]	Minnesota 33 lakes [6]	High Sierra 114 lakes [6]
	(max[1])	(median[2])	(min[1])	(mean)		(max)	(mean)				(mean)		
Cu	700	9	nd*	6	21	1000	270	21	15	1.5	7	5.2	1.2
Ni	830	6	nd		4	6400	2400	7	3	< 0.5	0.3		< 0.3
Pb	270	25	nd	20	34	100	58	17	4	14**	3		0.5
Zn	1500	120	21	77	107	180	93		8	0.8	20	7.5	1.5
Fe	2300	210	nd	31		730	370		156	23		38	1.3

[1]Kramer (1973), total, sites include Sudbury

[2]Kramer (1975)

[3]Shiomi and Kuntz (1973)

[4]Lazrus et al. (1970)

[5]Stokes et al. (1973)

[6]Chawla and Chau (1969)

[7]Biesinger and Christensen (1972)

[8]Turekian (1969)

* not detected
** two samples, 7 and 20 μg/l

then the atmospheric enrichment factor for lead of a little over 1000-fold varies scarcely at all in the seven sites. Many other elements (except for those of marine origin, such as sodium, chlorine, and bromine) exhibit a similar constancy. Figure 3, from Peirson et al. (1974), shows that at Chilton in the British Isles, atmospheric enrichment factors form a continuum ranging from 1 or less in one group of elements (aluminum, cerium, iron) to between about 10 and 1000 in another (vanadium, antimony, arsenic, zinc, selenium, lead), with a third group between about 2 and 6 (manganese, cesium, cobalt, chromium). The first three elements, which are not enriched relative to scandium, are almost certainly derived largely from soil dust, and the second group of highly enriched elements presumably derive chiefly from air pollution. The third group presumably represents elements enriched by pollution above normal soil levels, but to a lesser degree. Figure 3 also presents an estimate of dry deposition velocity, derived from the rate of dry deposition divided by the air concentration. This calculation shows that the elements of low atmospheric enrichment, and

TABLE X

Chemical composition of bulk precipitation in Southern Ontario (Shiomi and Kuntz, 1973)

	Main Duck Island	Trenton	Kingston Airport	Ancaster	Woodbridge	Hamilton	Toronto Island
	(arithmetic mean concentrations)						
Cu (µg/l)	9	6	5	5	5	9	6
Ni (µg/l)	4	4	3	3	4	5	6
Pb (µg/l)	7	7	7	17	39	28	40
Zn (µg/l)	114	60	52	120	66	104	65
Fe (µg/l)	27	10	17	35	29	32	48
SO_4 (mg/l)	6.6	8.0	6.6	10	8.8	12	12
Ca (mg/l)	3.5	4.4	3.8	4.5	4.3	7.0	6.5

Open lake ----------→ Strongly urban

derived chiefly from the soil, exhibit dry deposition velocities above 0.7 cm/sec, which suggests that the elements occur in rather large particles. Those elements showing high atmospheric enrichments, and derived largely from air pollution, exhibit dry deposition velocities less than 0.9 cm/sec, and these velocities decrease with increasing atmospheric enrichment. Presumably, therefore, the elements derived largely from air pollution occur in rather small particles. This conforms to the view (National Academy of Sciences, 1975) that atmospheric particles originating mechanically from soil dust are distinctly larger (diameter range approximately 1-100 um) than those originating by condensation during or after the combustion processes which give rise to air pollution (diameter range approximately 0.1-1 um). In connection with their studies of air chemistry, Peirson et al. (1974) analyzed a variety of elements in rainfall (from five sites in Britain, one in Holland, and one at a gas platform in the North Sea). The ranges of concentrations are given in Table XI. Highest concentrations are obs observed at the gas platform, and are believed to result from contamination by blown sea spray greatly enriched in elements which have become concentrated in the surface microlayers of the sea. Normal bulk sea water, also shown in Table XI, is very low in several of the elements highly concentrated at the gas platform site. The average concentrations for rain, also given in Table XI, exclude this extremely atypical site. A comparison with Table IX shows considerable similarity in the mean concentrations of elements analyzed in precipitation from Britain, the U.S.A., and Ontario.

In attempting to sort out cause and effect, Beamish (1974) has come to believe that high acidity from smelter pollution is the principal cause of the depletion and disappearance of fish populations in

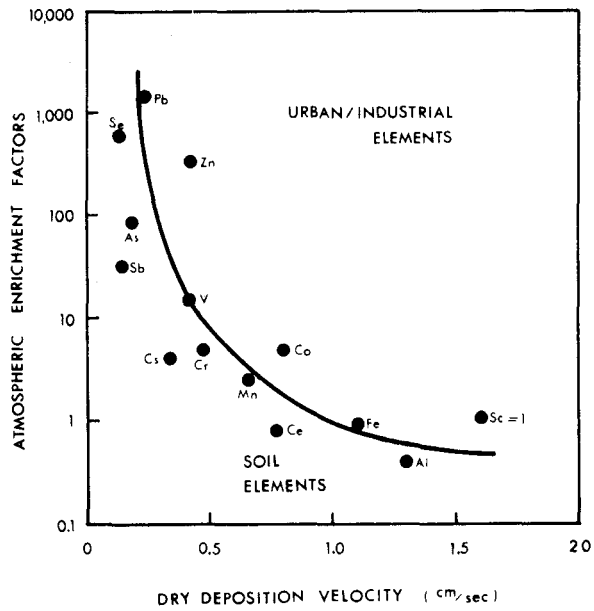

Figure 3. The relationship between atmospheric enrichment factors and dry deposition velocities for atmospheric elements at Chilton, England, after Peirson et al. (1974). Enrichment factors are normalized to the element scandium, which is derived predominantly from the soil, as follows:

$$\frac{\text{air concentration of element}}{\text{air concentration of Sc}}$$

$$\frac{\text{average soil concentration of element}}{\text{average soil concentration of Sc}}$$

Dry deposition velocities are calculated as:
rate of dry deposition/concentration in air.

lakes near Sudbury, Ontario. The addition of lime to acid lake waters has apparently been successful in facilitiating the restoration of fish populations (Wright, oral communication), but the degree to which treatment may have affected heavy metal contaminants or their influence upon the fish has not been established. In the case of aquatic macrophytes Gorham and Gordon (1963) suspected the implication of heavy metals because lakes near the smelters, but lying on calcareous glacial drift which neutralized the acid pollution, nevertheless exhibit a very restricted aquatic flora. Stokes et al. (1973), in a study of two lakes very close to smelters, also implicated metal pollution in the case of phytoplankton, because they observed that the surviving algae

TABLE XI

Elemental concentrations in rain at one Dutch and five British sites, at a gas platform in the North Sea, and in sea water (from Peirson et al., 1974)

Element	Mean (six sites)	Range	Gas platform N. Sea	Sea Water
Al	<503	< 230-770	2400	1-10
As	< 8	1.3-12	45	3.0
Br	446	33-1300	2300	65000
Ce	< 0.44	< 0.1-0.55	< 4	0.4
Cl	50700	3000-105000	210000	1.9×10^6
Co	0.46	0.19-0.68	3.2	0.2-0.7
Cr	3.4	1.9-5.0	20	0.13-0.25
Cs	< 0.125	< 0.03-0.19	1.7	0.5
Cu	28	23-41	82	0.24-1.7
Fe	413	135-570	3100	0.06-1.5
Mn	< 17	< 5-23	< 60	0.24-0.54
Na	25400	1700-56000	100000	1.06×10^7
Ni	5.9	3.8-7.2	23	0.16-0.51
Pb	33	11-53	190	< 0.05-0.8
Sb	0.96	0.3-2.0	5.9	0.5
Sc	0.081	0.021-0.11	0.49	0.04
Se	0.56	0.39-0.91	1.75	4.0 -6.0
Th	< 0.12	< 0.08-0.21	< 0.7	0.5
V	< 7.2	4.4-9.0	< 40	2.0
Zn	148	26-260	2000	1.5-6.9

were of metal-tolerant strains both in acid Baby Lake (pH 4.0) and in circumneutral Boucher Lake (pH 6.8). Later, Stokes and Hutchinson (1975) found that both metal and low pH were limiting these algae.

Lake acidification and consequent oligotrophication by acid precipitation may also lead to increasing coverage of lake bottoms by dense mats of Sphagnum mosses, including S. inundatum, S. cuspidatum, and other species (Grahn et al., 1974; Grahn, 1975). These mosses have strong cation-exchange properties, so that they can take up metal cations important to aquatic ecosystems and retard the recycling of these elements from sediments. Sphagnum can also take up anions such as phosphate rather strongly under acid conditions (Coffin et al., 1949), and this may be especially important because phosphorus is frequently a major factor limiting aquatic productivity.

The organic hydrocarbons which accompany atmospheric pollution are relatively little known, and virtually nothing is known of their effects upon ecosystems. In Great Britain (Parker, 1955) the yearly average of suspended smoke particles shortly after World War II ranged from 1 mg/100 m^3 or less in rural and coastal areas to about 50 mg/100 m^3 in densely populated industrial sites. Mean daily concentrations occasionally reached 400 mg/100 m^3, usually during severe fogs. Similarly, the deposit of total combustible matter ranged from about 44 g/100 m^2/month (about 8 mg/l of rain) in little-polluted areas to 540 g/100 m^2/month (about 98 mg/l of rain) in severely polluted sites. In the less polluted air of Sweden, precipitation has been observed to contain 0.8 to 3.4 mg/l of carbon (Neumann et al., 1959), approximately equivalent to 1.6 to 6.8 mg/l of organic matter. Ignition losses of clean precipitation samples are often equivalent to ignition residues, and in an agricultural part of Nova Scotia averaged 13 mg/l (Gorham, 1961).

Of the combustible material in British precipitation, tars soluble in carbon disulfide contributed 3 and 18 g/100 m^2/month in little polluted and heavily polluted sites, or 0.5 and 3.2 mg/l respectively. A detailed examination of organic (and potentially carcinogenic) components in the smoke of British air has been made by Stokes et al. (1961), as shown in Table XII. Given the hydrophobic nature of many smoke particles, they may travel long distances, and Brosset (1973, citing Rodhe et al., 1972) noted a strong correspondence between soot and sulfate concentrations in south and west Sweden, with many of the particles apparently originating 1000 km away. Their effect is most likely to be greatest upon terrestrial animals, or perhaps on tree leaves which scavenge them by impaction, but soot films do accumulate on lake surfaces during calm weather, where they may affect the surface-dwelling organisms (neuston), even in country areas such as the English Lake District (Gorham, 1961). Presumably such films are mixed to some degree into water masses during windier weather or by raindrops during precipitation (cf. Houk, 1975), and may affect the organisms living there. Probably the filter-feeders would be most affected.

TABLE XII

Annual averages for polycyclic hydrocarbons in British air (from Stocks et al., 1961)

		Total Smoke	3:4 Benz-pyrene	1:2 Benz-perylene	Pyrene	Flor-anthene	1:2 Benz-pyrene	Coro-nene	Anth-anthrene
		(mg/1000 m^3)			(µg/1000 m^3)				
Rural (n=2)	Min	100	11	11	7	10	8	2	2
	Max	140	15	12	6	10	9	3	3
Urban (n=16)	Min	150	15	14	4	7	9	3	3
	Max	620	108	73	38	58	52	12	20

So far acid precipitation with its accompanying inorganic elements and organic molecules has been treated as an unmitigated pollutant. It should, however, be pointed out that such precipitation may add nutrients to ecosystems, in particular nitrogen, calcium, and potassium (Gorham, 1955). For example, in rain in the English Lake District nitrate amounts to about 10 milli-equivalents % of sulfate, and correlates strongly with it. Calcium and potassium are also highly correlated with sulfate there (Gorham, 1955, 1958a), and calcium is strongly correlated with sulfate in urban British rain (Gorham, 1958b). Figures 1 and 2 demonstrate a strong correlation of ammonia with sulfate. Some of the added materials, such as calcium, tend to fall out closer to the point of emission than does sulfate (Gorham, 1955, 1958a). They may even neutralize acid fallout close to the source in some cases (Overrein, 1972), though not in others (Gorham, 1958b; Gordon and Gorham, 1963). Such additions of nutrients are especially significant in small upland lakes on crystalline igneous rocks, and in Sphagnum bogs on deep peat (Gorham, 1958a, 1967). Even some of the associated trace elements may presumably be beneficial in small amounts. Finally, sulfur itself is a nutrient deficient in certain soils (Missouri Botanical Garden, 1975) though seldom in aquatic habitats.

A question of interest here is whether appreciable amounts of phosphorus are supplied by acid precipitation. Table XIII presents a variety of data which suggest that in the northeastern U. S. A., where acid precipitation is prevalent, phosphorus is if anything rather low. However, differences in technique (digestion, filtration, etc.) may be responsible for some of the observed variation. Shiomi and Kuntz (1973) found no increase of phosphorus in urban as compared with non-urban sites (but their and Kramer's data are unusually high). According to Oden (oral communication) combustion of fossil fuels has been a significant source of phosphorus to aquatic ecosystems in Scandinavia. Probably a major source of widespread air-borne phosphorus is dust stirred up by agricultural operations, as suggested by the snow analyses of Table V and VI which range from 6 µg/l in the forests of western Ontario to 82 and 130 µg/l in clean and dirty snow from the North Dakota prairies. Barica and Armstrong (1971) point out that in the very dilute lakes of western Ontario, precipitation may supply as much as 80% of their phosphorus inputs.

TABLE XIII

Total phosphorus in precipitation

	Total P (µg/l)	
NE U.S.A.	13	Likens (1972)
Ithaca, clean	5	Likens (1972)
Aurora, clean	6	Likens (1972)
Hubbard Brook	8	Likens (1972)
Mays Point	22	U.S.G.S. (cited by Shiomi and Kuntz, 1973)
Lake Ontario	61	Shiomi and Kuntz (1973)
Northern Ontario	102*	Kramer (1973)
Western Ontario	18	Armstrong and Schindler (1971)
Northern Minnesota	28	Wright (1974)
Coshocton, Ohio	27	Weibel (cited by Likens, 1972), few samples
Cincinnati	80	Weibel (cited by Likens, 1972), few samples
N. England	14	Gore (1968)
N. England	27	Carlisle et al. (cited by Gore, 1968)
Sweden	17-34	Tamm (cited by Gore, 1968)

*median 81 (Kramer, 1975)

Another feature of acid precipitation that has both bad and good points is its capacity to leach materials, including macro- and micro-nutrients, from the soil (Overrein, 1972). Over the long term, such leaching is likely to be harmful (Air Pollution Across National Boundaries, 1971), but in the short run may make certain nutrients more accessible to organisms, particularly in aquatic ecosystems. Figure 4B shows that at an iron-sintering plant in Wawa, northwestern Ontario (Gordon and Gorham, 1963), the concentration of calcium in lake waters is sharply elevated in the intermediate pollution range, but decreases again (though not to unpolluted baseline levels) where sulfur pollution is great enough to exceed the neutralizing capacity of the soil and bring about severe acidification of lake waters (Figure 4A). In Scandinavia also, conductivity, calcium and magnesium have increased in lakes and rivers under the influence of acid precipitation which has replaced bases adsorbed in the soil exchange complex by hydrogen ions (Odén, 1975; Wright, 1975). Severe leaching, however, may acidify the entire soil column below pH 5, in which case aluminum is mobilized into soil waters and aquatic ecosystems where it can be distinctly toxic (Wright, 1975; Hutchinson and Whitby, 1975). According to Reuss (Missouri Botanical Garden, 1975), anion-adsorbing polymers of hydroxy-iron and aluminum ions increase considerably as soils become more acid, and can greatly increase retention in the soil of anions such as sulfate. Phosphate is also bound in this way (Brady, 1974), and so becomes less available to organisms, particularly in aquatic habitats.

A further consequence of severe acidification might well be the breakdown and solution of the iron/manganese oxidate crusts and nodules common in lakes on the Precambrian Shield and occasional elsewhere (Gorham and Swaine, 1965). These oxidates are efficient scavengers of trace elements, which would be released by such an acid attack and could perhaps reach toxic levels in some aquatic ecosystems (cf. Norton, 1975).

Although it is true that in certain circumstances a moderate degree of air pollution may supply nutrients beneficial to ecosystems, it is an extremely inefficient method of enrichment for two reasons. First, harmful components are always associated with the beneficial ones, with the balance likely to be tipped toward their side. Second, air pollution usually obeys a power law of dilution by dispersion (see sulfate, Figure 4C) so that concentration decreases very rapidly away from point sources. This usually means highly toxic concentrations near the source as a heavy price for marginal (if any) benefit farther away.

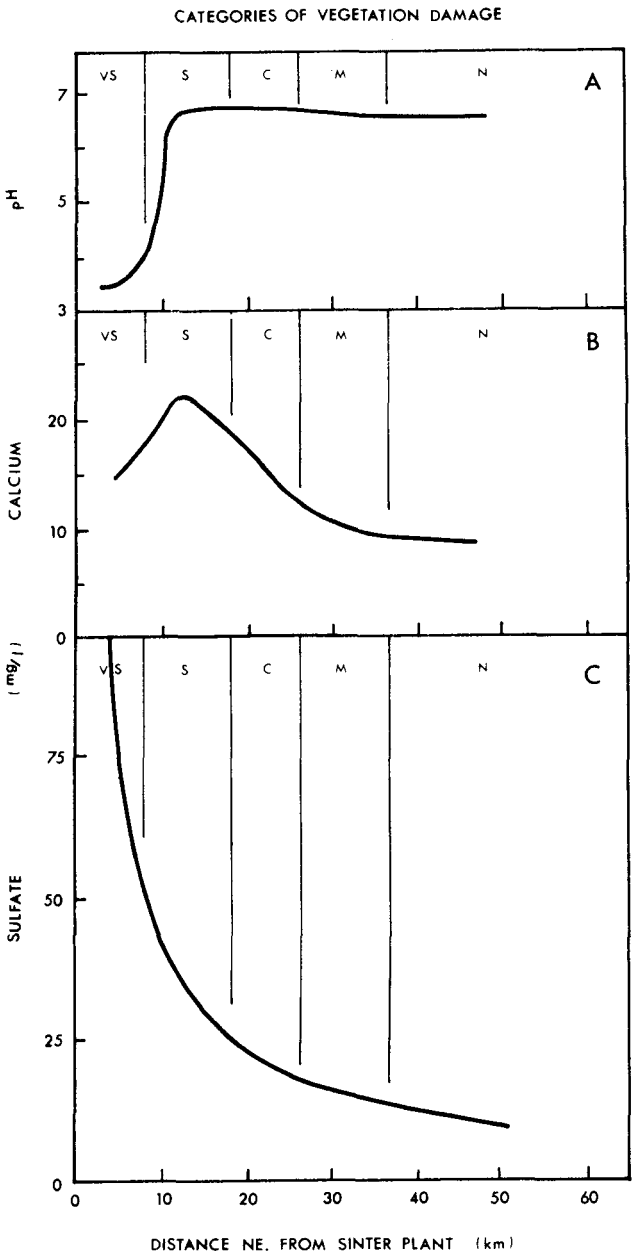

Figure 4. The relationships of sulfate, calcium, and pH in lake and pond waters at Wawa, northwestern Ontario, to distance from an iron-sintering plant, after Gordon and Gorham (1963). Subjective aerial estimates of forest damage are given as very severe (VS), severe (S), considerable (C), moderate (M), and not obvious (N).

6. THE QUESTION OF THRESHOLDS

A final question deserving consideration is whether there is a threshold for ecosystem damage from acid precipitation. In the sense that every species probably has a slightly different threshold for damage from each of several toxins included in acid fallout (and for their various combinations) it becomes difficult to look for a single ecosystem threshold. However, the rapid power-law increase of fallout

as one approaches a pollution source may produce rather sudden changes in vegetation which simulate a threshold effect, for example in the forest ecosystem at Wawa in northwestern Ontario (Figure 5, from

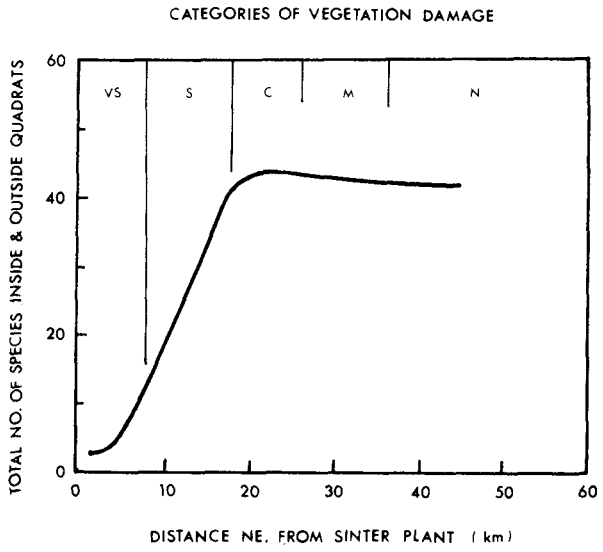

Figure 5. The relationship of the diversity of terrestrial flora at Wawa, northwestern Ontario, to distance from an iron-sintering plant, after Gordon and Gorham (1963). Subjective aerial estimates of forest damage are given as very severe (VS), severe (S), considerable (C), moderate (M), and not obvious (N).

Gordon and Gorham, 1963). There most forest species (with the unfortunate exception of white pine, Pinus Strobus) seem able to survive the relatively low levels of sulfur pollution beyond about 20 km from the source. However, once sulfur begins to rise rapidly within that distance, species disappear equally rapidly from the ecosystem and it becomes progressively less diverse. This apparent threshold for the influence of pollution upon species diversity is, however, misleading. Although most species survive beyond 20 km, many are far from healthy (see Gordon and Gorham, 1963, and their Table I) and show (in differing degree) a progressive deterioration as one approaches the sinter plant. It is important, therefore, to look

beyond the diversity of an ecosystem to the health of each of its component species in order to assess adequately the influence of acid fallout. Once this is done, the concept of a threshold for ecosystem damage becomes difficult to sustain, unless one considers the threshold for the single most sensitive species in the ecosystem to be the ecosystem threshold as well (cf. Woodwell, 1975).

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IMPACT OF ACID PRECIPITATION ON FRESHWATER ECOSYSTEMS ON NORWAY[1]

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ABSTRACT

Extensive studies of precipitation chemistry during the last 20 years have clearly shown that highly polluted precipitation falls over large areas of Scandinavia, and that this pollution is increasing in severity and geographical extent. Precipitation in southern Norway, Sweden, and Finland contains large amounts of H^+, $SO_4^=$, and NO_3^- ions, along with heavy metals such as Cu, Zn, Cd, and Pb, that originate as air pollutants in the highly industrialized areas of Great Britain and central Europe and are transported over long distances to Scandinavia, where they are deposited in precipitation and dry-fallout.

In Norway the acidification of fresh waters and accompanying decline and disappearance of fish populations was first reported in the 1920's, and since then in Sørlandet (southernmost Norway) the salmon have been eliminated from several rivers and hundreds of lakes have lost their sport fisheries.

Justifiably, acid precipitation has become Norway's number-one environmental problem, and in 1972 the government launched a major research project entitled "Acid Precipitation - effects on forest and fish", (the SNSF-project). Studies of freshwater ecosystems conducted by the SNSF-project include intensive research at 10 gauged watersheds and lake basins in critical acid-areas of southern Norway, extensive surveys of the geographical extent and severity of the problem over all of Norway, and field and laboratory experiments on the effect of acid waters on the growth and physiology of a variety of organisms.

Large areas of western, southern, and eastern Norway have been adversely affected by acid precipitation. The pH of many lakes

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[1]SNSF-contribution FA 2/75

is below 5.0, and sulfate, rather than bicarbonate, is the major anion. Lakes in these areas are particularly vulnerable to acid precipitation because their watersheds are underlain by highly resistant bedrock with low calcium and magnesium contents.

Apart from the well-documented decline in fish populations, relatively little is known about the effects of acid precipitation on the biology of these aquatic ecosystems. Biological surveys indicate that low pH-values inhibit the decomposition of allochthonous organic matter, decrease the species number of phyto- and zooplankton and benthic invertebrates, and promote the growth of benthic mosses.

Acid precipitation is affecting larger and larger areas of Norway. The source of the pollutants is industrial Europe, and the prognosis is a continued increase in fossil-fuel consumption. The short-term effects of the increasing acidity of freshwater ecosystems involve interference at every trophic level. The long-term impact may be quite drastic indeed.

INTRODUCTION

Extensive studies of precipitation chemistry during the last 20 years have clearly shown that highly polluted precipitation falls over large areas of Scandinavia and that this pollution is increasing in severity and geographical extent (Barrett and Brodin 1955, deBary and Junge 1963, Odén 1968, Bolin et al. 1970, Ottar 1972). Precipitation in southern Norway, Sweden, and Finland contains large amounts of H^+, $SO_4^=$, and NO_3^-, ions along with heavy metals such as Cu, Zn, Cd, and Pb, that originate as air pollutants in the highly industrialized areas of Great Britain and central Europe and are transported over long distances to Scandinavia, where they are deposited in precipitation and dry-fallout (Odén 1968, Holt-Jensen 1972, Brosset 1973, OECD 1973, Rühling and Tyler 1973, Nordø 1975, Semb 1975). Only a small fraction of the H^+, $SO_4^=$, and NO_3^- deposited in southern Norway comes from local sources (Fredriksen 1973, Skogvold 1974, and Førland 1973) has firmly established that precipitation falling from air masses that have passed over industrial Europe has much higher concentrations of these ions than does precipitation from other air masses.

Because much of Norway is underlain by highly resistant granitic rocks with only a thin cover of unconsolidated glacial till and soil (Figure 1), the inland waters are characterized by low conductivities (less than 20 micromhos/cm), low concentrations of major ions, and extremely low buffer capacities. Thus large areas of Norway are quite vulnerable to inputs of pollutants from the atmosphere, and the potential damage to Norway's 300,000 lakes is indeed great.

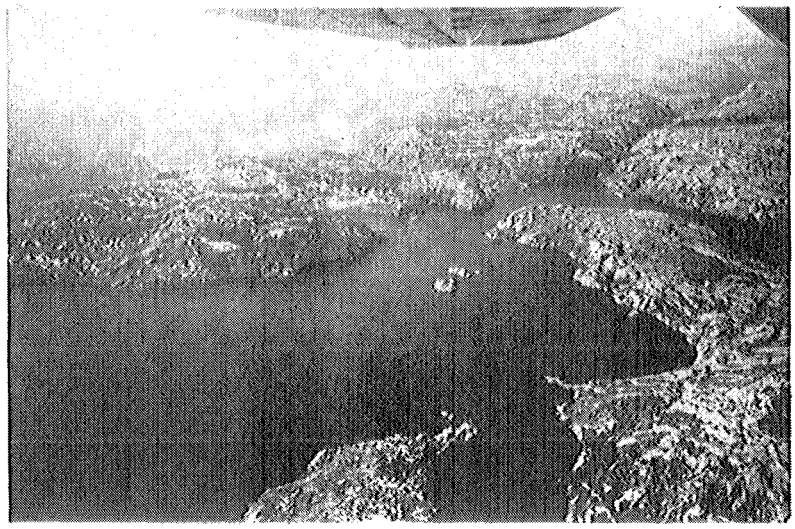

Figure 1. Air view of a mountainous area of southern Norway showing the typical thin soil cover, sparse vegetation and many lakes.

Acidification of fresh waters and accompanying decline and disappearance of fish populations was first reported in the 1920's (Sunde 1926, Dahl 1926), and since then in Sørlandet (southernmost Norway) the salmon have been eliminated from several rivers, and hundreds of lakes have become devoid of fish (Jensen and Snekvik 1972).

Justifiably, acid precipitation has become Norway's number-one environmental problem, and in 1972 the government launched a major research project entitled "Acid precipitation - effects on forest and fish", (the SNSF-project) (Overrein and Abrahamsen 1975). Studies of freshwater ecosystems conducted by the SNSF-project include intensive research at 10 gauged watersheds and lake basins in critical acid-areas of southern Norway, extensive surveys of the geographical extent and severity of the problem over all of Norway, and field and laboratory experiments on the effect of acid waters on the growth and physiology of a variety of organisms (Table 1).

EFFECTS ON FRESH WATERS

The impact of acid precipitation on the chemistry and biology of Norwegian freshwaters is well illustrated by the results from a survey of 155 lakes conducted in October 1974. To obtain a statistically valid sample of lakes in Southern Norway, a 10 × 10 km block was selected at random from each square of a 50 × 50 km grid covering Norway south of 63° N latitude (Figure 2). Two small lakes were chosen from each block under the conditions that they have minimal local sources of pollution and that they be large enough to permit access by light float-plane (Wright and Lysholm 1974).

Table 1. Research on aquatic ecosystems conducted by the SNSF-project in 1975.

	LAKES			RIVERS	
	regional surveys	intensive studies	sediment studies	regional surveys	intensive studies
CHEMISTRY					
major ions	+	+	+	+	+
nutrients	+	+	+		+
heavy metals	+	+	+		+
BIOLOGY					
decomposers		+	+		+
bacteria		+	+		
phytoplankton	+	+	+		
benthic algae					+
macrophytes		+			
zooplankton	+	+			
benthic fauna	+	+		+	+
fish	+	+		+	+

At each lake water samples were collected, and at 57 lakes the phyto- and zooplankton, and zoobenthos were sampled. The physiography, vegetation, and geology of the lake watersheds were described on the basis of field observations, photographs, and maps. This survey is similar to the study of 50 lakes near the smelter at Sudbury, Ontario described by Conroy et al. (1974), and to the survey of 400 lakes in southwest Sweden reported by Almer et al. (1974).

CHEMISTRY

Isopleth maps of the concentrations of various components in the surface water samples show that the chemistry of Norwegian lakes is strongly influenced by inputs from the atmosphere. The map for chloride, for example, clearly reflects its seawater source and its deposition in orographic rainfall (Figure 3). The concentrations of sulfate also reflect a seawater source for this ion (Figure 4), but the high sulfate concentrations in lakes along the south and southwest coasts are the result of an atmospheric input of sulfate in excess of that associated with the chloride (Figure 5). The source of this excess sulfate is most certainly anthropogenic. Air masses moving from industrial Europe transport sulfur compounds over long distances, and these pollutants are removed in orographic precipitation along the mountainous coastal areas of Norway (Nordø 1975).

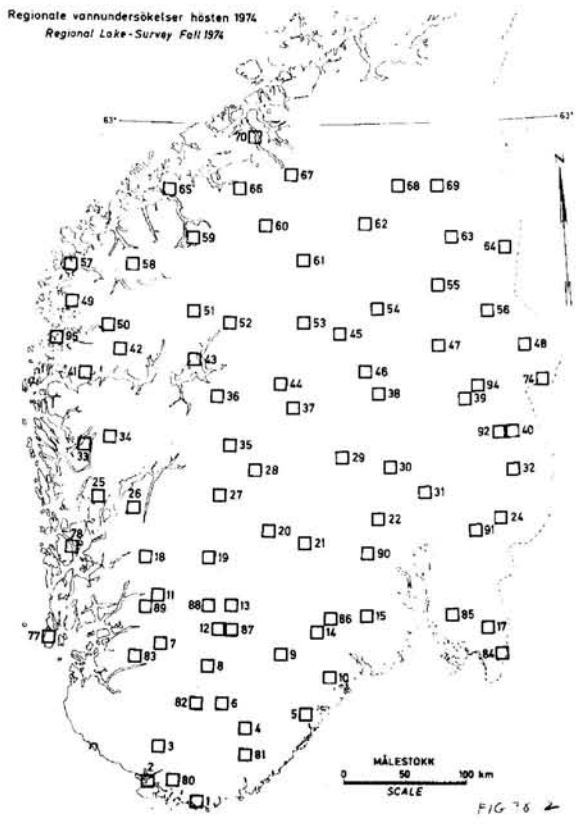

Figure 2. Location map of the 10 × 10 km blocks selected at random from each square of the 50 × 50 km grid (from Wright and Lysholm 1975).

The isopleth map of pH thus also reflects the very great impact of acid precipitation on lakes in large areas of Norway (Figure 6). Whereas unpolluted lakes in granitic basins in central Norway have pH values above 6.0 and bicarbonate is the major anion, lakes in large areas of western, southern, and eastern Norway have pH values below 5.5; many lakes in Sørlandet and southeastern Norway are below 5.0. As a result of the atmospheric loadings of sulfuric acid, sulfate has replace bicarbonate as the major anion.

The isopleth maps for other components demonstrate additional effects of acid precipitation. For example, the aluminum map (Figure 7) shows that the acidic, high-sulfate lakes also have unusually high Al concentrations. Since precipitation contains very little Al, the Al in the lake waters must be supplied from the watersheds, probably due to the washout of Al by acid precipitation. Because the solubility of Al is negligible at pH greater than 5.0 (Norton 1975), the mobilization of Al indicates that the soil pH has been depressed to levels below 5.

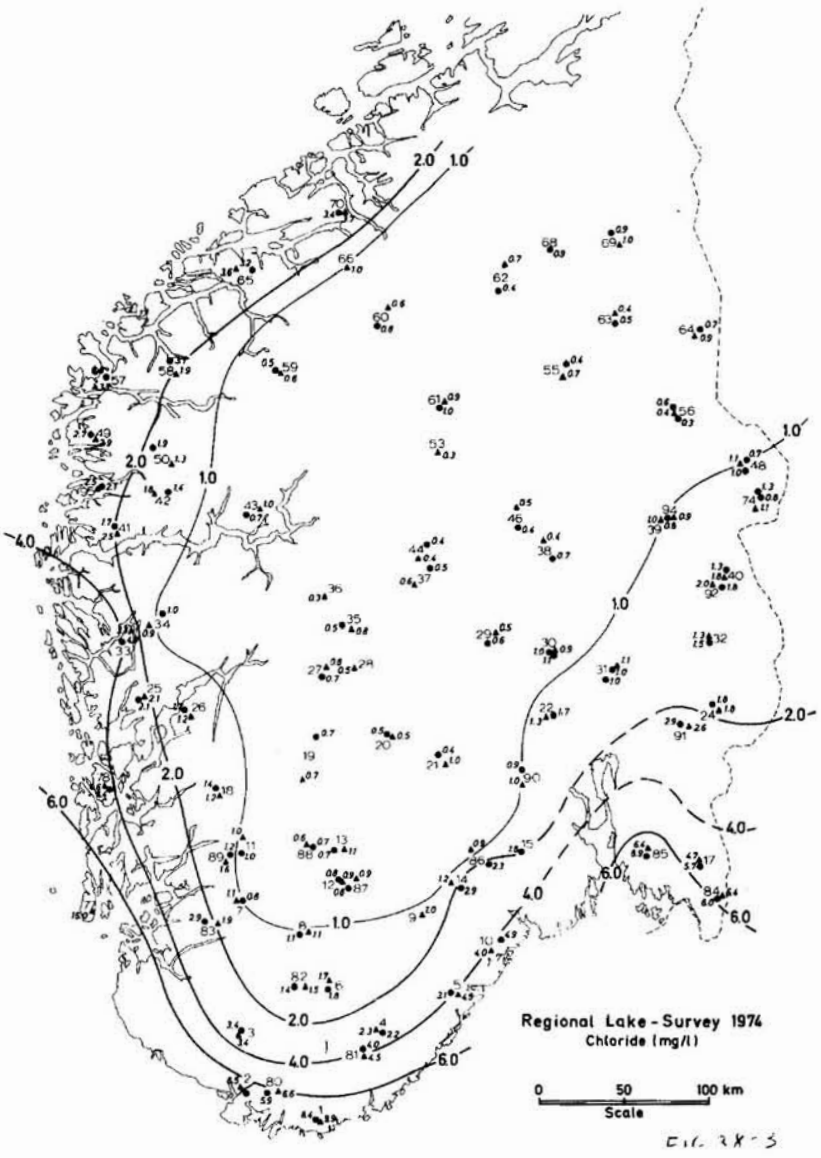

Figure 3. Isopleth map Cl (mg/l) in surface-water samples (from Wright and Lysholm 1975).

Although the washout of alkaline earths (Ca + Mg) by acid precipitation in Norway has been reported (Overrein 1972, Henriksen 1972), washout of Al represents the next, more severe stage in the alteration of soil chemistry (Malmer 1973).

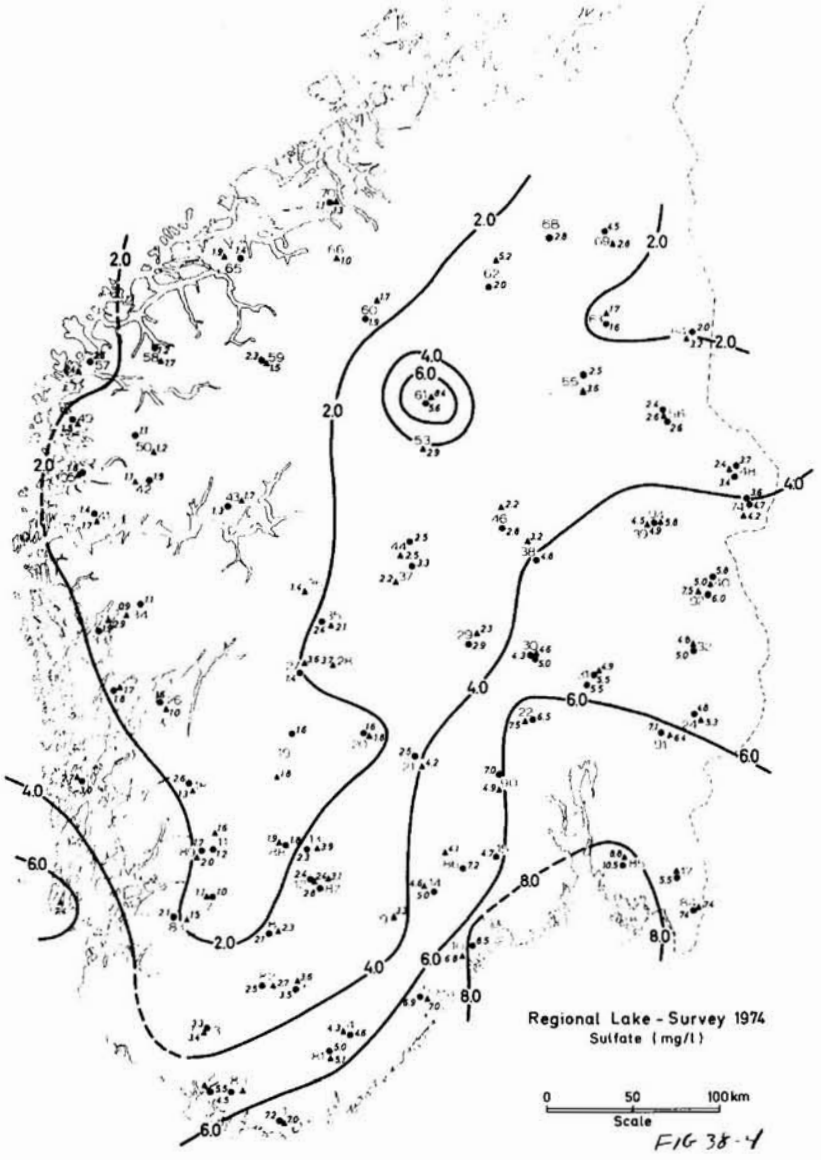

Figure 4. Isopleth map of SO_4 (mg/l) in surface-water samples (from Wright and Lysholm 1975).

BIOLOGY

The altered water chemistry in lakes and rivers of Norway appears to have affected organisms at every trophic level in these ecosystems. Experiments underway in the SNSF-project indicate that at low pH levels bacterial decomposition is retarded while fungal growth increases on aquatic sediments. The decomposition of cellulose is reduced by 50% when the pH is lowered from 7.0 to 5.2 (Traaen 1974). Inhibition of decomposition results in an increased accumulation of organic debris and a decreased rate of nutrient recycling. Organic debris and fungal mats

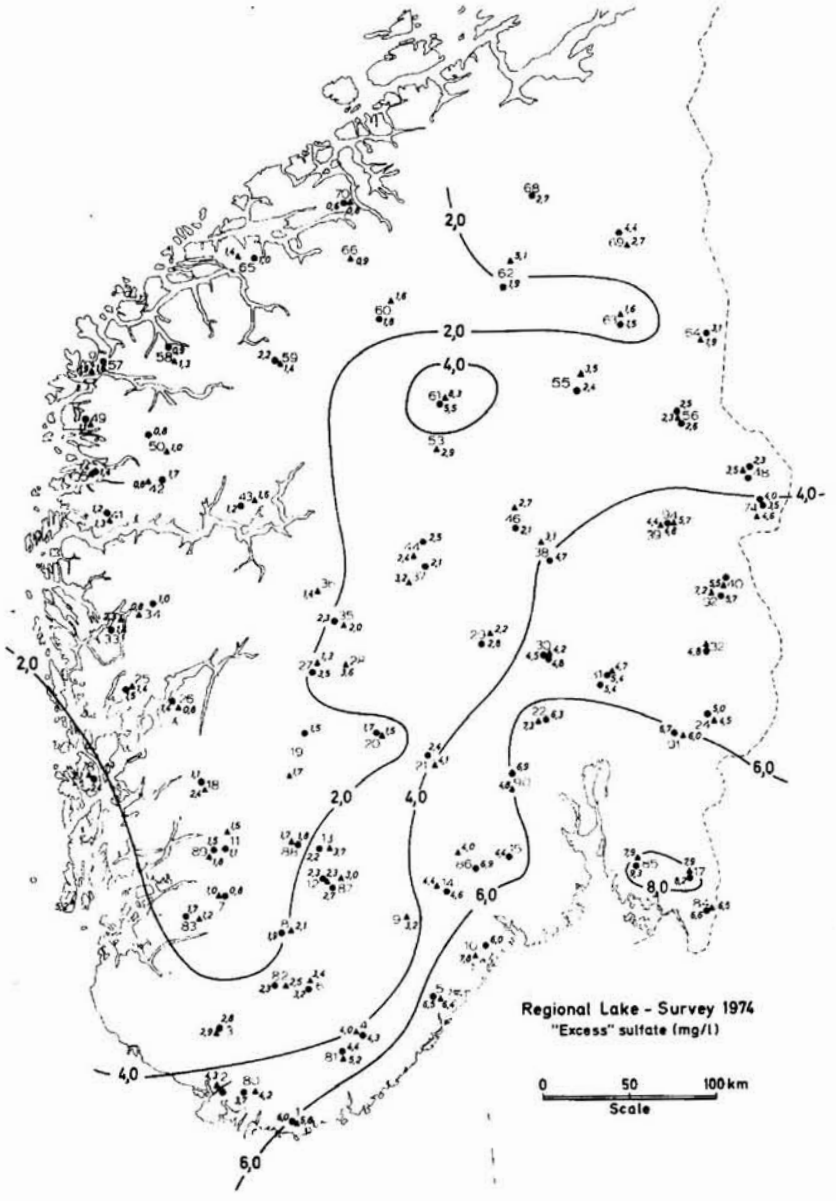

Figure 5. Isopleth map of excess-SO_4 (mg/l) in surface-water samples.

cover the lake sediments and thereby apparently inhibit nutrient exchange with the overlying water (Grahn et al. 1974). Since the nutrient recycling rate is an important control of the primary production in many lakes, reduced recycling in acid lakes would contribute to the "self-accelerating oligotrophication" proposed by Grahn et al. (1974), Hultberg (1975), and Grahn (1975).

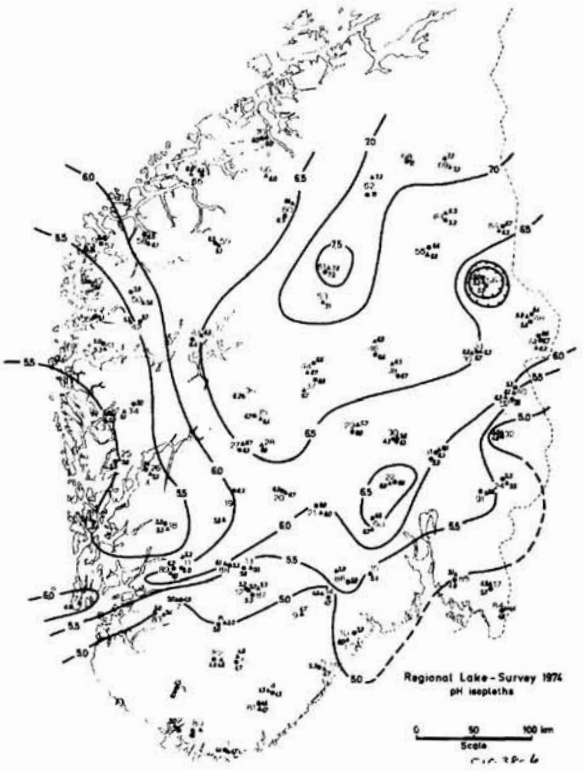

Figure 6. Isopleth map of pH in surface-water samples (from Wright and Lysholm 1975).

Acidification of lake waters alters phytoplankton species-composition and abundances. Analysis of phytoplankton samples from 57 lakes of the regional survey indicates that lakes with pH less than 6.0 have fewer species and, in particular, that the Chlorophyceae (green algae) are affected (Figure 8). Almer et al. (1974) also found decreased species numbers and altered species-compositions in a survey of 115 lakes in southwestern Sweden.

The number and type of zooplankton species also are related to pH; at a low pH fewer species are present (Figure 9). There is also evidence from investigations in Sweden that *Daphnia* species are absent in low-pH lakes (Almer et al. 1974, Hanson 1974).

Preliminary results from the regional lake-survey also indicate that the benthic fauna is sensitive to pH, with again fewer species present at pH levels below 6. Studies on the distribution of *Gammarus lacustris*, another aquatic invertebrate, indicate that this important food source for fish is rarely found in waters with pH below 6.0 (Økland 1969, 1970). Data from England show that in streams with pH below 5.7 the insect fauna is greatly impoverished (Sutcliffe and Carrick 1973).

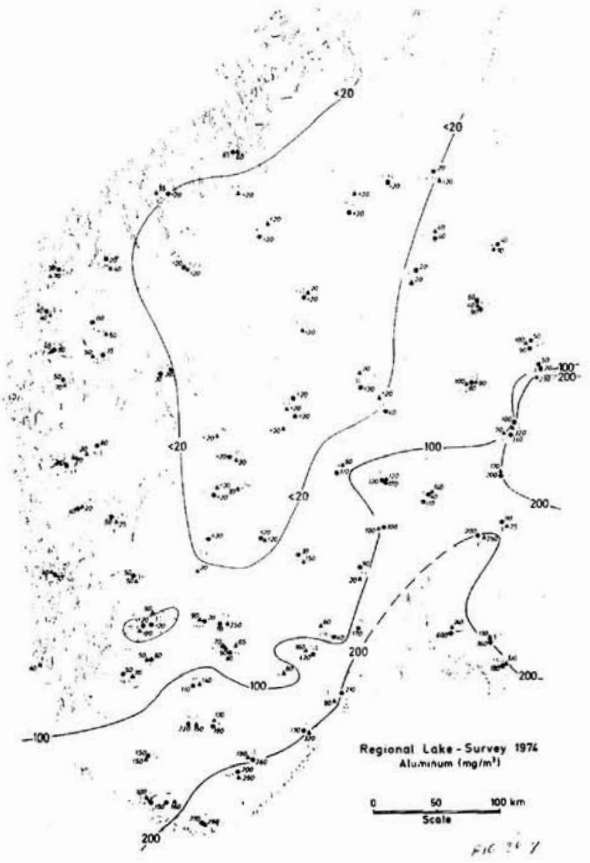

Figure 7. Isopleth map of Al (mg/m^3) in surface-water samples.

Information on the impact of acidification on fresh-water biology is thus mostly of a descriptive nature, and as Almer et al. (1974) points out, very little is known about the effect of low pH on the morphology, physiology, and nutrition of phyto- and zooplankton.

FISH

A great deal, however, is known about fish, primarily because of their economic and recreational value (cf. EIFAC 1968). Dahl (1926) first reported the adverse effects of acidification on fish in Norway, and in 1959 Dannevig (1959) suggested that acid precipitation was the cause of the increased acidity and adverse effects on fish.

Salmon-catch records for 79 Norwegian rivers recorded since the late 1800's show that the catch from 9 rivers in Sørlandet declined rapidly between 1885 and 1925 and was essentially zero by 1968 (Jensen and Snekvik 1972). The salmon catch for the entire country, however, shows

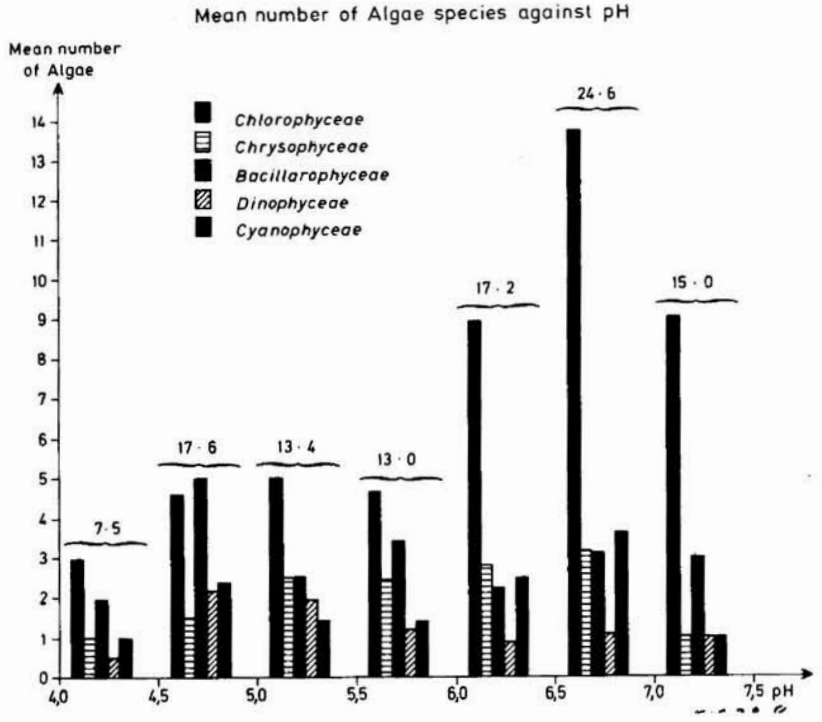

Figure 8. Mean number of algal species against pH in samples from 57 lakes of the regional lake-survey

no such decrease (Figure 10). These 9 rivers are now quite acidic (pH 4.5-5.5), and their acidity is still increasing (Henriksen 1972). There can be little doubt that acid precipitation is the cause (Hagen and Nordby 1967). The dissappearance of salmon from these rivers is not usually marked by massive fish kills (although fish kills were reported in 1911, 1921, 1948 and most recently 1975), but rather by the failure of reproduction and recruitment (Jensen and Snekvik 1972). Indeed laboratory experiments indicate that acid water first affects fish eggs and fry; the lower limit for normal reproduction is 5.0-5.5 for salmon, 4.5-5.0 for sea trout, and about 4.5 for brown trout (Jensen and Snekvik 1972).

Fish have also been disappearing from lakes in Sørlandet because of inputs of acid precipitation. Information on the fish-status of 2083 lakes in Sørlandet was gathered in 1971 by E. Snekvik and K. W. Jensen (Norwegian Directorate for Game and Fresh-Water Fish) from local fishery authorities. Of these lakes, 741 now have no fish, and 477 have become devoid of fish since 1940 (Jensen and Snekvik 1972). pH data for 516 of these lakes show clearly that at pH levels below about 5.5 the fish are either entirely absent or present only in reduced numbers (Figure 11).

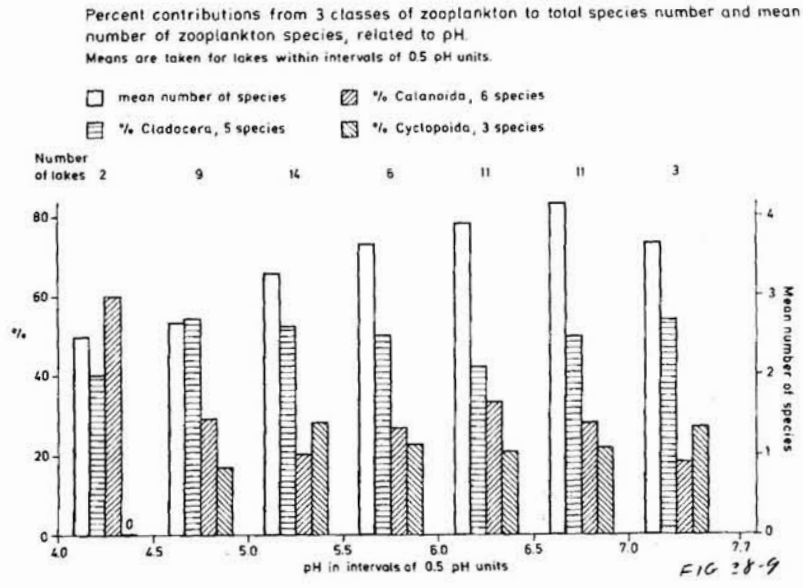

Figure 9. Percent contributions from 3 classes of zooplankton to total species number and mean number of zooplankton species, related to pH. Data from 57 lakes of the 1974 regional lake-survey.

Acid precipitation has resulted in the decline and loss of fish populations in other areas of Norway as well. A preliminary survey of the fish status for lakes over all of southern Norway was conducted during 1974 as part of the SNSF-project. Lakes with no fish or only sparse populations occur over large areas of western and east-central Norway as shown in Figure 12, and these lakes are acid, generally below pH 5.5 (Muniz 1975).

The disappearance of fish from lakes as pH decreases often follows a characteristic pattern. Long-term increases in acidity apparently first interfere with reproduction and spawning such that the remaining adult fish increase in size and age until the only fish left are large and old. This pattern has been described in Norway (Jensen and Snekvik 1972), in Sweden (Hultberg and Stenson 1970, Almer et al. 1974, Andersson et al. 1971, Almer 1972 a, Almer 1972 b), in Canada (Beamish 1975), and in the United States (Schofield 1975).

Another mode of fish mortality is caused by large, rapid changes in pH. Sudden drops in pH cause severe physiological stress that may produce fish kills at pH levels *above* those normally toxic to adult fish. Resistance to such shocks is also species dependent. Sudden drops in pH are often observed in the early spring when the pollutants accumulated in the snowpack are released in high concentrations during the first phases of melting (Hagen and Langeland 1973, Hultberg 1975).

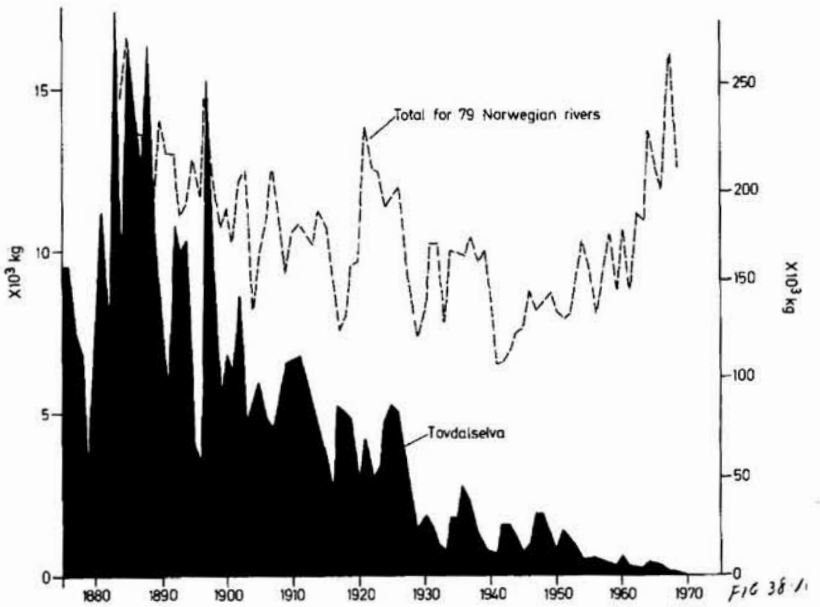

Figure 10. Salmon-catch statistics for 79 Norwegian rivers and for Tovdalselva, an acidic river in Sørlandet, over the period 1880-1970 (data from Sndkvik 1970).

SUMMARY

The precipitation over much of southern Scandinavia contains large amounts of H^+, $SO_4^{=}$, NO_3^- that originate as air pollutants in the highly industrialized areas of Great Britain and central Europe. Because much of Norway is underlain by highly resistant granitic rocks with only a thin cover of unconsolidated glacial till and soil, the inland waters have extremely low buffer capacities and are thus quite vulnerable to inputs of atmospheric pollutants.

The continually growing inputs of acidic pollutants have resulted in major changes in the chemistry of lakes and rivers in southern Norway. Regression analysis on 10 years of data from several rivers in Sørlandet (southernmost Norway) show significant decreases in pH and increases in conductivity and total hardness, the latter due to the washout of Ca and Mg from the watersheds. The inputs of sulfate have resulted in the replacement of bicarbonate by sulfate as the major anion in many lakes.

High concentrations of aluminum in acid lakes in southernmost Norway suggest that pH levels in the watershed soils have dropped below 5, resulting in the mobilization and washout of Al.

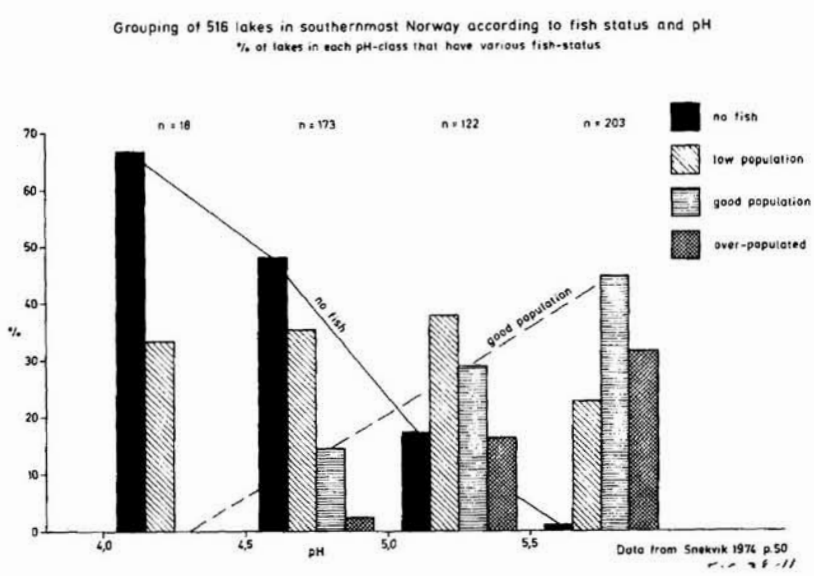

Figure 11. Grouping of 516 lakes in southernmost Norway according to fish status and pH. Percent of lakes in each pH-class that have various fish-status (data from Snekvik 1974).

Information from the survey of 57 lakes in southern Norway indicates that increasing acidity results in a decline in the number of phytoplankton species, and in particular, a decrease in the abundance of green algae. The composition of zooplankton and zoobenthos species are similarily affected. These decreases begin to occur at about pH 6.0.

Data on the annual salmon catch, pH, and success of fish hatching indicate that acidic precipitation began affecting fish as early as the 1920's. Since then the salmon have been eliminated from many major rivers, and thousands of lakes have become devoid of fish (Jensen and Snekvik 1972). Fish are eliminated from lakes and rivers because of gradual increases in acidity that cause interference with reproduction and spawning. Sudden drops in pH, especially during snowmelt cause severe physiological stress and often death in fish. The tolerance of fish to both long-term and short-term changes in acidity is species dependent.

Acid precipitation has affected large areas of Norway. These adverse effects are occuring over greater geographical areas with both increasing frequency and severity. The source of the pollutants is industrial Europe, and since the prognosis is for a continued increase in fossil-fuel combustion, the situation will continue to deteriorate. The short-term effects of the increasing acidity of freshwater ecosystems involve interference at every trophic level. The long-term impacts may be quite drastic indeed.

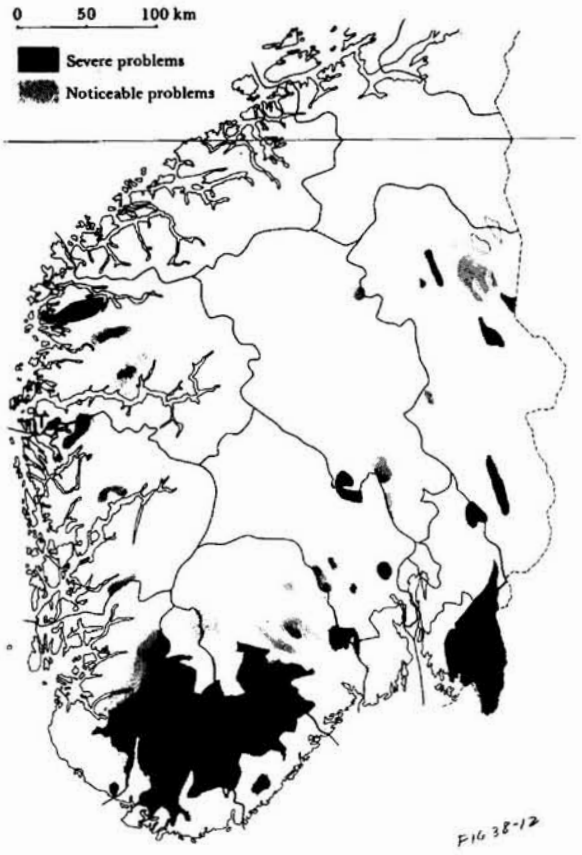

Figure 12. Fisheries status in lakes of southern Norway showing areas that have been moderately and severely affected by acid precipitation (from Muniz 1975).

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LAKE ACIDIFICATION IN THE ADIRONDACK MOUNTAINS OF NEW YORK: CAUSES AND CONSEQUENCES

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ABSTRACT

Current and historic geographic distributions of acidity in Adirondack lakes were examined in relation to regional edaphic, climatic, and physiographic features. Acid conditions are currently predominant in high elevation drainage lakes having small watershed/surface area ratios. Comparable levels of acidity were found only in small seepage lakes and bog ponds during the 1930's. Increased acidity in the high elevation lakes can be quantitatively related to the occurrence of excess acid forming anions of atmospheric origin. Knowledge of this stoichiometric relationship and the morpho-edaphic factors which regulate cation supply permits modeling of the acidification process and prediction of the consequences of changes in precipitation chemistry, both in terms of variations in lake acidity and in terms of the numbers and location of lakes likely to be affected. Recent surveys suggest that fish populations have been adversely affected by acidification in approximately 75% of the high elevation lakes. Effects range from complete extinction of populations to alterations in density, size structure, and growth rates. Interspecific and intraspecific differences in acid tolerance exhibited by Adirondack fishes are examined in relation to factors such as life history, size, age, and secondary water quality parameters. Management alternatives are discussed in relation to the problem of lake acidification.

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ACIDIFICATION OF LAKES IN CANADA BY ACID PRECIPITATION AND THE RESULTING EFFECTS ON FISHES

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ABSTRACT

There are several areas in Canada that could receive acidic fallout. Only in the area that produces Canada's largest single source of sulfur oxides has there been appreciable research. In the Sudbury region of Ontario, Canada, fallout of sulfur oxides has been shown to be responsible for damage to vegetation, lakes and fishes.

The acidic fallout has been shown to effect a rate of acidification in many lakes that over several decades has resulted in the extinction of many species of fishes. Fishes exhibit profound differences in acid tolerance but show some similarities in their physiological response to levels within the range of their individual susceptibilities. Prior to extinction most females of a particular species did not release their ova to be fertilized. The failure of females to spawn was coincident with an inability to maintain normal serum calcium levels. In some species growth was reduced despite an adequate supply of preferred food items. High concentrations of acid were considered to be the principle factor stressing the fish populations. Elevated concentrations of some heavy metals may add to the stress caused by high concentrations of acid.

As a result of damage in one area to trees, lakes and fishes by the fallout of sulfur oxides the Canadian Government started court proceedings against the companies alleged to be responsible for the pollution. After 4 years the suit was settled out of court just days before the trial was scheduled to commence.

It is the intention of this paper to discuss the effects of acid precipitation on Canadian lakes and fishes. However, it is only in the Sudbury, Ontario area that such effects have been well documented. The principle source of acid entering the Sudbury lakes comes from local nickel mining and smelting industries. In 1969 it was estimated that 2.6 million metric tons of sulfur oxide were released into the atomsphere from the Sudbury area (Beamish and Harvey, 1972). In 1970 the emissions were estimated to be equivalent to half of Canada's total emissions (EPS, 1973) or about 10% of the total United States of America emissions (Beamish, 1974a). In fact the Sudbury area may have the dubious distinction of being the largest single source of sulfur dioxide in the world. The second largest point source (about 700,000 metric tons) in Canada is at Noranda, Quebec about 138 km north of Sudbury (EPS, 1973) (Figure 1). Excluding the major cities of Toronto

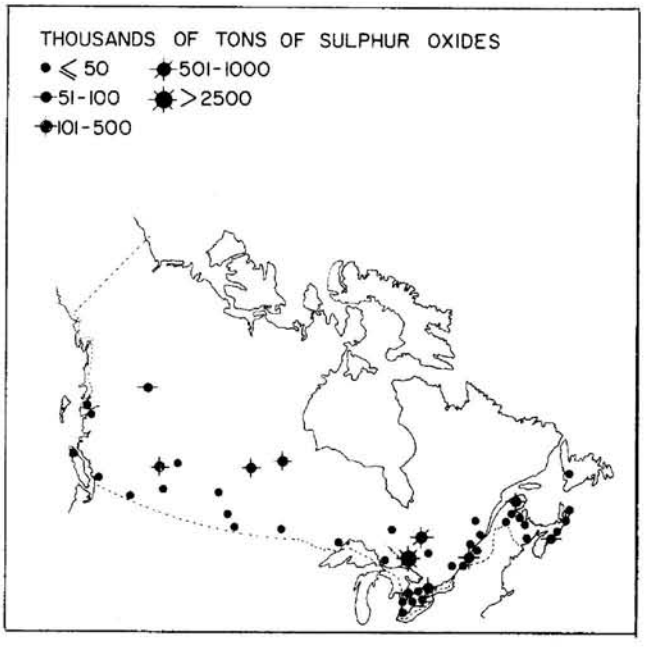

Figure 1. Summary of principle sources of sulfur oxide emissions in Canada (from EPS, 1973).

and Montreal and the important emission areas of Sudbury and Noranda there are only four or five other point sources ranging in annual emissions of 200,000 to 400,000 metric tons that can be considered to be potential sources of acid precipitation to nearby lakes. In one of these areas, near Flin Flon, Manitoba a survey in 1973 of 27 lakes in the vicinity of the smelter revealed only one lake with a pH below 6.5 (Van Loon and Beamish, 1976). The one acid lake (pH 4.0-5.0) received acid effluent in the spring from a holding area. At present there is no other information that identifies other point sources of sulfur dioxide in Canada as causing the acidification of lakes.

Similarly there is no published study at present that identifies long-range transportation of acid (from many point sources) as affecting Canadian lakes. Several studies have reported that fallout of acid has occurred and with hindsight long-range transport of acid may have been involved. On April 9, 1970 Barica and Armstrong (1971) recorded a snow at the Experimental Lakes Area (E.L.A.), in northwestern Ontario that contained excessive particulate material and sulfate concentrations five to 10 times greater than measured in previous samples. Since there are no major industrial areas in the vicinity of E.L.A. it appears that this fallout could have originated somewhere in the north central United States. Precipitation may also be the principle source of nutrients to the E.L.A. Lakes (Schindler, 1971). In Halifax County, Nova Scotia acid lakes were found (Gorham, 1957) in which the acidity could not be completely accounted for by natural processes. Gorham felt that rain was a major source of SO_4 for some of these lake waters as "suggested by recent analyses of Herman (unpublished), who found an average of 0.96 ppm total sulfur, equivalent to 2.9 ppm SO_4, in rain collected over a 2-year period at the Dominion Experimental Station, Kentville, Nova Scotia." This is one of the earliest records of acid precipitation in Canada and it is possible that the source of this acid was either from the Halifax area or from combined areas on the east coast of North America.

ACID PRECIPITATION IN THE SUDBURY AREA

The effects of acid fallout on plants and soils in the Sudbury area have been demonstrated in numerous studies over the past 30 years (McCallum, 1944; Linzon, 1958, 1966, 1971; Gorham and Gordon, 1960a, 1960b; McGovern and Basillie, 1972, 1973; Whitby and Hutchinson, 1974; Le Blanc et al., 1972; Stokes et al., 1973; and others). However, the effects of Sudbury emissions on lakes have not been as extensively studied. Studies undertaken in the early 1960's did show a deterioration in water quality of lakes and ponds in the immediate Sudbury area (Gorham and Gordon, 1960a, 1963) and recently lakes located in the La Cloche Mountains some 65 km southwest of the smelters have been found to be extremely acidic (Beamish and Harvey, 1972).

There is good evidence that indicates the Sudbury smelters are the principle source of acid entering the La Cloche Mountain lakes. As previously mentioned it is known that extremely large quantities of SO_2 are released annually into the atmosphere around Sudbury. A summary of the average percentage of wind hours as recorded at Sudbury, Ontario from 1961 to 1973 (Department of Transport, monthly record of meteorological observations in Canada) indicates the prevailing wind directions are northeast and southwest (Figure 2a). By comparing the mean ground

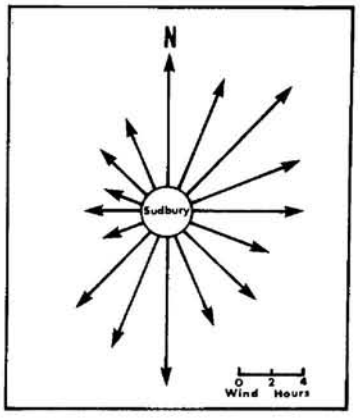

Figure 2a. Average percentage of time wind blew in each of 16 compass directions. Length of arrows indecates the average percentage of wind-hours that were recorded for each direction from 1961 to 1972. Data obtained from Department of Transport, Monthly meteorological observations in Canada.

sulfur dioxide concentrations from 1964 to 1968 (Figure 2b redrawn from Dreisinger and McGovern, 1970) it is apparent that sulfur dioxide falls out in decreasing concentrations from the smelters in the direction of the prevailing winds. A similar fallout pattern occurs for nickel, iron and copper (McGovern and Basillie, 1973; Kramer, 1973a). It is also known that the Sudbury smelters release large quantities of heavy metals into the atmosphere. Stack emission reports prepared by one of the companies indicate that approximately 14,500 tons of iron, 2,000 tons of nickel and 1,800 tons of copper have been released annually into the atmosphere over the last decade (Falkowski, 1973).

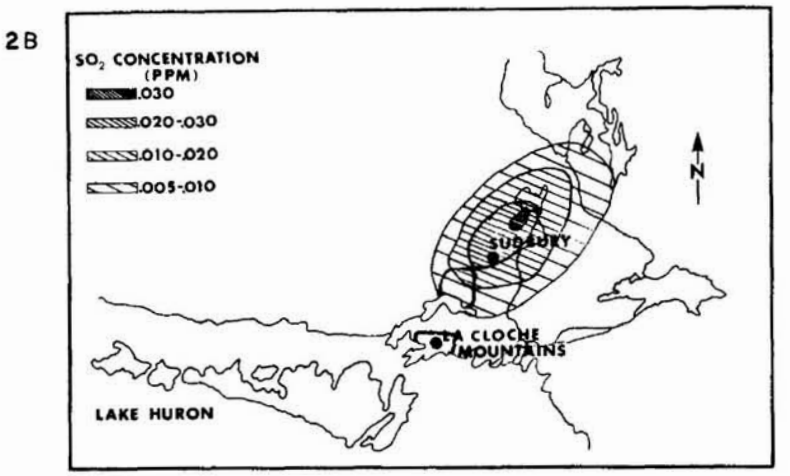

Figure 2b. Average ground concentrations of sulfur dioxide in the Sudbury area from 1964 to 1968 (Figure reproduced from Dreisinger and McGovern, 1970).

A study of the dispersion of the Sudbury smelter plumes showed the plumes from the four main smelters combined to form a plume approximately 25 km wide and contained sulfur dioxide concentrations ranging from 0.3 to 0.02 ppm at a distance of 40 km from Sudbury (Whaley and Lee, 1971). Whaley and Lee (1974) used the plume dispersion study to show that high ground-level sulfur dioxide concentrations measured at a site 36 km southwest of the Sudbury smelters during fumigation conditions could be attributed to Sudbury smelter emissions. These authors computated ground-level sulfur dioxide levels using the plume dispersion study and Sudbury smelter production figures, and were able to obtain a good correlation between observed and predicted ground-level sulfur dioxide concentration over the period 1961-1971.

In the immediate Sudbury area the pH of precipitation has been reported to average about 4.5 with an extreme low of 3.2 (Kramer, 1973a). In the La Cloche Mountains, the average pH of 18 precipitation events from 1972 to 1973 was 4.3 (Beamish and Van Loon, 1975) and the average pH of monthly precipitation collections for this period was 4.4. The lowest pH measured was 2.9 (Beamish and Harvey, 1972). As mentioned, precipitation in the Sudbury area also contains high concentrations of nickel and copper (Beamish and Van Loon, 1975; Kramer, 1973b). Kramer (1973b) claimed that most of northern Ontario has been subjected to rates of fall of nickel that are 10 times the rate observed in the Continental United States. The consistent observation that substances or byproducts of substances known to be emitted from the smelters, occur in precipitation; the evidence that concentrations decrease with distance from the smelters in the direction of the prevailing winds; the

calculations showing that the plume disperses over great distances and ground-level concentrations can be related to concentrations of sulfur dioxide in the plume; the effective "labelling" of this plume by the high levels of nickel emitted by the industries and the anomalously high nickel concentrations in precipitation leave little doubt that fallout of substances from the plume is occurring in the Sudbury area.

It can be shown that this fallout has altered the water quality of lakes in the Sudbury area. Harvey (1975a) has measured the sulfate concentration of over 100 lakes and found concentrations were highest close to the smelters and decreased with distance from the smelters. Sulfate ions were partially balanced to hydrogen ions indicating that part of the sulfate that was entering the lake from the atmosphere was in the form of sulfuric acid. A survey of 150 lakes in the La Cloche Mountain area indicated that some 33 lakes had a pH of 4.5 or less and one-half of the lakes had a pH of 5.5 or lower (Beamish and Harvey, 1972). From a study of the pH change in one lake over a period of 5 years it was shown that the lake was acidifying at a rate of approximately 0.13 pH units per year (Beamish et al., 1975a). This compares with estimated average decrease of 0.16 pH units for 22 La Cloche Mountain Lakes for which determinations measured in 1971 could be compared to readings taken 10 years earlier (Beamish and Harvey, 1972).

A detailed examination of the precipitation loading of acid to a small lake in the La Cloche Mountains from 1972 to 1973 showed that this 21 ha lake received approximately 2100 kg of sulfuric acid from precipitation in 1972, that would be capable of depressing the pH below its January 1972 value (Beamish and Van Loon, 1975). A titration curve, calculated using lake water obtained during an earlier period of higher pH, predicted that the addition of this much acid would reduce the pH of the lake from 5.2 to 4.8. The actual measured change was from 5.2 to 4.7. In 1973, 600 kg H_2SO_4 were added to the lake from precipitation that would be capable of depressing the pH below the January 1973 concentration. The titration curve for the lake predicted a pH change from 4.8 to 4.74. By January 1973, the lake pH had risen from 4.7 to 4.8 and there was no net change in pH throughout the year. Thus the pH of this lake during this 2-year period was closely related to the acid content of the precipitation.

This study and others (Beamish, 1974a; Beamish et al., 1975a, 1975c) also indicated that lakes in the La Cloche Mountains contained high concentrations of nickel and copper when compared to concentrations measured in lakes remote from major areas of industrialization. The remote area used for a comparison was part of the Canadian Shield as were the La Cloche Mountain lakes (Beamish et al., 1975b).

It has been shown that the Sudbury plume was responsible for the deposition of sulfur dioxide, acid and nickel. It has also been shown that many La Cloche Mountain lakes were acid, contained elevated concentrations of nickel and probably responded to atmospheric loadings of acid as closely as the one lake studied. Therefore, there can be little

doubt that industry in Sudbury has been a major contributor to the atmospheric pollution that has altered the water quality of these lakes.

CHANGES IN WATER CHEMISTRY

Changes in water chemistry of Canadian lakes as a result of atmospheric inputs of acid have been described in only a few reports. Also it is difficult to examine changes in lake chemistry when the lake chemistry was not described before the change occurred. However, by comparing the chemistry of acidified lakes with the chemistry of unpolluted lakes from a similar geological area it is possible to gain some insight into the changes that have occurred.

As might be expected, sulfate concentrations have been shown to be high in many acidified lakes (Gorham and Gordon, 1960a; Harvey 1975a; Beamish and Van Loon, 1975). The high sulfate concentrations were found in association with low pH and by balancing anions and cations it was possible to demonstrate that part of the sulfate ion is balanced with hydrogen ion, indicating the pH results from the presence of sulfuric acid (Beamish, 1974a). A comparison of the major ions in four of the acid lakes with unpolluted lakes (Table I) (see also Beamish, 1974a) indicated that the ionic composition was similar except for hydrogen and sulfate ions. Hydrogen ions were two to three orders of magnitude greater in the acidic lake than in the E.L.A. lakes and sulfate represented approximately 90% of the anions compared to an average of about 40% for the E.L.A. lakes.

Calcium concentrations were slightly higher in the acid La Cloche Mountain lakes (average 2.6 mg/ℓ, Table II) than the average (2.0 mg/ℓ) for the 102 E.L.A. lakes (Tables I). Gorham and Gordon (1960) reported that calcium in ponds near Sudbury smelters appeared to decrease between pH 6 and pH 5 while below pH 5 calcium concentrations appeared to increase. There is some historic data of unknown analytical quality for the La Cloche lakes that suggests the calcium concentrations were at least double their present values. The historic data is to some extent corroborated by the observation that the less acidic Kakakise Lake (Table II) has a calcium concentration almost double the values of the nearby acid lakes. Since calcium appears to be very important to the survival of fishes (Beamish et al., 1975) more information concerning the effect of acidification on the calcium content of lakes may be necessary for a thorough understanding of the response of fishes to acidification.

It is apparent that bicarbonate alkalinity (as mg/ℓ $CaCO_3$) will be greatly reduced in any lake of low pH. Alkalinity of the acidic La Cloche Mountain Lakes was less than 0.5 mg/ℓ which was at the limit of detection. By comparison alkalinity of the E.L.A. lake averaged 11.4 mg/ℓ (Table I).

Table I. Chemical composition of four acid lakes and non-polluted lakes in a remote area of N.W. Ontario. For details of water chemistry see references. Range in brackets.

	O.S.A.*	Muriel*	George**	Lumsden***	E.L.A.	102 lakes N.W. Ontario****
pH	4.5 (4.4-4.9)	4.7 (4.5-4.8)	5.0 (4.8-5.3)	4.8 (4.7-5.3)		6.5
Sulfate mg/ℓ	15 (14-17)	15 (14-15)	14.3 (12-16)	10.7 (10.0-12.6)		3.8
Chloride mg/ℓ	1 (<1-1)	<1 (<1-1)	1.0 (0.6-1.6)	0.7 (0.5-1.2)		0.8
Sodium mg/ℓ	0.6 (0.6-0.8)	0.6 (0.6-0.7)	0.8 (0.7-1.0)	0.4 (0.4-0.8)		0.9
Calcium mg/ℓ	3.2 (2.9-3.7)	3.4 (3.1-3.4)	3.2 (1.8-4.0)	2.2 (1.4-2.9)		2.0
Magnesium mg/ℓ	0.9 (0.7-1.0)	0.9 (0.7-0.9)	1.0 (0.9-1.6)	0.7 (0.5-1.0)		0.6
Potassium mg/ℓ	0.4 (0.3-0.5)	0.3 (0.3-0.4)	0.5 (0.3-0.6)	0.3 (0.2-0.4)		.0.3
Hardness (as $CaCO_3$) mg/ℓ	11 (10-14)	11 (11-12)	12.3 (7.9-16.4)	8.4 (5.6-11.3)		7.5
Total dissolved solids mg/ℓ	23 (7-39)	16 (15-16)	28 (10-49)	18 (10-25)		-
Total suspended solids mg/ℓ	1 (0-2)	1 (0-1)	<1 (<1-4)	<1 (< 1-4)		2
Bicarbonate alkalinity (as $CaCO_3$) mg/ℓ	0.5	<0.5	<0.5	< 0.5		10
Conductivity μmho/cm²	48 (46-53)	32 (8-47)	40 (35-45)	32 (27-35)		19
Iron μg/ℓ	23 (18-29)	40 (34-46)	27 (7-45)	35 (13-77)		143
Nickel μg/ℓ	11 (8-13)	12 (10-15)	10 (5-15)	8 (6-9)		<3
Copper μg/ℓ	4 (2-6)	2 (2-4)	2 (1-8)	4 (2-16)		2
Zinc μg/ℓ	36 (30-48)	29 (25-31)	24 (8-45)	32 (17-35)		<1
Cadmium μg/ℓ	<1	<1	<0.5 (<0.5)	0.4 (0.2-0.5)		<0.1
Lead μg/ℓ	4 (2-6)	1 (0-3)	<2 (<2)	2 (1-3)		<1
Manganese μg/ℓ	-	-	220 (160-260)	258 (210-310)		3

*Beamish, 1974a.

**Beamish et al., 1975a.

***Beamish and Van Loon, 1975.

****Beamish et al., 1975b.

Heavy metal concentrations in the La Cloche lakes appeared to be greatly altered during the acidification process. As previously mentioned nickel and to a lesser extent copper concentrations were higher in the acidic lakes than in the E.L.A. lakes. Nickel concentrations ranged from 8 to 12 μg/ℓ, many times higher than found in most lakes (Table I; Beamish, 1974a). Copper concentrations averaged 2 to 5 μg/ℓ but were only slightly higher than found in the E.L.A. lakes. As previoulsy discussed the higher concentrations of nickel (and copper) appear to result from precipitation loadings (Beamish and Van Loon, 1975; Kramer, 1973a and b). Zinc concentrations (25-46 μg/ℓ) were rather normal when compared to an average concentration of 49 μg/ℓ obtained for over 1,500 samples from waters within the United States of America (Kopp and Kroner, 1969). They were, however, much higher than the average value for E.L.A. lakes. Zinc concentrations were similar in the acidic La Cloche Mountain lakes and lakes of similar pH in Sweden (Beamish and Van Loon, 1975; Hörnström et al., 1973). Manganese concentrations were also high in both the La Cloche lakes and Swedish lakes. While the higher levels of zinc may be partly due to precipitation loading and increasing solubility at lower pH, the higher concentrations of

Table II. Calcium concentrations (mg/ℓ) for acidic lakes in the La Cloche Mountains.

Lake	pH average	pH (range)	Ca average	Ca (range)	Lake	pH	Ca
George	5.0	(4.8-5.3)	3.2	(0.8-4.0)	1A*	4.4	2.2
Lumsden	4.8	(4.7-5.3)	2.2	(1.4-2.9)	2A	4.8	2.2
O.S.A.	4.5	(4.4-4.9)	3.2	(2.9-3.7)	3A	4.1	2.0
Muriel	4.7	(4.5-4.8)	3.4	(3.1-3.4)	4A	4.4	2.1
Kakakise	5.6		4.1		5A	4.5	1.1
A.Y. Jackson	4.4		2.9		6A	4.5	2.3

*Not named. See Beamish et al. 1974a for locations.

manganese appear to be the result of increased solubility (Beamish and Van Loon, 1975).

EFFECTS OF LAKE ACIDIFICATION ON FISHES

Extensive fishing operations have documented the absence of fish populations for several of the acidic La Cloche Mountain lakes (Beamish and Harvey, 1972; Beamish, 1974a; Beamish et al., 1975a). Less intensive netting operations enabled a greater number of lakes to be examined and it was found that 28 of 67 lakes in the La Cloche Mountain region had lost the majority of their fishes (Harvey, 1975b).

In Lumsden Lake (Beamish and Harvey, 1972), O.S.A. and Muriel lakes (Beamish, 1974a) and George Lake (Beamish et al., 1975a) the condition of the ovaries of female fish were examined before, during and after the lake pH was reduced to levels that affected various species. It was found that most species which had reproduced normally each year, stopped reproduction when the pH of the lake reached a certain level. The pH at which reproduction ceased varied among species. Failure to reproduce did not appear to result from egg to fry mortalities as most females did not release ova to be fertilized. Ovaries were mature prior to the normal spawning period but few, if any fish, were found with spawned ovaries after the normal spawning period. Ova became flaccid and watery and fish appeared to resorb material from ovaries. Some old fish were found in this condition (Beamish, 1974a) suggesting that the development of ova but the failure to spawn may continue in some species for many years. With the absence of recruitment, the numbers in a

population appear to decrease rapidly in response to the natural mortality rate which may be increased because of the added stress of the low pH. Mortalities due to acid stress would be expected to be related to the lake conditions, species tolerance, and to the rate of acidification. It could not be determined if some loss in production due to partial mortalities of eggs or fry occurred prior to the complete failure of females to release ova.

Because different species responded to different levels of acidification and because reproduction appeared to be the most sensitive major physiological process that was critical to the survival of the species, it was necessary to determine the approximate pH at which species ceased reproduction. The term "critically acidic" was adopted and defined to be the pH which was sufficient to inhibit reproduction of a particular species (Beamish, 1974a). A lake was then considered to be critically acidic at a pH which was sufficient to inhibit the reproduction of the most acid sensitive species in the lake. Fish populations from the acidic La Cloche Mountain lakes appeared to be affected in the pH range of 4.5 to perhaps as high as 6.0 (Beamish et al, 1975a). The most sensitive species (Table III), smallmouth bass, walleye, lake trout, were also the most desired sportfish. Smallmouth bass appeared to be the most sensitive species in the area as they had disappeared from most lakes before this study commenced in 1966. Local residents reported this species to be abundant in several lakes prior to the late 1950's. It is possible that this species ceased reproduction at pH values above 6.0. Walleye is another important sportfish that appears to be very susceptible to additions of acid. This species disappeared by the mid 1960's from most lakes in the La Cloche Mountains. Lake trout were of intermediate tolerance, becoming extinct at pH values below 5.0 and ceasing reproduction at about 5.5. However, in one lake the occasional female lake trout was observed to have spawned when the lake pH was 5.2 to 5.0. The titration curve for several dilute lakes (Beamish and Van Loon, 1975) indicates that equal additions of acid in the range of pH from about 5.5 to 5.0 cause greater decreases in pH than at other pH values. Thus fish of intermediate susceptibility, lake trout, trout perch, brown bullhead, white sucker, and northern pike (Table III) may exhibit a shortened "long-term" response to changes in lake chemistry. Cyprinids (minnows) were the most resistant species. The lake chub was observed to reproduce at pH of 4.5. Yellow perch, lake herring and rockbass also were tolerant of low pH values.

The minimum pH of 6.0 established for aquatic organisms by the National Technical Advisory Committee (1968) would probably be acceptable for most fishes. However, if smallmouth bass and walleye were desired species as they are in most areas then the acceptable pH may be at some value greater than 6.0. The pH range of 5-9 considered by the EIFAC Working Party on Water Quality (1968) not to be directly lethal for fishes should be ignored as it has been shown that in the La Cloche lakes two to four important species were extinct before pH 5.0 was reached.

Table III. Approximate pH at which fish in the La Cloche Mountain lakes stopped reproduction.

pH	Species	Family
6.0+ to 5.5	Smallmouth bass	Centrarchidae
	Micropterus dolomieui	
	Walleye	Percidae
	Stizostedion vitreum	
	Burbot	Gadidae
	Lota lota	
5.5 to 5.2	Lake trout	Salmonidae
	Salvelinus namaycush	
	Troutperch	Percopsidae
	Percopsis omiscomaycus	
5.2 to 4.7	Brown bullhead	Ictaluridae
	Ictalurus nebulosus	
	White sucker	Catostomidae
	Catostomus commersoni	
	Rock bass	Centrarchidae
	Ambloplites rupestris	
4.7 to 4.5	Lake herring	Salmonidae
	Coregonus artedii	
	Yellow perch	Percidae
	Perca flavescens	
	Lake chub	Cyprinidae
	Couesius plumbeus	

The extinction of fishes did not appear to be an indirect effect caused by an earlier loss of food items. Predators such as smallmouth bass, walleye lake trout, and northern pike all became extinct while major prey species such as lake herring and yellow perch and cyprinids remained abundant. White suckers in Lumsden Lake were observed to become extinct even though approximately 10 times the biomass of preferred benthic food items was present (Beamish, 1974b). A decrease in feeding intensity was observed for white suckers held for several months in sublethal concentrations of acid (Beamish, 1972) and it is possible white suckers and other species responded to acid stress in the natural

environment in a similar manner by reducing feeding or food utilization or both. Changes in plankton composition of the La Cloche lakes have been reported (Sprules, 1975) but may not be important as the species most dependent upon plankton for food (lake herring) was one of the last species to become extinct (Beamish, 1974b).

Growth of some species did appear to be affected by the decreasing pH. Between 1966 and 1968 in Lumsden Lake the mean size of similar aged white suckers decreased as the population was becoming extinct (Beamish, 1974b). In 1972 and 1973 white suckers in George Lake were found to be significantly smaller than similar aged fish sampled earlier (Beamish et al., 1975a). Many of the remaining lake trout and northern pike in George Lake in 1972 and 1973 were observed to be emaciated and generally in poor condition. The changes in growth of these species occurred during the period that the fish first stopped reproducing. During this same period, yellow perch increased in numbers then increased in mean size (Beamish et al., 1975a). An increase in size as a lake became more acidic has also been reported for fishes from acid lakes in other areas (Almer, 1972; Schofield, 1975). Since there is a wide range of tolerance to pH among fishes one might expect there is also a wide range of pH values in which growth of a species may be altered. Therefore it is important not only to identify changes in growth but to relate these changes to other physiological changes that may be occurring such as the failure to reproduce. If species are observed to increase in mean size at a specific age and the species have ceased to reproduce then such an observation would indicate that the response of white suckers and perhaps lake trout and northern pike in the La Cloche lakes may be characteristic only of the species or of the area.

It was found that female fish from the acid lakes had abnormally low serum calcium concentrations during the period of ovarian maturation (Beamish et al., 1975a). The cause of this reduction in serum calcium of females was not determined but because changes occurred when pH was depressed to critical levels it did appear that the changes in normal calcium metabolism have resulted from the increased acid content of the lake and these changes caused or resulted from the reproductive failures. Another indication that normal calcium metabolism might be altered by the changes in water quality was found in the increased occurrence of deformed white suckers in George Lake (Beamish et al., 1975a). The occurrence of deformities in fish during periods of sublethal acid stress has also been described in laboratory acid toxicity tests (Mount, 1973; Beamish, 1972). The similar response of white suckers in an acidifying acid lake and from a controlled laboratory experiment is accepted as corroboration that this species was responding to the stress of increased acidity.

OTHER EXPLANATIONS FOR OBSERVED RESPONSE OF FISHES

It has been assumed that the cause of the reproductive failures and the ultimate extinction of the fish populations were a result of the increasing acid content of the lake. Another possibility would be that some unknown very toxic chemical was causing the observed responses. Such a possibility always is present in research and while there appears to be a more reasonable explanation for the observed responses, the presence of some unknown agent should not be completely discounted. A more probable alternative would be that the fish were responding to heavy metal toxicity, increased in effect because of the low pH. In the La Cloche lakes only zinc concentrations were sufficiently high (20-40 µg/ℓ) to be potentially hazardous to fishes (Canadian Department of the Environment, 1972). The observed zinc concentrations were well below incipient LC50 values considered representative for most salmonid fishes in water of a hardness similar to the La Cloche lakes (Candian Department of the Environment, 1972). The zinc concentrations were well within the range of "safe" concentrations of 30 µg/ℓ which had no effect and 180 µg/ℓ which caused an 83% reduction in egg production of fathead minnows (*Pimephales promelas*) in hard water (Brungs, 1969). Zinc concentrations were also lower than concentrations considered to be "safe" for *Daphnia magna* (Biesinger and Christensen, 1972). Mangenese and nickel concentrations were high in all acid lakes, however, they were well below concentrations that caused a minimum of reproductive impairment to *Daphnia magna* (Biesinger and Christensen, 1972). Nickel concentrations were much lower than the 380 µg/ℓ considered "safe" for fathead minnows in hard water (Pickering, 1974). Copper concentrations ranged from 2 to 4 µg/ℓ and were much lower than the value of 17 µg/ℓ that did not affect survival, growth or reproduction of adult brook trout (*Salvelinus fontinalis*) in soft water (McKim and Benoit, 1971). Cadmium (< 1 µg/ℓ) was well below the range of 4.5 to 37 µg/ℓ that had no adverse effect on survival, growth or reproduction of fathead minnows in hard water (Pickering and Gast, 1972).

These tests of toxicity were performed at higher pH values and it is possible that the "safe" levels are too high for the acidic La Cloche Mountain lakes. Conversely heavy metal concentrations probably increased gradually as the lakes acidified, allowing fish to acclimate to the increasing concentrations. Schofield (1965) found that only brook trout that were acclimated to higher zinc concentrations could be introduced into an acidic lake with high zinc concentration. Also, if heavy metal concentrations increased as the lake acidified then the loss of the more sensitive species occurred at even lower concentrations than presently found.

In contrast to the lack of a good relationship between concentrations of heavy metals in the lakes and the concentrations observed to affect fishes in controlled laboratory experiments, there was a good correlation between pH and the observed responses of fishes. Mount (1973) showed that the survival of fathead minnows in hard water was not

affected at pH 7.5 to 4.5 but at pH 5.9 and lower, egg production and hatchability were reduced. At pH 5.2 to 4.5 females did not spawn. It was in the range of pH 5.2 to 4.7 that five species in George Lake were first observed to stop reproducing (Beamish et al., 1975a). The occurrence of decreased egg production and reduced hatchability were not studied in the acidic La Cloche Mountain lakes and may have influenced total fish production. Water quality standards allowing pH values lower than pH 6 were not considered acceptable for fathead minnows. Mount (1973) recommended that a minimum pH of 6.5 be maintained for fish populations.

In George Lake five species were observed to cease reproduction after pH dropped from 5.5 to 4.7 in the early spring of 1971, followed by a brief winter rise to 5.2, and a fall again to 4.8 in the summer of 1972 (Beamish et al., 1975a). This is an increase from .003 to .020 mg/l of hydrogen ion in 1971 and a change from .006 to .016 mg/l in 1972. It also appears that small increases in copper, nickel, and manganese may have occurred when the George Lake pH decreased from about 5.5 to 4.7 (Table IV). Zinc may have doubled in concentration from about 15 µg/ℓ to 30 µg/ℓ. Iron determinations were so variable that comparisons could not made. There was no significant correlation ($p = 0.05$) between pH and copper, nickel, or manganese from February 1972 to November 1973 (Table IV). The decrease in zinc concentrations was significantly correlated ($p = 0.05$) with increasing pH. A comparison of heavy metal concentrations in George Lake with concentrations from a nearby less acidic lake (Kakakise Lake, Table IV) indicates that heavy metal concentrations may have doubled in George Lake when the pH dropped from 5.5 to 4.7. However, the more than sixfold increase in hydrogen ion that lowered the pH into a range known to prevent fish from spawning (Mount, 1973) appeared to be a more important stress then the heavy metal increases that still were below concentrations considered to be safe for fishes. Thus there were small changes in heavy metal concentrations in relation to the very large increase in hydrogen ion concentration during the time many species in the lake first ceased spawning. Finally, there is a substantial literature describing the levels of pH that are lethal to fishes (EIFAC, 1969; McKee and Wolf, 1963; Daudoroff and Katz, 1950; and others). While such literature in general does not consider the wide range of sensitivities exhibited by fishes and the effects of prolonged sublethal concentrations of acid and resulting reproductive failures, it is unanimous in its agreement that pH values below 5.0 are harmful to fishes.

It is possible that synergistic effects of acid and heavy metals, or additive effects of heavy metals and acid may cause stress at a slightly higher pH than if heavy metals were not present. A fish may be responding to an acid stress modified by heavy metal toxicity but there does not appear to be any justification for considering that the failure of reproduction and ultimate extinction of fish populations has resulted primarily from the toxic effect of heavy metals. It is important to consider that the elevated concentrations of heavy metals such as zinc,

Table IV. Heavy metal concentrations and 3 m pH values* for George and Kakakise lakes.

Date	Cu	Ni	Cd	Zn	Pb	Fe	Mn	pH
George Lake								
February 1972	<2.5	-	<1	27	1.2	41	-	-
July	3	7	nd	20	1	19	260	5.0
August	3	11	-	31	3	20	260	4.9
September	4	8	nd	26	3	19	200	5.1
October	4	9	nd	27	nd	22	200	5.0
December	2	14	nd	20	nd	12	210	5.2
January 1973	3	9	0.3	32	1	7	-	4.8
February	2	10	<.2	24	nd	27	-	5.0
April	3	5	nd	21	nd	33	210	5.0
May	3	5	nd	21	nd	33	200	5.0
June	1	9	.5	11	<2	6	-	5.0
August	<1	9	<.5	25	3	32	220	5.1
November	1	9	.3	13	2	22	240	5.3
Kakakise Lake								
November 1972	<1	5	.2	10	<2	8	150	-
February 1973	2	6	<.2	12	nd	8	190	5.7

*See Beamish et al. (1975a) for methods of chemical analysis.

- indicates no measurement; nd indicates not detected.

manganese, and perhaps other substances may occur because of increased weathering and solubility due to acidification of soils and lakes. If this is true then it is practical to think of fish populations as being stressed by an association of factors of which acid is the principle stressing agent as well as controlling the concentrations of the less important factors.

COURT ACTION

In 1970 a court action was initiated by the Federal Department of Indian Affairs in cooperation with the Department of Justice. It was alleged that the major mining and smelting companies in Sudbury had

caused damage to forests and lakes on a nearby Crown Indian Reserve as a result of their sulfur dioxide and heavy metal emissions. For the purposes of the action, special investigations were conducted of the dispersion of the plume of sulfur dioxide as it left the companies stack; the correlation of quantities of sulfur dioxide in the plume with measured ground-level concentrations, the effects of these emissions over the past few decades on forest in the Reserve; and the effects of emissions on lakes and fish populations. After discovery hearings, and subsequent trial postponements at the request of the companies, the action was settled out of court for an undisclosed sum without any liability being assessed. The settlement occurred in October 1974 just days before the trial was scheduled to commence.

Such a settlement while probably being beneficial to the Indian Reserve in that monies became available for the compensation of damages suffered, did not appear to be particularly helpful to those concerned with maintaining and improving the quality of the environment. However, because there was a settlement on the part of the companies, the action was important because it demonstrated that it is possible to provide evidence that at least can encourage major polluters to control the emissions of pollutants into the atmosphere.

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THE EFFECTS OF ACID AND PARTICULATE PRECIPITATION ON PHYTOPLANKTON AND LAKE CHEMISTRY IN THE SUDBURY REGION OF ONTARIO, CANADA

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ABSTRACT

The Sudbury basin, Ontario is the source of more than 60% of the free world's nickel and is also a major producer of copper, iron, cobalt and other metals. The sulfur dioxide and particulate discharge from the Sudbury smelters have been described and discussed in a number of publications and information will also be presented at the present conference.

A survey of some of the lakes in the Sudbury area (commencing 1958) revealed high sulfate concentration in lakes within 1.9 km of the smelters. Many of these lakes also had abnormally low pH values. In our own studies, a survey of the phytoplankton revealed severely depauperate populations and a low productivity. Bioassays with algal test species, on waters from lakes within 1.9 km of one of the smelters, indicated pH limitations to growth and survival, and severe but complicating metal problems, both from metals occurring in rocks and from particulate fallout. Algal isolates from these contaminated lakes proved to be metal tolerant (Stokes, Hutchinson and Krauter, 1973) and acid tolerant.

The use of increasingly tall stacks has extended the area of occurrence of acid rain. Other studies revealed acidification of lakes at least 24.8 km from the smelter, with changes in phytoplankton composition, even though overall phytoplankton biomass might not always be decreased. Destruction of the fish population of these latter lakes has already been described (Harvey and Beamish, 1973).

It is hypothesized that acid precipitation into lakes, especially shield lakes of low buffering capacity, would not only lower the pH and increase the solubility and availability of toxic heavy metals, but might also result in wide and rapid fluctuation in pH. Shifts in species population composition of algae such as we have observed would presumably also have effects on the primary consumers in the lakes. Possible consequences of acid rainfall on lake ecology in this and similar areas will be Possible consequences of acid rainfall on lake ecology in this and similar areas will be briefly discussed.

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THE MIXING OF RAIN WITH NEAR-SURFACE WATER

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ABSTRACT

Rain experiments were run with various temperature differences between the warm rain and the cool receiving water. The rain intensities were uniform and the raindrop sizes were usually uniform (2.2 mm, 3.6 mm, and 5.5 mm diameter drops). Two drop size distributions were also used.

The depth of mixing varies from 8 cm for raindrops less than 1.5 mm in diameter at an intensity of .9 cm/hr to 42 cm for drops 5.5 mm in diameter at 2.3 cm/hr. The mixed layer depth was found to be directly proportional to the rain's kinetic energy, to the 1/3 power of time, and inversely proportional to the rain-induced heat transfer through the water surface. The proportionality constants vary with raindrop size. Large raindrops strongly affect the depth of mixing even though they are a small fraction (2 - 4%) of the total rain volume. For natural rain, which consists of a broad spectrum of drop sizes, the constant representative of the largest few percent of the drop sizes should be used to predict the mixed layer depth. Maximum errors using the equations developed for predicting the depth of mixing were found to be 24% of the observed depth.

The rain dilution of the near-surface water may be estimated (to 24%) when the depth of mixing is known. If rain is acidic then the pH of unbuffered surface waters will be lowered depending on the mixed layer depth (dilution). The pH values of unbuffered surface waters could be estimated.

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THERMALLY STRATIFIED ACID WATER IN LATE WINTER - A KEY FACTOR INDUCING SELF-ACCELERATING PROCESSES WHICH INCREASE ACIDIFICATION

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ABSTRACT

Ion separation of acid air pollutants out of snow causes sudden, deep pH-drops in lakes and running waters at an early stage of snowmelting. These pH-drops have drastic effects on fish populations and are suggested to be the main cause of *Sphagnum* invasion and changes in the microflora already at an early stage of acidification, i.e. when summer pH-values are about 6. These effects in turn reduce the nutrient recycling and accelerate the acidification process.

INTRODUCTION

During the last ten to fifteen years, fish and crayfish populations in thousands of lakes and running waters in Sweden and Norway have suffered from increasing water acidity (Hultberg and Stenson 1970, Anon 1971, Jensen and Snekvik 1972, Almer et al. 1974, Svärdson 1974).

Odén and Ahl (1970) and Snekvik (1972) have shown that sharp pH-drops occur at snowmelting in rivers and lakes in Sweden and Norway.

In southern Norway polluted snow was found to have considerable influence on the quality of the water in lakes and brooks in winter and spring. Great quantities of e.g. SO_4^{--}, NO_3^{-}, Zn and Pb were found together with high acidity in the upper strata of lakes. A poor bottom fauna consisting mainly of *Sialis* sp., *Chironomidae* and *Oligochaetes* were found in shallow areas (1 m depth) while the number of species and biomass increased at greater depths (Haugen and Langeland 1973).

Oligotrophic Lakes and brooks with low buffer capacity would be especially susceptible to pH-drops. Grahn and Hultberg (1974) observed acidification effects in a lake with summer pH-values just below 6. *Sphagnum* sp. had invaded lake Örvattnet in the province of Värmland in 1967 when summer pH-values were about 5.8.

Effects such as fish kill, reduced fish reproduction, death among groups of invertebrates, *Sphagnum* invasion, and changes in the microflora already at an early stage of acidification cause feed-back mechanisms which delay nutrient recycling and accelerate the acidification process (Grahn et al. 1974). Sharp pH-drops at the time of snowmelting are suggested to be a main factor inducing these biological perturbations in aquatic ecosystems.

INVESTIGATED AREAS AND METHODS

The annual variations in pH have been studies in lakes in two areas in south-western Sweden: ten in the province of Bohuslän since late 1969, and three in the province of Värmland since 1973 (Figure 1). Since the discovery of drastic pH-drops in Bohuslän in April 1970, effects on fish populations in running waters have been studied by means of electrofishing at three stations, fish mortality tests (fish in net-cages at ten stations), and by studying the occurrence of false annuli in seatrout otoliths. Also, fishing with survey nets and rotenone treatment has been used at three stations to study fish populations in the lakes (Figure 2). In addition, skindiving has been used to study macrophytes and the microflora in both areas.

RESULTS AND DISCUSSION

Among the investigated lakes in Bohuslän, the yearly pH-variation is greatest at 1 m depth in lakes with summer pH-values around 5.2 - 5.5. In the very acid lakes, the variations are small. In all the lakes, a sharp drop in pH occurred in the spring of 1970. No such drop has been observed during any of the following winters. As an example, the yearly variation in pH in Lake Härsevatten and Lake Timmervatten is shown in Figure 3.

Figure 4 gives a more detailed example of the drastic pH-drop from 5 to 4.2 in April 1970. The winter 1969-70 had unusually much snow, with an average snow depth of around 0.7 m. The temperature was low from mid November and no snowmelting occurred until mid April. pH was 4.4 - 4.5 in snow profiles in the area, but the pH-drop at the start of snowmelting at 1 m depth in Lake Timmervatten and other lakes in the

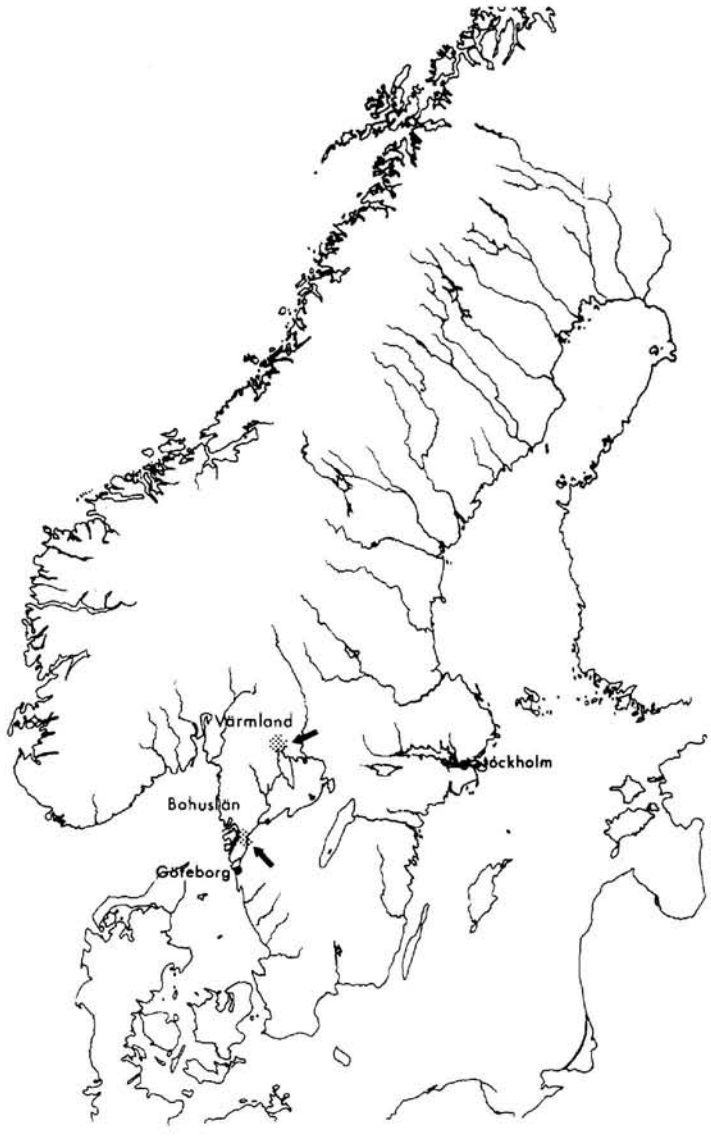

Figure 1. Scandinavia. Arrows mark investigated lake areas in the provinces of Värmland and Bohuslän in Sweden.

area was even greater. In a thin layer between the snow and the ice cover on the lakes, pH-values as low as 3.7 - 4.0 were measured. These values show that acid had been concentrated from the snow by means of ion separation at the beginning of snowmelting, forming this acid water layer. Due to mild winters and no snow cover, no such short-term, deep pH-drops have occurred in the lakes in Bohuslän since the one recorded in April 1970.

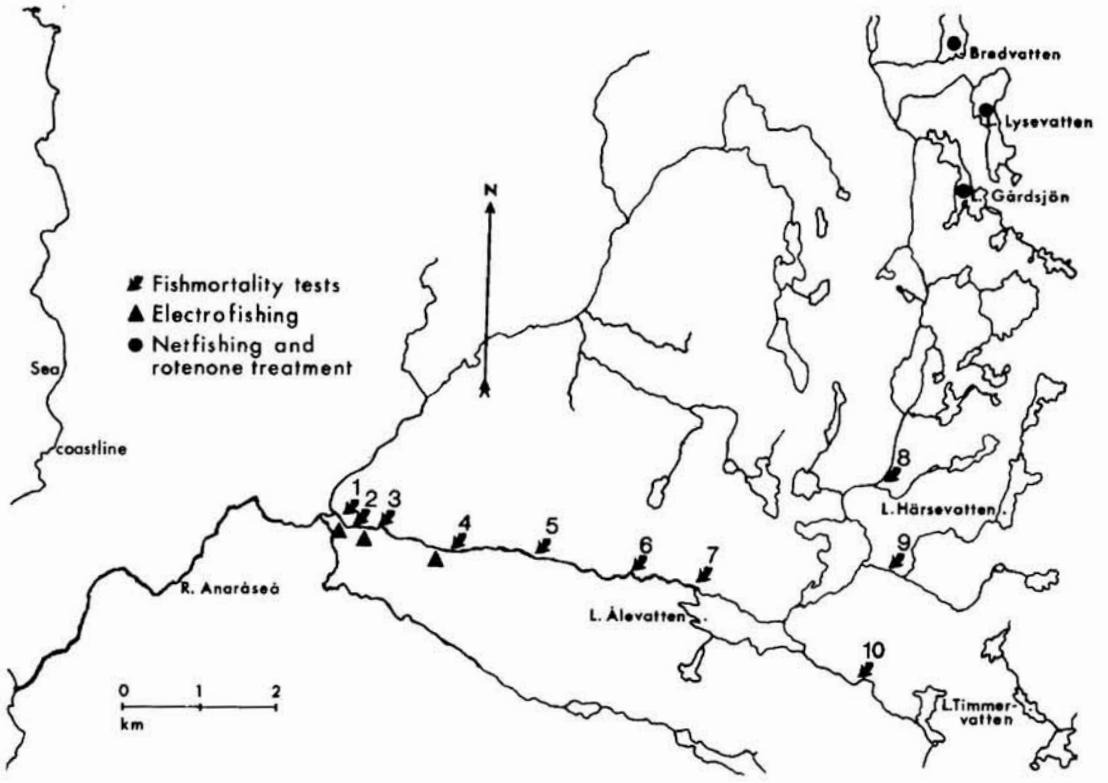

Figure 2. Tests on fish populations in the investigated lake area in Bohuslän.

As from June 1973, monthly pH-profiles have been measured in three lakes in the snow-rich province of Värmland. In all the lakes, a sudden sharp pH-drop occurred in mid February 1974. In Lake Stensjön, the drop was spectacularly deep, from 5 to 3.4 just below the ice cover, and from 5 to 3.8 at 1 m depth (Figure 5). The pH-drop was observed down to 5 m depth near the shore, but only to 3 m depth in the middle of this 34 ha lake. Comparing these low values to pH values in precipitation and in the snow pack, it is clear that during a mild period in mid February, ion separation had concentrated the acid substances from the snow into the lake. The rise in pH in the two lakes in Bohuslän and Värmland (Figures 4 and 5) following the pH-drop makes the duration of the extremely acid layer short (14-30 days) and these sharp drops can therefore be recorded only through frequent measurements.

Odén and Bergholm (1973) point out that the first fraction collected during laboratory-controlled snowmelting is a very acid salt-solution, and that the pH rises and the salt content is gradually reduced during the melting process. The last 50 percent of the meltwater is almost distilled water.

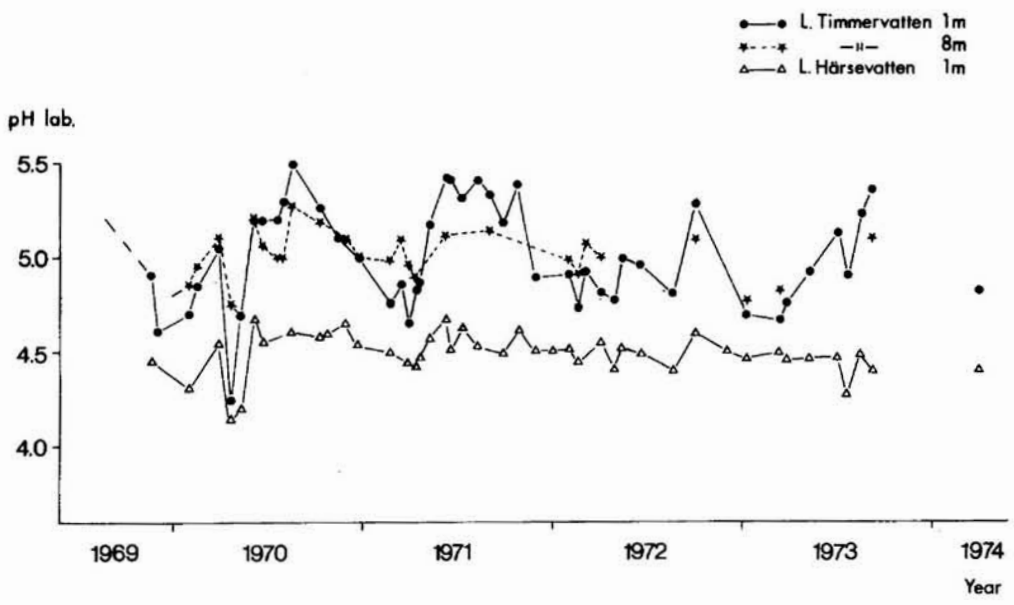

Figure 3. Yearly pH-variations (laboratory measurements) in L. Timmervatten and L. Härsevatten in Bohuslän, 1969-1970.

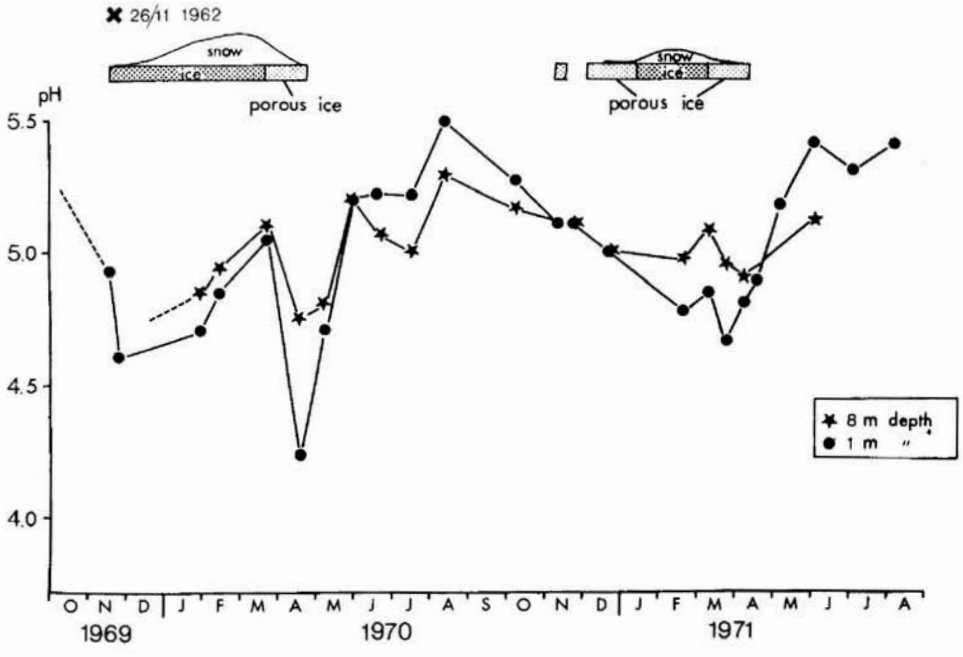

Figure 4. pH-variations in L. Timmervatten showing the sudden sharp pH-drop in April 1970 as compared to spring 1971.

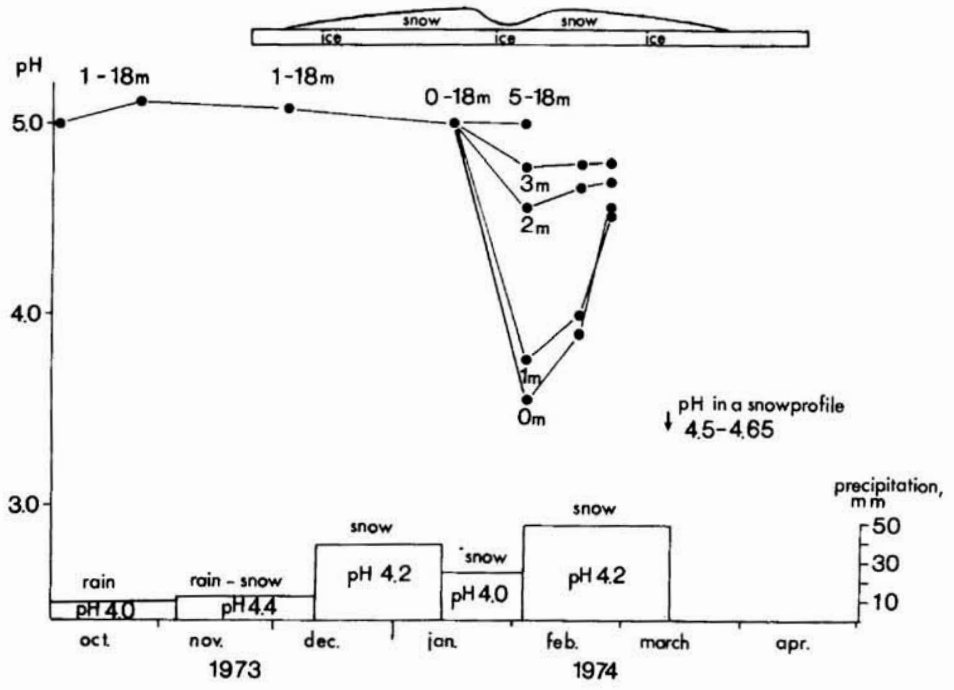

Figure 5. pH-variation during winter 1973-74 (field measurement) in L. Stensjön in Värmland. Note the pH and amount of precipitation, and pH in snow profiles.

In a similar study, Henriksen et al.(1974) show that 75 percent of the divalent and 58 percent of the monovalent ions are removed from the snow pack when only 30 and 31 percent respectively of the snow has melted in a thermostated (2.0 ± 1.0°C) lysimeter.

To study the pH-drop effects on fish populations in small running waters in Bohuslän, a test was performed with two species: seatrout *(Salmo trutta)* and minnows *(Phoxinus phoxinus)*, both with a mean length of 65 mm, and collected in the outlet of lake Ålevatten. Two-three net cages were placed at each of 10 test stations, seven along the outlet and three upstreams lake Ålevatten (Figure 2). The test was performed during the winter 1971-72 and the following pH-fluctuations were recorded:

TABLE I. pH-RANGE (FIELD MEASUREMENTS) AT TEST STATIONS 1-10, L. ÅLEVATTEN

Station No.	pH-range	Station No.	pH-range
1	5.50-6.00	6	4.80-5.60
2	5.40-6.00	7	4.65-5.10
3	5.35-5.80	8	4.30-4.70

Station No.	pH-range	Station No.	pH-range
4	5.25-5.60	9	4.40-5.20
5	5.00-5.50	10	4.40-5.50

An example from station no. 5 (Figure 6) illustrates the pH-fluctuation and the fish survival during the test. The mortality for

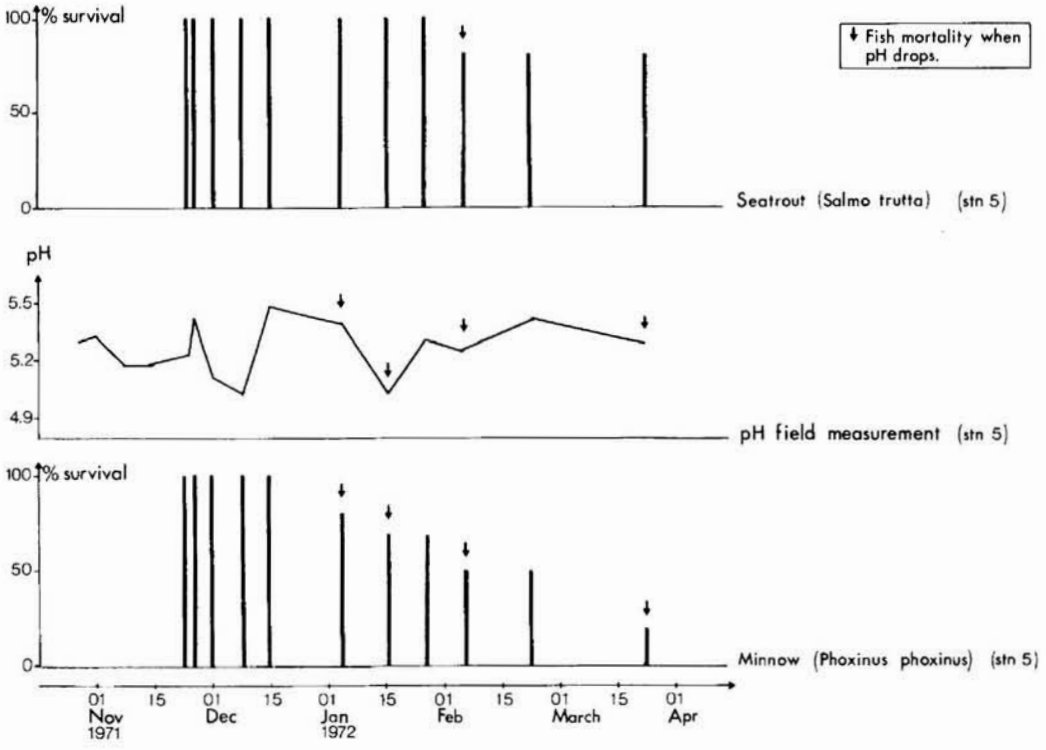

Figure 6. Fish mortality test at station No. 5 in the outlet of L. Ålevatten in the winter 1971-72

pH-drop, pH-rise, and unchanged pH was recorded. A total of 131 seatrouts and 128 minnows were tested. The pH at the least acid station (No. 1, 5 km downstreams the lake) ranged from 5.50 to 6.00, while pH gradually sank upstreams to station No. 8 where the pH-range was 4.30-4.70. 53 percent of the seatrouts and 91 percent of the minnows died during the test (Figure 7). All but three of the test stations (No. 1-3) were within localities where minnows have disappeared during the last ten-year period.

A dominating part (i.e. 68 percent of the seatrouts and 59 percent of the minnows) died when pH dropped although these drops were much less pronounced (due to lack of snow) than that in April 1970 described earlier. Obviously, fish mortality during pH-drop and pH-rise cannot

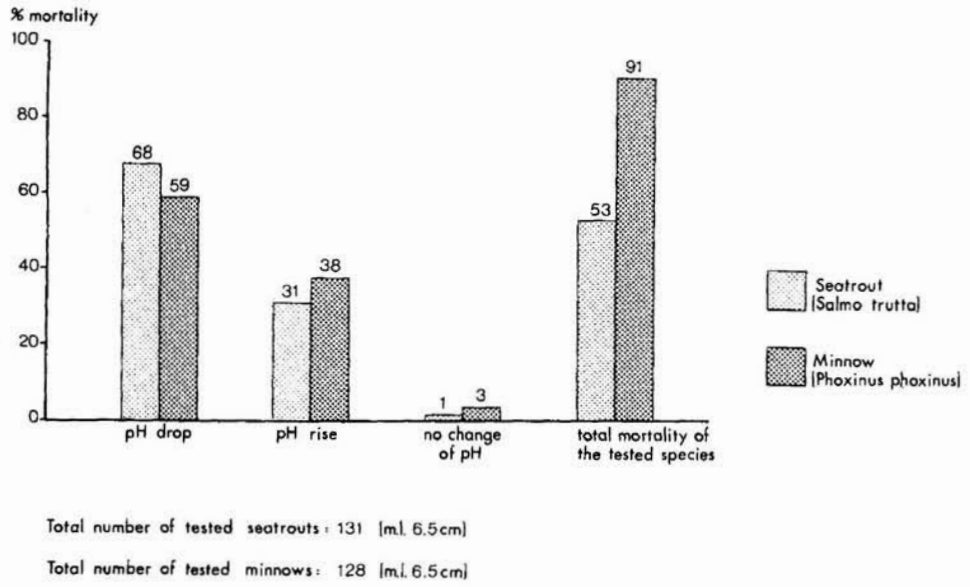

Figure 7. Percent of the number of seatrouts and minnows that died during the test period, as well as during drop, rise and unchanged pH, respectively.

be separated. However, the results indicate that pH-drops cause the most severe effects.

Already in 1957, the fishery administration in Sweden carried out electrofishing at two stations downstreams lake Ålevatten in Bohuslän to check the trout population (Edman, 1970). These checks were continued within the author's research project, starting in August 1970 about four months after the sharp pH-drop in the lakes, and electrofishing was repeated every autumn until 1973.

Compared to the results from 1957, 1971, 1972 and 1973, the trout reproduction in 1970 (number of 0+) was extremely low, and at the station nearest to the lake there were no fry at all (Figure 8).

In 1971, the reproduction was higher at all three stations, especially at 4.5 and 4.9 km downstreams the lake. The number of two-summers and older trout was seriously affected in 1971 by the limited or non-existent reproduction in 1970. As no such sharp pH-drop as the one in April 1970, when the trout fry had hatched, has occurred afterwards, and as the trout population has increased in the following years, one can argue that the thermally stratified acid water from the lakes had caused the serious effects on the trout population.

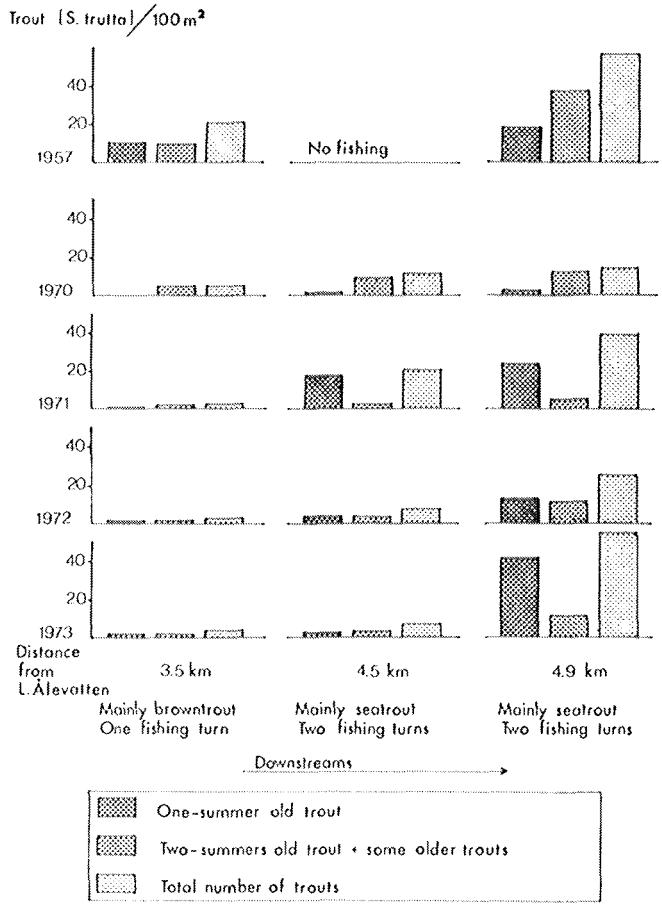

Figure 8. Number of one-summer old (0+), two-summers old and some older seatrouts as well as total number of trouts/100 m^2 at three stations in the outlet of L. Ålevatten from 1957 and 1970-73. Total catch figures are not equal to total fish biomass. The number of 0+ is probably much too low for 1957 due to fishermen catching the big ones first.

Figures 9, 10 and 11 show seatrout otoliths. These are part of the fish auditory mechanism as organs of equilibrium, containing prisms of calcium carbonate and an organic matrix.

Of the three otoliths in Figure 9, all from young of the year (0+) seatrout 5.0-5.7 cm, two have a broad zone with no calcium carbonate and are from seatrouts caught in the outlet of lake Ålevatten. The otolith without this false annuli is from a seatrout caught in a part of the watersystem where no sharp pH-drop occurred in the spring of 1970.

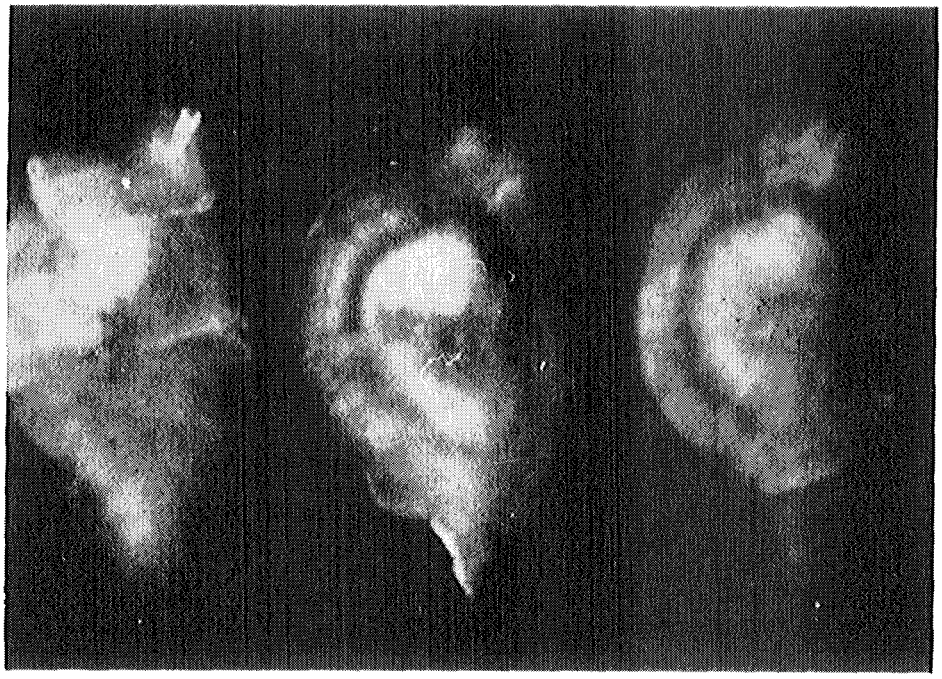

Figure 9. Three otoliths of young of the year (0+) seatrouts. The two with a broad zone (without calcium carbonate) were collected in the outlet of L. Ålevatten in August 1970, and the one without the broad zone is from a part of the water system where no deep pH-drops occurred in April 1970.

Figures 10 and 11 show otoliths from a young of the year (0+) seatrout 5.7 cm, and a two-summers old (1+) 10.4 cm, both caught in August 1970. It is obvious that the broad zones (acid zone, spring 1969, etc.) in these otoliths correspond to the annual occurrence of pH-drops in the studied area. The seatrout fry in this area actually register the acid periods, and the broad zones in the otoliths show when the acidity of the water have caused stress and death in the seatrout population.

Figure 12 shows the year of birth of 253 pearches *(Perca fluviatilis)*, some fished by net in 1970, 1971, 1972 and 1973, and some collected after rotenone treatment in the autumn of 1973 in three lakes in Bohuslän (figure 2). From 1970 and onwards, the reproduction was low or non-existent (1972). Actually there were no fish at all in one of the lakes, and only 60 and 37 respectively in the other two, in 1973. The poor reproduction in 1970 compared to the extremely good reproduction in 1969 is most probably directly or indirectly an effect of the extreme pH-drop in 1970. The abundant reproduction in 1969 is well-known from other lakes and species in other parts of Sweden, and is a result of an unusually early and warm spring that year.

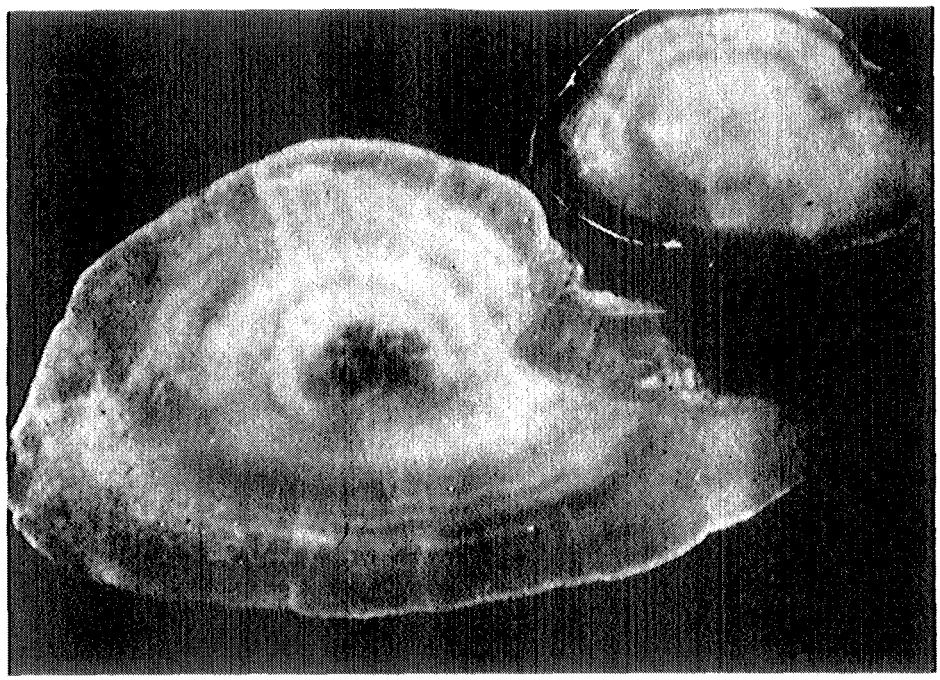

Figure 10. Two otoliths, one from a one-summer (0+) old, the other from a two-summers old seatrout, both caught in August, 1970 in the outlet of L. Ålevatten.

In acid lakes, the *Sphagnum* mats and fungus hyphae felts are thicker and cover greater bottom areas in the littoral than in the other depth zones (Figure 13). This corresponds to observations by Haugen and Langeland (1973) of acidification effects on invertebrates in the littoral and in deeper water respectively in lakes in southern Norway. As mentioned above, *Sphagnum* species invaded a lake in the snow-rich province of Värmland when summer pH-values were as high as 5.8. The pH-drop in the littoral zone in winter induces the *Sphagnum* invasion and affects the microflora, which in turn leads to further expansion of *Sphagnum* and fungus hyphae on the bottoms in shallow areas.

CONCLUSIONS

Through ion separation out of snow at an early stage of snowmelting, acid substances cover the littoral bottoms with a highly acid layer. This leads to poor fish reproduction and death among groups of invertebrates; it induces the Sphagnum invasion and affects the microflora in both lakes and running waters already at an early stage of acidification.

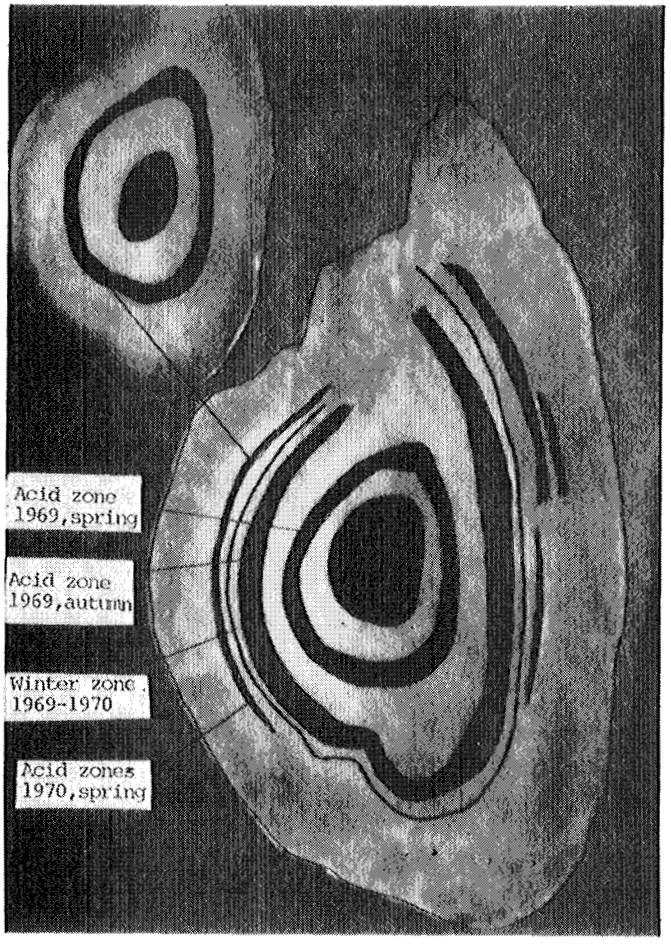

Figure 11. See figure 10.

These biological disorders brought about by thermally stratified acid water in late winter lead to oligotrophication which in turn accelerates the acidification process.

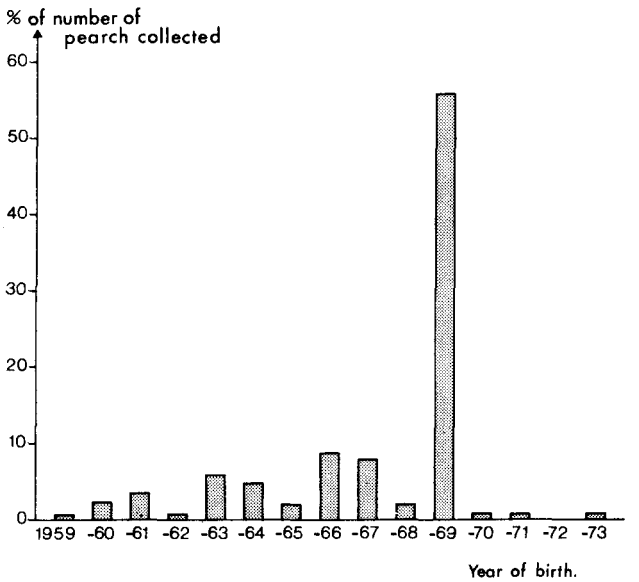

Figure 12. Year of birth and percent of the number of 253 perches caught by survey nets and collected after rotenone treatment in L. Bredvatten, L. Lysevatten and L. Gårdsjön (see Figure 2).

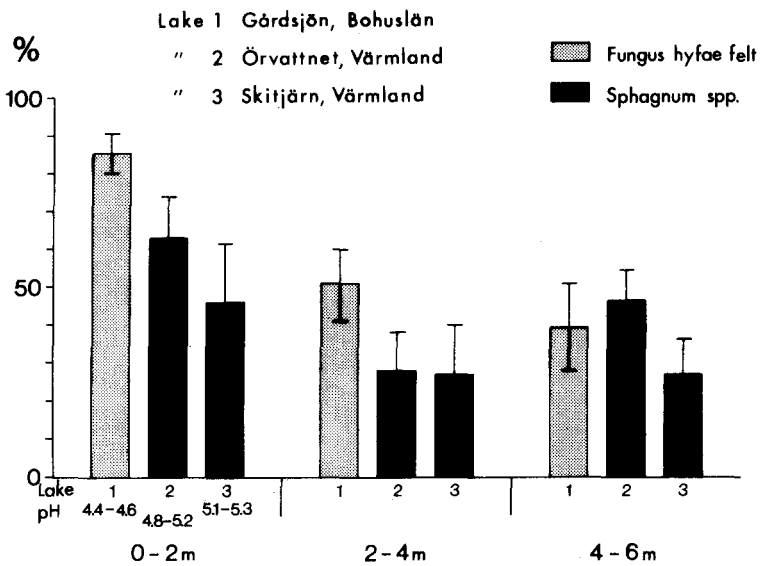

Figure 13. Coverage of fungus hyfae felt in L. Gårdsjön (Figure 2) and *Sphagnum* spp. in L. Örvattnet and L. Skitjärn in Värmland at different depth zones.

ACKNOWLEDGEMENTS

The field and laboratory work performed by L. M. Lindén and J. Kjellarson in the fish mortality tests is very much appreciated. I. Torbrink. E. Nordquist, A. Ahlfors and M. Eastmond provided valuable technical assistance in completing the investigation and preparing the manuscript.

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MACROPHYTE SUCCESSION IN SWEDISH LAKES CAUSED BY DEPOSITION OF AIRBORNE ACID SUBSTANCES

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ABSTRACT

Recurrent biological investigations have been made in six lakes in two areas in western Sweden. It has been found that the supply of acid substances induces long-term biological perturbations at all trophic levels in the lake ecosystem. Among these changes, the *Sphagnum* expansion is believed to strongly affect the dynamics in the lake. A quantification of the *Sphagnum* expansion in different depth zones of a lake was made. The rate of this invasion was found to be highest in shaded and sheltered areas of the littoral. The abundance of *Sphagnum* mats is furthermore negatively correlated to the pH of the lake water.

The further consequences for the lake ecosystem of this occupation of ever-larger bottom areas by dense *Sphagnum* mats are discussed.

INTRODUCTION

In 1968, Odén presented results of studies which clearly pointed to an increasing acidity in precipitation and in a number of rivers in Sweden. He also discussed the long-term consequences of this acidification for our soil and water resources (Odén 1968). The large number of reports on this subject published since then, particularly in Sweden, Norway, and Canada, have justified the misgivings previously expressed by Odén (Henriksen 1972, Jensen and Snekvik 1972, Almer et al. 1974, Beamish 1974, Grahn et al. 1974). Consequently, in Scandinavia today a large number of lakes and running waters are suffering irreversible biological damage, with total fish kill in some areas, as a result of increasingly acid water (Hultberg and Stensen 1970, Jensen and Snekvik 1972).

For several years now, the effects on lake ecosystems of the increasing acidification have been studied within the framework of a

current research project at the Swedish Water and Air Pollution Research Laboratory (Grahn el al. 1974).

The study comprises six small lakes (16-78 ha), three in the province of Bohuslän just north of Gothenburg on the Swedish west coast, and three in the province of Värmland, 300 km further north (Figure 1).

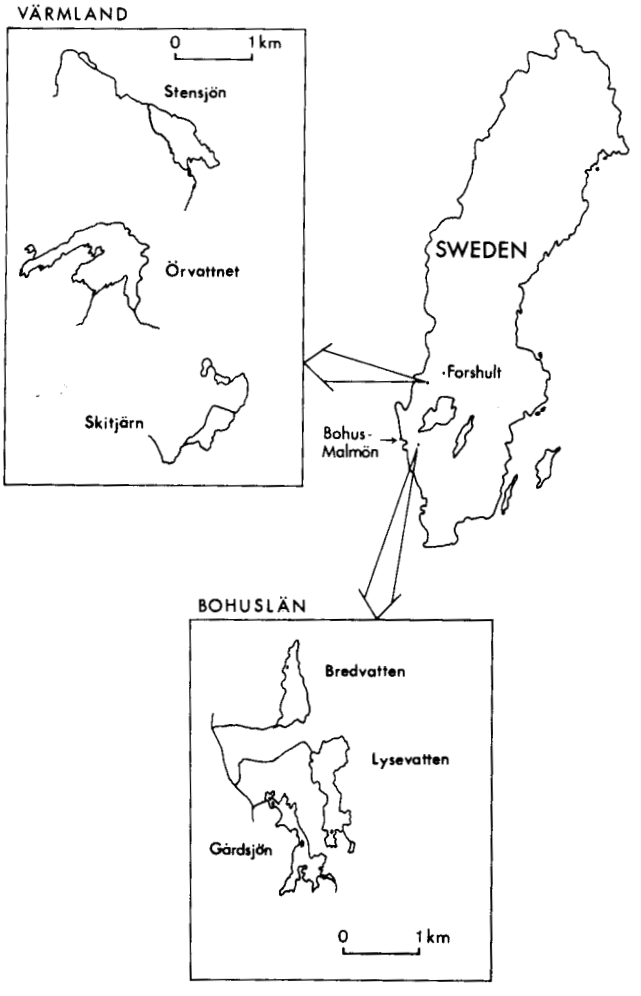

Figure 1. Investigated lakes, and stations for precipitation sampling (Bohus-Malmön, Forshult).

All the lakes except for one are clear-water lakes, situated high above sea level and surrounded by moraine ground. There are no industrial or populated areas in the surroundings, and thus no direct discharges of pollutants into the lakes.

The investigations so far have shown that disturbances occur on all trophic levels: among fish, macrophytes, bottom fauna, plankton as

well as among micro-organisms. Of these ecological changes, the macrophyte succession, in particular that of *Sphagnum*, is one that may strongly affect the dynamics in the lake.

No distinction was made in this study between the different *Sphagnum* species.

Unless otherwise stated here, "*Sphagnum*" therefore refers to all *Sphagnum* species observed in this investigation.

CHEMICAL DATA

In both investigated lake areas, sulphur and nitrate in precipitation have increased, and the pH in precipitation decreased by more than one pH-unit since 1955 in Värmland and 1958 in Bohuslän (Figure 2a and b).

In Bohuslän, pH in the lake water has fallen 1.4 - 1.6 units since 1948, and a drop of the same order has occurred in Värmland since 1937-39. No pH-measurements were made during the '50s and '60s except in Lake Örvattnet, where pH fell 0.8 units from 1967 to 1973 (Figure 3 and 4b).

Compared to older secci-depth measurement data, transparency in all lakes, expecially those in Värmland, has increased. In Lake Örvattnet, the secci-depth in July 1939 was 4 m and in July 1973 it was 8 m. The oxygen content is high in all lakes and the oxygen curve regularly shows a metalimnial oxygen maximum during the summer stagnation.

The conductivity, which is a measure of the total salt content of the lake water, differs in the two investigated areas. In the Värmland lakes, the specific conductivity is about 30 uS and in the Bohuslän lakes the corresponding value is about 70 uS. The higher specific conductivity in Bohuslän is due to the marine influence through salt-spray and especially the ions Na^+, Mg^{2+}, Cl^- and SO_4^{2-} occur in higher concentration of HCO_3^{2-} is not measurable in any of the lakes, and SO_4^{2-} has replaced HCO_3^{2-} as the dominant anion.

MATERIAL AND METHODS

In order to study the macrophyte succession in the lakes, quantification of *Sphagnum* coverage on the bottoms was made in different depth zones at two localities in Lake Örvattnet between 1967 and 1974.

One locality is exposed to wind and sun, whereas the other is sheltered and shaded. The bottom was sampled by means of a 1 m^2 frame

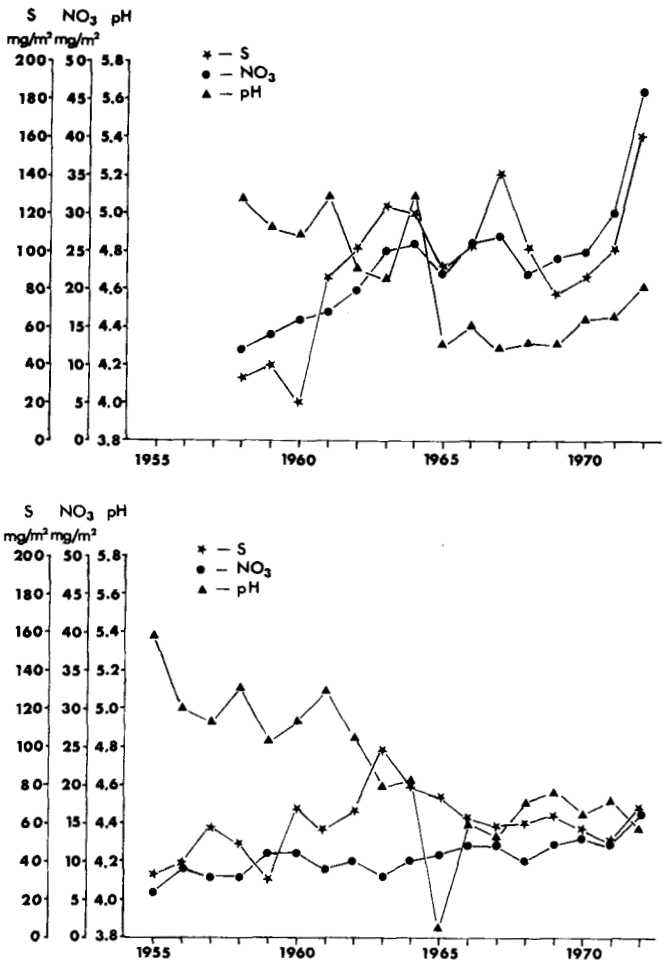

Figure 2a. Annual means of S, NO_3 and pH in precipitation at Bohus-Malmön in Bohuslän 1958-1972. (Data from the European Atmospheric Chemistry Network, Dept. of Meteorology, University of Stockholm).

Figure 2b. Annual means of S, NO_3 and pH in precipitation at Forshult in Värmland 1955-1972.

thrown out at random from a boat, and the degree of coverage determined by a diver according to a linear 7-degree scale.

Furthermore, an assessment of the *Sphagnum* coverage exceeding 40 percent was made together with an inspection of *Isoetides* throughout the lake by ocular inspection of the bottoms down to 6 m depth.

In addition, a quantification of *Sphagnum* at a shaded and sheltered locality and an inspection of the *Isoetides* were made in each of the other five lakes in 1974, employing the same technique as in Lake Örvattnet.

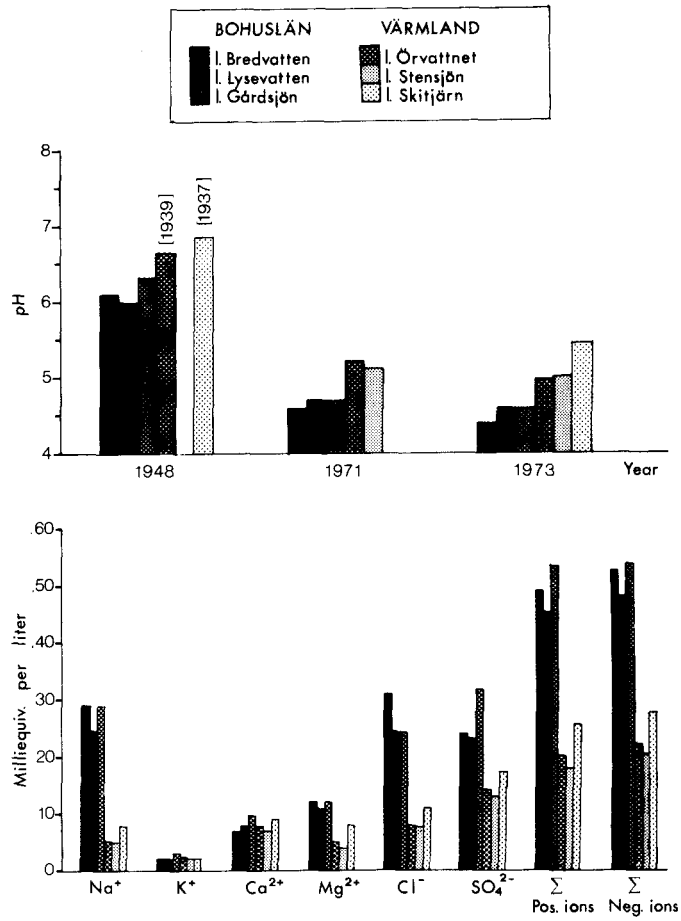

Figure 3. pH (in July 1948, 1971, 1973) and major ion constituents (July 1973) in the six investigated lakes.

RESULTS

In Lake Örvattnet there has been a considerable expansion of *Sphagnum* growth during the last seven years. Figure 5 shows the degree of coverage of *Sphagnum* in different depth zones at two localities in the lake from 1967 to 1974. Dominant among the *Sphagnum* species is *Sphagnum subsecundum* coll. Each annual value is a mean of 15 sampling squares (1 m^2). As can be seen from this figure, the expansion has been the largest in the depth zone 0-2 m at the sheltered and shaded locality of the lake. Here, the degree of coverage increased from 8 to 63% between 1967 and 1974. In the 2-4 m depth zone, a significant change from 10 to 26% occurred, whereas *Sphagnum* in the 4-6 m depth zone increased from 4 to 30%.

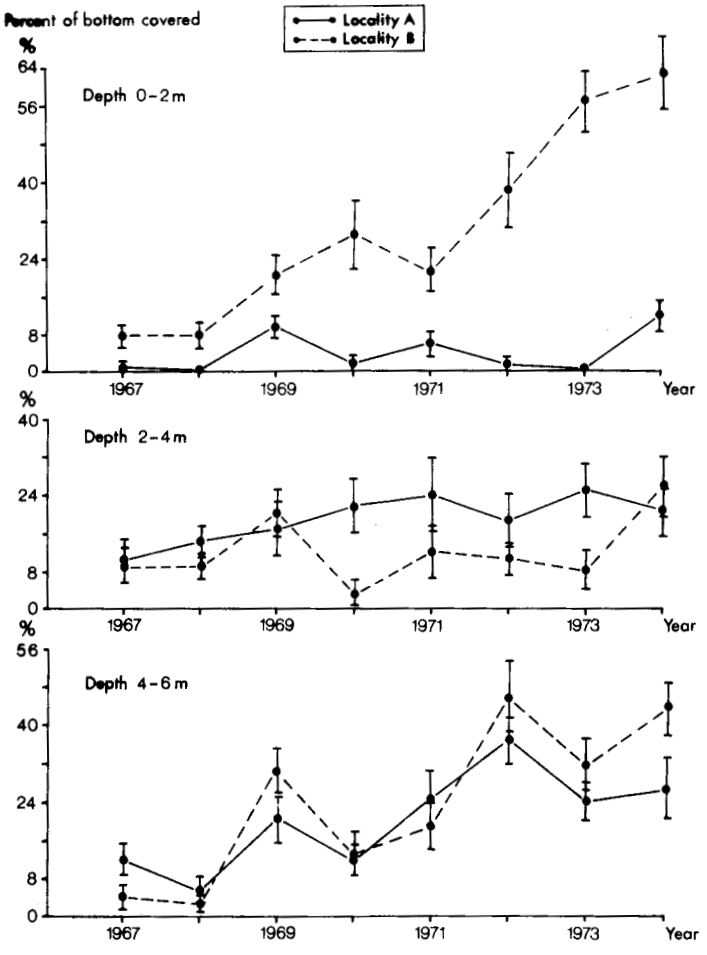

Figure 4a. Coverage of *Sphagnum* spp. on the bottom i different depth zones at two localitees in Lake Orvattnet in July 1967 - 1974. Each value is the mean of 15 sampling squares (1 m^2). Locality A: exposed to wind and sun. Locality B: sheltered and shaded.

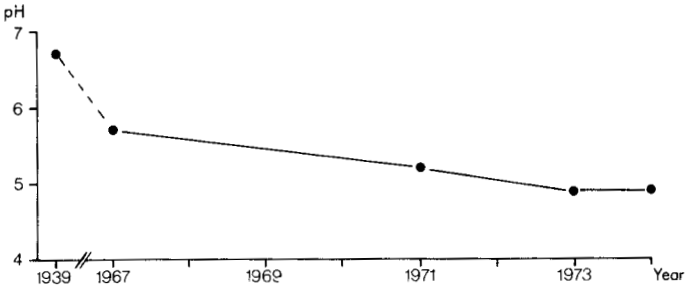

Figure 4b. pH at 1 m depth in Lake Örvattnet in July 1939, 1967, 1971, 1973 and 1974.

At the locality exposed to wind and sun, on the other hand, no significant increase occurred in the 0-2 m depth zones, whereas the degree of *Sphagnum* coverage at 4-6 m increased from 12 to 26%.

The two localities A and B in Lake Örvattnet differ with respect to both exposure to light and to wave effects. Locality A is situated on the NE side of the lake, with no tall trees near the shoreline, and is therefore exposed to the sun from the early morning hours. Southwesterly winds predominate in the area, which leads to strong wave effects. At locality B, softwoods grow all the way down to the shoreline. It is situated on the SW side of a bay, which reduces the number of sunny hours, as well as the wave effects.

At both localities, the depth zone 4-6 m is at a 100 m- distance from land and therefore exposed to the sun for the same number of hours. This makes possible a similar *Sphagnum* expansion in this depth zone at both A and B.

Areas in Lake Örvattnet covered with more than 40 percent of *Sphagnum* are represented by the dark areas on the map in Figure 5. Despite the subjective quantification it is, nevertheless, obvious that the coverage of *Sphagnum* is most extensive in shallow and sheltered bays. *Sphagnum* mats do occur on deeper bottoms down to 10-12 m, and observations of *Sphagnum* down to 18 m depth have been made.

It was found that the abundance of *Sphagnum* mats on the bottom is negatively correlated to the pH-value in five of the investigated lakes - the exception being Lake Stensjön which is humic. Figure 6 lists the six lakes in the order of their increasing pH as a function of the degree of coverage of *Sphagnum* at different depth zones in each lake. In Lake Lysevatten, Lake Gardsjön and Lake Bredvatten, *S. cuspidatum* and *S. palustre* occur beside *S. subsecundum* coll., whereas in Lake Skitjärn and Lake Stensjön, *S. subsecundum* coll. dominate. In the most acid lakes (Bredvatten, Lysevatten, Gardsjön), the coverage of *Sphagnum* at 0-2 m depth is about 70-80 percent, whereas it is about 50 percent in the least acid lake (Skitjärn). In the depth zones 2-4 m and 4-6 m, the occurrence of *Sphagnum* is less frequent than at 0-2 m in all lakes except in the most acid, Lake Bredvatten, where the coverage is about the same from 0 to 6 m.

In the littoral of oligotrophic lakes, *Lobelia dortmanna* and *Litorella uniflora* usually dominate in the depth zone 0-2 m and *Isoetes lacustris* and *Isoetes echinospora* dominate in the depth zone 2-4 m. In the investigated lakes, the *Isoetes* have, as a result of the *Sphagnum* expansion, been driven out of large littoral areas which have been overgrown with thick mats of *Sphagnum*. In July 1973 and 1974 a large number of dead plants were found under the moss in five of the six investigated lakes. Also the change induced by acidification of the micro-organism community negatively affects the *Isoetides* flora. In the acid clearwater lakes the bacteria have been largely wiped out and replaced by fungus (Grahn et al. 1974). The result has been a much retarded decom-

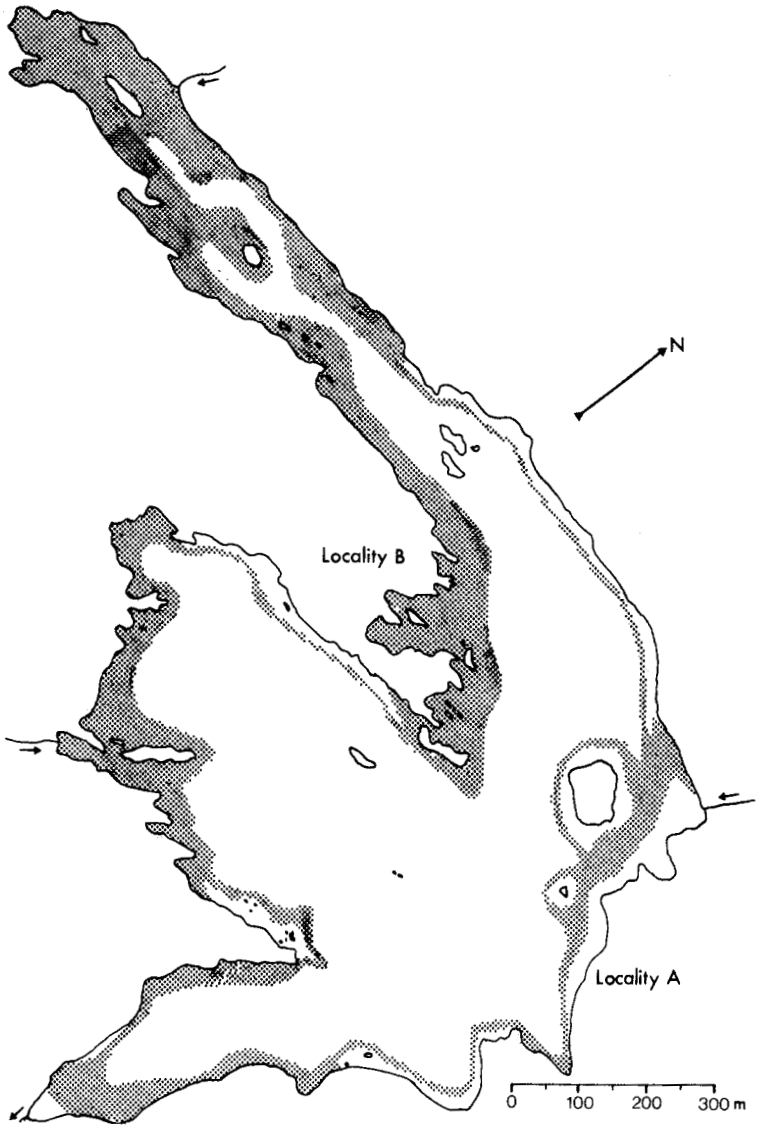

Figure 5. Bottom areas with > 40% coverage of *Sphagnum* spp. in Lake Örvattnet in 1974.

position rate and a more organic sediment. The upper sediment layer thus consists of a thick felt, where fungus hyphae, filamentous algae and remains of *Sphagnum* dominate, with *Isoetides* overgrown by or incorporated in the felt. Both the *Sphagnum* and the felt have thus contributed to the considerable reduction in the *Isoetides* flora in the littoral areas of the lakes.

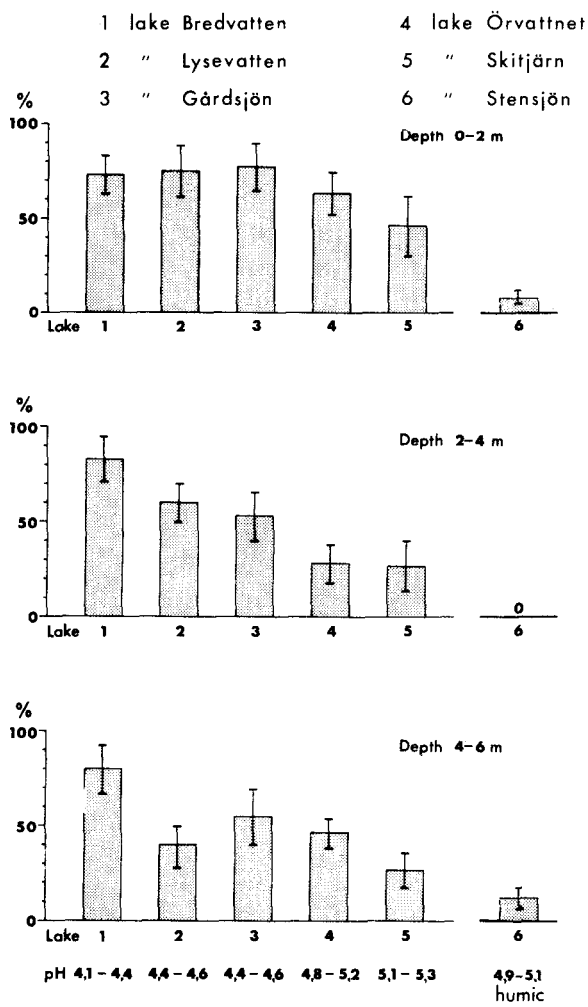

Figure 6. Coverage of *Sphagnum* spp. in different depth zones as a function of pH in the six investigated lakes, 1974.

DISCUSSION

The macrophyte surveys made during 1967 - 1974 in Lake Örvattnet clearly show that a succession of the plant community has taken place, and that a negative correlation exists between the pH of the water and the *Sphagnum* occurrence in five of the six investigated lakes. In both areas studied, the acidity of precipitation has increased during the last decades, resulting in pH-drops in the lakes. For this reason, one can assume that *Sphagnum* expansion is dependent on factors which are

directly or indirectly associated with the changes in pH in the lake water.

One of these factors is the state of the hydrogen carbonate buffer system which in freshwater is often the dominant buffer system. The pH of the water is due to the relative concentration of the components of the buffer system. When pH is below 5.3, as in the investigated lakes, most of the inorganic carbon is present as free CO_2. No carbon is present as carbonate ions and the concentration of hydrogen carbonate is less than 6 percent.

There is experimental proof that many aquatic plants directly utilize hydrocarbonate ions for their carbon supply, whereas others, among them several aquatic mosses, lack this ability and must therefore use free CO_2 for their carbon assimilation (Steeman Nielsen 1944, 1946, 1947; Ruttner 1948, 1953).

The occurrence of *Sphagnum* in acid waters has been observed before: E. g. Harrison (1958) found *Sphagnum truncatum* growing in dense mats in deeper parts of a river polluted with acids, whereas in a nearby, unpolluted stream *Sphagnum* was non-existent.

In unpolluted waters, *Sphagnum* and other mosses are often found in habitats which are rich in free CO_2, such as springs, streams with subsoil-water inflow, and moorland pools (Ruttner, 1960).

Similar habitats rich in free CO_2 may be found just below the ice cover in lakes containing HCO_3^{2-}, when acid water from heavy rainfalls or from snowmelting continuously mixes with the lake water. This may be a contributing cause of the moss in certain lakes migrating to the littoral in the early stage of the acidification process, e.g. in Lake Örvattnet at a pH of > 5.8.

Another factor of importance for the *Sphagnum* expansion is the light conditions in the lake. It is well known that *Sphagnum* prefers shaded habitats (Clymo 1973). However, in acid lakes, *Sphagnum* occupies not only the shaded areas in the littoral but also deep bottoms, given more favourable light conditions through the increased transparency.

The further consequences for the lake ecosystem of this occupation of ever larger bottom areas by dense *Sphagnum* mats are that several ions, most of which are important for biological production, are bound to the moss membrane and the peat, due to their strong ion-exchange capacity (Skene 1915, Ramaut 1954, Anschütz and Gessner 1954, Clymo 1963). In order to maintain electro-neutrality between *Sphagnum* and the water, protons are emitted.

The dense mats together with the remains of *Sphagnum* and fungus hyphae may also reduce the exchange of plant nutrients between the water and the sediment, reduce the mineralizing processes, as well as drive Isoetides out of the area. The living conditions for many members of

the bottom fauna also deteriorate because the moss is a very poor substratum for these organisms, especially for fish food organisms, and most of the fauna consists of small species of chironomide larvae. The recycling of nutrients bound up in the plant biomass therefore slows down.

CONCLUSION

The investigation has shown that a succession in the plant community in the lakes occurs over a short period and that these changes are correlated to the increasing acidity of the lake water.

The lakes have changed from being a kind of 'equilibrium systems' to biologically accumulating systems similar to acid biogene peat and forest soils. This type of biologically accumulating system may cause an acceleration of the acidification process, which in turn leads to further disorders in the lake ecosystem.

ACKNOWLEDGEMENTS

Thanks are due to M. Eastmond, I. Torbrink and L. Nordquist for their valuable assistance in this investigation. The investigation was financed by grants from STU and CDL.

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ACID PRECIPITATION AND REPRODUCTIVE SUCCESS OF *AMBYSTOMA* SALAMANDERS

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ABSTRACT

The two species of mole salmander that occur in the Ithaca, New York, region (*Ambystoma maculatum* and *A. jeffersonianum*) breed in temporary ponds that are formed by accumulation of melted snow and spring rains. Water in many of these pools during the breeding season is acid; pH values as low as 3.5 have been measured. In laboratory experiments *A. maculatum* tolerated pHs from 6-10 and had greatest hatching success at pH 7-9. *Ambystoma jeffersonianum* tolerated pH 4-8 and was most successful at pH 5-6. Mortality rose abruptly beyond the tolerance limits. The pH optimum shifted upward with increasing temperature for *A. jeffersonianum* and downward for *A. maculatum*.

Judging from our laboratory studies, the acidity measured in breeding ponds should cause mortality in *A. maculatum* and permit normal development in *A. jeffersonianum*. In a four-year study of a large acidic vernal pond, 938 adult *A. maculatum* produced 486 metamorphosed juveniles (0.52 juvenile/adult), while 686 adult *A. jeffersonianum* produced 2157 juveniles (3.14 juveniles/adult). Because the effects of acid precipitation on the salamanders' breeding ponds are cumulative from year to year, profound changes in the salamander populations can be anticipated.

INTRODUCTION

Certain species of amphibians may be the vertebrate animals most immediately and directly affected by acid precipitation. Their vulnerability to this form of pollution derives from their reproductive habits. Especially in temperate regions, many species of amphibians congregate at ponds to lay eggs which hatch into aquatic larvae. This pattern is particularly characteristic of frogs and toads; 90% of the

species in the United States adhere to it (Salthe and Duellman 1973, Table 8). Salamanders show more diversity of reproductive modes but half of the terrestrial salamander species of the United States lay eggs in water. (In tropical regions a majority of amphibians lay eggs out of water. In some of these species the aquatic larval stage is also omitted.)

Temperate-zone amphibians are not only largely aquatic in their reproduction, but many species breed in temporary pools formed each year by accumulation of rain and melted snow. Approximatley 50% of the species of frogs and toads in the United States regularly breed in ephemeral pools of this nature. Calculating a similar percentage for salamanders is more complicated because there are permanently aquatic species as well as completely terrestrial ones. One-third of the species that have aquatic eggs and larvae and terrestrial adults breed in temporary pools.

These temporary pools are usually completely empty at some time during the year and are refilled by rain and/or melted snow shortly before the amphibians enter them. For many species of amphibians the heavy rains that fill the pools are also the stimulus that initiates breeding activity. Because there is no water in the pools at the end of the dry season, the precipitation that fills them is not diluted by water already present as is the case in a permanent pond. Furthermore, most of these pools are small and collect drainage from a limited area. As a result, precipitation has relatively little contact with soil buffer systems before it enters the pools. In many regions amphibians breed early in the spring, before deciduous trees have sprouted leaves, so precipitation is not buffered by passage through the forest canopy. Because of these characteristics of amphibian breeding sites, the acidity of the water in the pools is strongly influenced by the pH of the precipitation that fills them and the pools are more acid than adjacent permanent bodies of water. During the spring amphibian breeding season in 1975, pH was measured in ponds used by frogs or salamanders near Ithaca, New York. The average pH of 12 temporary ponds was 4.5 (range 3.5-7.0). Permanent ponds are less acidic, the average of 6 used as amphibian breeding sites was pH 6.1 (range 5.5-7.0) (Pough, in prep.). Amphibian eggs and larvae in the temporary pools are exposed to these acid conditions.

There is virtually no information about the effect of pH on amphibian embryonic development, especially in an ecological context. the single study we have found, Gosner and Black (1957) reported that only acid-tolerant species of amphibians could breed in sphagnaceous bogs in the New Jersey Pine Barrens. Less tolerant species were excluded from the Pine Barrens or occurred only in more alkaline pools, most of which were products of human activity.

Temperature is another potential environmental stress to which amphibian eggs are exposed. Some amphibians breed when pools are partly ice-covered and water temperatures near freezing. Sunlight

penetrating the leafless forest canopy can raise water temperatures to 25 C or higher before the eggs hatch. In contrast to the paucity of information about the effects of pH on amphibian development, there is a massive body of information about the effects of temperature. Both the ecological and evolutionary significance of rate of development and tolerance limits of particular species have been extensively considered. (See Zweifel 1968 for a recent review.) We know of no study that has considered the effects of temperature and pH in combination, and data of this sort are essential in predicting the effects of acid precipitation on amphibian populations.

MATERIALS AND METHODS

Two species of mole salamanders widely distributed in eastern North America were studied. The geographic range of the spotted salamander (*Ambystoma maculatum*) extends northward from the Gulf of Mexico into southern Canada. The Jefferson salamander (*A. jeffersonianum*) has a more northern distribution extending southward from the Canadian border to northern Kentucky and Virginia. Both species occur in the Ithaca region, although the Jefferson salamander is found only in local populations. Both species breed in vernal ponds formed by accumulation of melted snow and rainwater, or in small permanent ponds. Freshly laid eggs were collected in the field or inseminated females were brought to the laboratory and held at field temperature until they laid their eggs. Eggs and salamanders were obtained from three sites, all in Tomkins County, New York: a small pond on the Cornell University Golf Course (n 42° 27' 30" W 76° 28' 00" pH 7-8), the Lloyd-Cornell Wildflower Preserve (N 42° 27' 00" W 76° 22' 26" pH 5-6), and several pools on Connecticut Hill (N 42° 22' W 76° 40' pH 5.5-6.5). Only eggs that had not reached gastrulation were used, and every combination of temperature and pH was tested at least once with eggs in the temperature-sensitive stages of early cleavage.

Incubation temperatures were controlled (± 1 C) at 5 C intervals from 5 to 35 C. The eggs were placed 40-60 cm from a 20 W cool white flourescent tube and a 12-hour photoperiod centered on noon EST was maintained. Sulfuric acid or NaOH was added to dechlorinated tap water to produce pH values from 4 to 11. The ionic content of the water approximates that of water in the breeding ponds. Sulfate is the predominant anion in these ponds (average concentration 3.9 mg/l, range 2.9-4.9, n = 5; Pough, in prep.). Nitrate concentration in the breeding ponds is low because of biological activity.

Solutions were prepared in advance and stored at the test temperature, pH was checked with a pH meter before the solutions were used. For each temperature/pH combination 20-30 eggs were placed in 300 ml of solution in a capped, ventilated plastic dish (9.5 × 9.5 × 6.5 cm). After eggs were added the pH of these unbuffered solutions drifted as

much as 0.5 pH units toward neutrality in the intervals between daily changes. Critical temperature/pH combinations were tested repeatedly with eggs from different clutches, and total sample sizes for different combinations range from 20 to over 100. We tried to retain the eggs within the gelatinous mass in which they were deposited, but handling expelled some eggs from the jelly. Eggs outside the mass appeared to develop slightly faster than those that remained in the jelly, but no other effects of separation were noted and no distinction was made in the analyses between individual eggs and eggs *en masse*.

Eggs were examined daily and development recorded by reference to the Harrison stage (Rugh 1962) except at 5 C where examinations were made on alternate days. We had no difficulty comparing different temperature/pH combinations until the later embryonic stages were reached. At that point developmental stages are defined largely on the basis of gill development, and gills of individuals at high temperatures were hypertrophied while those of individuals at low temperatures were small. Our criterion of success was development of an embryo without gross abnormalities to the gill circulation or hatching stage. Hatching sometimes preceded gill circulation, but in every case in which one occured the other followed. If neither had been achieved in 100 days the experiment was terminated. Larvae that appeared normal were released in the breeding ponds.

Field temperatures were measured with calibrated Wesco Museum Special thermometers or calibrated thermistors. Pond water pH was measured in the field with a Fisher portable pH meter or with LoIon pHydrion paper. Data were graphed on an IBM 1120 computer using a program written by Dr. Donald Allen.

RESULTS

HATCHING SUCCESS

We have followed previous authors in distinguishing several levels of hatching success. "Extreme" conditions never produced successful development. "Severe" mortality was < 50% hatching, and "moderate" mortality was 50-89% hatching. "Optimal" conditions produced ≥ 90% hatching. The optimal conditions were different for the two species. For *A. maculatum* these were pH 7-9 at 10-15 C, while for *A. jeffersonianum* the greatest success was achieved at pH 5-6 at 5-10 C (Figure 1). There was a similar but less pronounced difference in conditions that produced moderate and severe mortality. As temperature increased, the pH giving the greatest success increased in *A. jeffersonianum*, but not in *A. maculatum*.

A two-way analysis of variance was performed on the ungrouped data. For *Ambystoma maculatum* the effects of temperature and of pH were

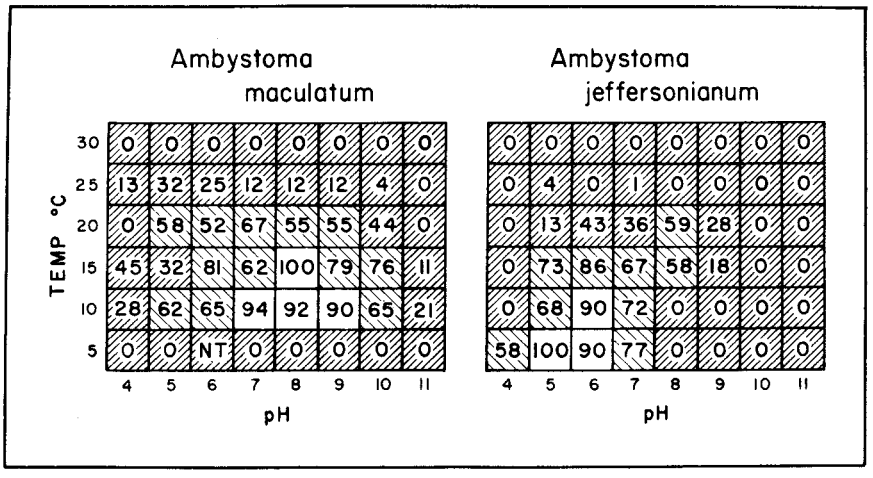

Figure 1. Hatching success of *Ambystoma maculatum* and *A. jeffersonianum* at different combinations of temperature and pH. The figure in each square is the percentage of eggs tested under those conditions that developed successfully.

significant (Table I) but the interaction between temperature and pH was not significant.

For *Ambystoma jeffersonianum* significant effects of temperature and of interaction between temperature and pH were demonstrated (Table I). Additional comparisons involving cell means were computed. At 5 C survival at pH 5 and 6 was significantly greater than survival at pH 4, 7, 8, or 9 ($F_{1,53} = 30.43$, $p < 0.001$). At 10 C survival at pH 6 was significantly greater than survival at pH 4, 5, 7, 8, or 9 ($F_{1,53} = 5.763$, $p < 0.025$).

SUBLETHAL EFFECTS

Temperature profoundly affected the rate of development. The average time from gastrulation (stage 10) to hatching is shown in Figure 2. *Ambystoma jeffersonianum* developed more rapidly than *A. maculatum* at all temperatures; the difference was greatest at low temperatures. *Ambystoma maculatum* did not develop successfully at 5 C, and *A. jeffersonianum* did not tolerate 25 C. Neither species survived at 30 or 35 C.

The pH had little effect on rate of development (Figure 3). The experiments illustrated were conducted at 10 C which is within the optimum temperature range for both species. There is some variation in the stage of development of different pHs on a given day, but development was not consistently faster or slower than the average at any pH

Table I. Two-way analysis of variance of survival at different temperatures and pHs.

Source	SS	df	MS	F
Ambystoma maculatum				
Temperature	1.266	3	0.422	3.802*
pH	2.791	7	0.399	3.596*
Temperature x pH	1.835	21	0.087	0.784 n.s.
Error	4.896	44	0.111	
Ambystoma jeffersonianum				
Temperature	1.640	3	0.547	4.675**
pH	0.640	5	0.128	1.094 n.s.
Temperature x pH	5.741	15	0.383	3.274***
Error	6.189	53	0.117	

n.s. = $p > 0.05$

* = $p < 0.05$

** = $p < 0.01$

*** = $p < 0.001$

and the daily variation resulted largely from the stepwise character of the Harrison stages. In each species only one pH produced hatchlings in this experiment (pH 6 for *A. jeffersonianum*, pH 8 for *A. maculatum*) but development proceeded as rapidly at pHs that were to prove lethal as it did at the optimal pHs.

STAGES AT WHICH ABNORMAL DEVELOPMENT APPEARED

Under extreme conditions of temperature or pH death occurred within a few hours of the eggs' being placed in the test solutions. In some cases development ceased at the stage at which the egg was put into the solution, in others irregular cell divisions continued for several hours. These eggs became mottled without a differentiation between the animal and vegetal poles. By blastula (stages 7-9) the eggs were shriveled and no further development occurred. Mortality produced by high temperatures occurred in these early stages. Lethal effects of acidity were expressed at different developmental stages depending upon the severity of the stress. Under severe pH stress developmental anomalies appeared during late gastrulation. Yolk plugs failed to retract or retracted incompletely. Some embryos died at this stage, others

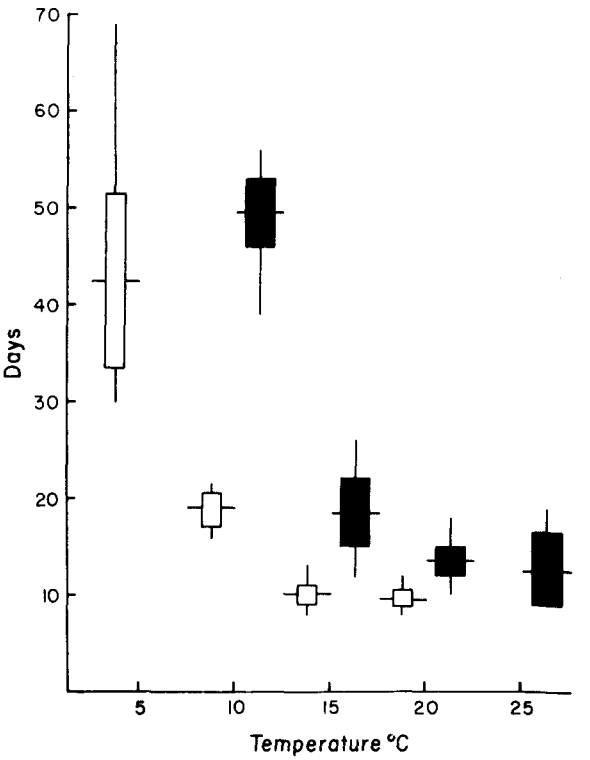

Figure 2. Effect of temperature on rate of embryonic development in *Ambystoma maculatum* (dark symbols) and *A. jeffersonianum*. The vertical axis shows the time in days for development from gastrulation to hatching. At 5 C *A. maculatum* eggs did not hatch, and 25 C was lethal to *A. jeffersonianum*.

survived with deformations of the spine and tail. The body usually arched dorsally. Those embryos that hatched retained this deformity, rested on their sides, and were barely able to swim. Moderate mortality was associated with abnormalities appearing late in the embryonic period, especially at gill development (stages 37-40). A swelling on the body wall near the heart was often seen, and the gills were asymmetric, sharply kinked, and stunted.

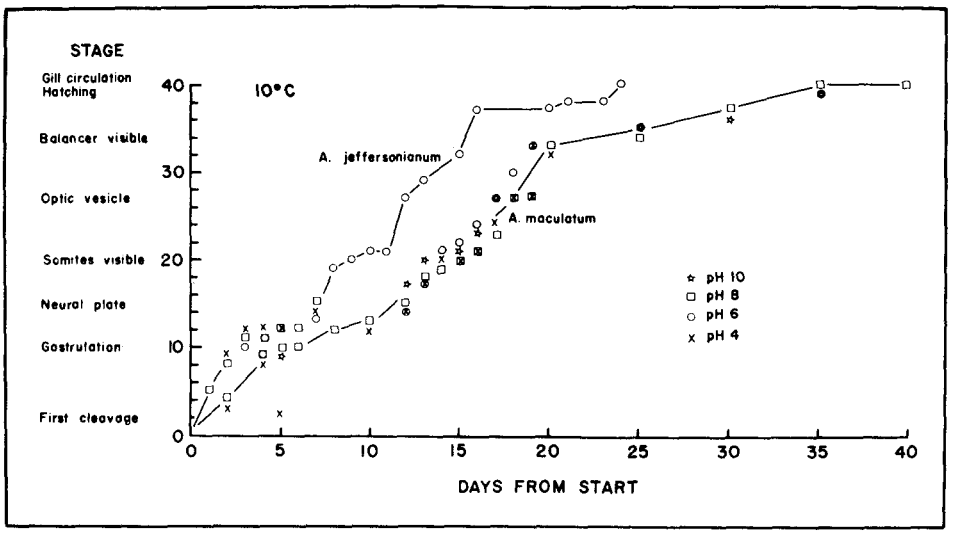

Figure 3. Effect of pH on rate of embryonic development of *Ambystoma maculatum* and *A. jeffersonianum*. Although only one pH produced hatchlings in each species, development proceeded at the same rate at all pHs to the point of embryonic death.

SPECIAL CASES

At 5 C *A. maculatum* eggs progressed to stage 37 at all pHs that permitted development, but did not hatch nor initiate gill circulation. If the eggs were moved to warmer temperatures they hatched after several days.

At pH 4 *A. maculatum* egg membranes shrank, forcing embryos into a sharp curve. Development of some embryos was apparently normal except that they had little space to move and did not engage in the muscular activity that normally characterizes late embryos. These embryos did not hatch spontaneously, and when they were removed from the egg membranes they were unable to straighten their bodies to swim. Although this occurred in every trial of *A. maculatum* eggs, it was seen only once in *A. jeffersonianum*.

DISCUSSION

TEMPERATURE TOLERANCE AND RATE OF DEVELOPMENT

The temperature relationships of the two species of *Ambystoma* conform to Moore's (1939) conclusions concerning anurans; northern forms that breed at lower water temperatures than southern forms have lower minimal and maximal temperatures for development than the southern forms, and develop more rapidly at low temperatures. Normal development was confined to a temperature range of only 10-15 C in the salamanders compared to a 22-24 C range in the frogs Moore studied.

Anderson (1972) studied six populations (four species) of *Ambystoma*. He concluded that rate of development and temperature tolerance reflected adaptation to life history pattern and the climate of a species' range rather than its geographic location *per se*. Inasmuch as *A. maculatum* and *A. jeffersonianum* breed in the same pools in the Ithaca region, Anderson's conclusions do not appear to apply to this case.

TOLERANCE OF pH EXTREMES

The most interesting results of the present study concern the effects of pH on hatching success. Mortality resulting from acid conditions can be distinguished from that produced by temperature extremes; high temperatures killed eggs at early developmental stages while low temperatures (in *A. maculatum*) permitted development but inhibited hatching. Furthermore, temperature profoundly affected the rate of development. In contrast, stressful pHs appeared to act as a series of hurdles in the embryonic process. Mortality occurred at specific developmental stages and development proceeded normally between these stages. Embryonic deformities produced by stressful pHs appear identifiably different from those resulting from temperature-induced chromosomal abnormalities (Fankhauser 1945), low oxygen (Hall 1924), and metal salts (Deuchar 1966). Some mutations described in a related salamander, the Mexican axolotl (*A. mexicanum*) are grossly similar to the deformities seen at stressful pHs, especially mutations *f*, *g*, and *v* (Malacinski and Brother 1974). They differ from pH stress in morphological detail and time of expression (Humphrey 1948, 1959, 1960, 1962; Briggs and Humphrey 1962; Justus and Humphrey 1964; Tompkins 1970). The similarities that do exist probably indicate only that both the mutations and stressful pHs cause profound cellular and subcellular rearrangements at early developmental stages. For example, acid or alkaline stress causes rearrangement of RNA in amphibian eggs (Brachet 1960) similar to that produced by mutation *v* (Briggs and Humphrey 1962), and varying the

acidity of the medium changes surface charges differentially in different germ layers (Schaeffer *et al.* 1973).

In 1957 Gosner and Black published a study of the effect of pH on development of several species of anurans that occur in or near the New Jersey Pine Barrens. They concluded that the low pH (3.6-5.2) associated with sphagnaceous pools in the Pine Barrens limited the breeding sites of most anurans to less acidic areas such as grassy ponds and gravel pits. Only *Hyla andersoni* and *Rana virgatipes*, species endemic to the Pine Barrens, could breed successfully in sphagnaceous pools. Ten of 12 amphibian breeding sites in temporary pools near Ithaca, New York, had pHs below 6 (the approximate lower limit of tolerance of *A. maculatum*). Six of the 12 pools were pH 5 or lower. On the basis of laboratory results, these acidic pHs should cause significant mortality in *A. maculatum*. Egg masses with a high proportion of embryos dead were frequently observed in this study, as in previous work with *Ambystoma* by other investigators (Anderson *et al.* 1971, Shoop 1974). Recent field work conducted by the senior author (Pough, in prep.) indicates that mortality of *A. maculatum* in natural breeding ponds closely corresponds to mortality seen at similar pHs in the laboratory. In a series of ponds ranging from pH 4.5 to 7.0, hatching success fell from > 90% at pH 6.5 and above to 40-60% at pHs lower than 6.5. An abrupt transition from high to low success occurred between pH 7 and pH 6 in the field as it does in the laboratory.

Relative reproductive success of the two species of *Ambystoma* at a common breeding site, an acidic (pH 5.0-6.5) pond in the Lloyd-Cornell Wildflower Preserve, is consistent with the hypothesis that there is an environmental stress that affects *A. maculatum* more severely than *A. jeffersonianum*. From 1968 through 1971 the pond was enclosed by a fence and virtually every adult entering the pond and juvenile leaving it was counted (Wilson 1976). In the four years of the study, 938 adult *A. maculatum* produced 486 juveniles, an average of 0.52 juvenile/adult. In the same perios 686 *A. jeffersonianum* (most of which bred biennially) produced 2157 juveniles, an average of 3.14 juveniles/adult.

PROBABLE ECOLOGICAL EFFECTS OF ACID PRECIPITATION

We suspect that acid precipitation has already had a deleterious effect on the reproduction of *A. maculatum* in the Ithaca region. The annual mean pH of precipitation of Ithaca, New York, in 1970-1971 was 3.98 (Likens and Bormann 1974). Likens (1972) calculated that 1 meter of precipitation at pH 4 leaches the equivalent of 50 kg $CaCO_3$/hectare. This represents the approximate annual loss of soil buffering capacity in the Finger Lakes region of New York. The effect is cumulative, and in terms of amphibian breeding sites is increased by the fact that the water comes in contact only with leaf litter and superficial layers of the soil before entering the pools. It seems inevitable that the pH of

the breeding pools will continue to fall toward the pH of incident rain and snow. If the pH in the pools reaches those levels, *A. maculatum* will be unable to reproduce and *A. jeffersonianum* will experience significant mortality. Lack of precise information on water pH and reproductive success of any *Ambystoma* before the advent of acid rain prevents documentation of its effects. The data presented here will provide a baseline for future study.

Presently *A. maculatum* is more abundant than *A. jeffersonianum* in the Ithaca region. We know of many sites at which only *A. maculatum* breeds, but none utilized exclusively by *A. jeffersonianum*. This situation probably reflects human land use in the 18th and 19th centuries; there is little indication of direct competition between the species (Wacasey 1961, Wilson 1976). A century ago central New York was largely farm and pasture land. Now much of that land is reverting to woods, and second growth forest is widespread. *Ambystoma maculatum* breeds in overgrown pastures and second growth woods, but in our experience *A. jeffersonianum* occurs only in or adjacent to areas of relatively undisturbed woods. The pH of breeding sites does not explain the present distribution of *A. jeffersonianum*. They breed successfully in ponds in undisturbed woods near Ithaca at pHs of 7.0 and 7.25 as well as in ponds with pHs from 4.5 to 6.0 in the Wildflower Preserve, but are absent from ponds in second growth woods with pHs of 4.5 to 7.0, and from ponds in meadows (where *A. maculatum* breed) with pHs of 6.0 to 7.0.

We believe that *A. maculatum* was able to tolerate land clearing associated with agriculture, maintaining populations in hedgerows and small patches of woodland, while *A. jeffersonianum* could not utilize these habitats and persisted only in undisturbed woods. As farms were abandoned and succession returned fields to woodland, the small populations of *A. maculatum* formed nuclei to invade the restored habitats, but *A. jeffersonianum*, confined to a few limited populations, has not been in a position to exploit second growth woods. Strips of cleared land between woodlots are probably a greater barrier to a dispersal of *A. jeffersonianum* than they are to *A. maculatum*. Attempts to reintroduce *A. jeffersonianum* into apparently suitable habitat by moving egg masses or larvae from pond to pond would probably be successful. One population was established this way in 1969 in a small permanent pond (pH 7.0-8.0) with larvae produced in the experiments described here. It is still in existence and appears to be growing. Before that attempt is made on a large scale, however, more should be known about the ecological relationships of *A. jeffersonianum* and *A. maculatum* to ensure that introduction of *A. jeffersonianum* does not add to the stress to which *A. maculatum* is subjected.

ACKNOWLEDGMENTS

We appreciate the technical assistance of Edward Francolini who also prepared the illustrations. Donald Allen wrote the computer program used to graph the experimental data. Morton Goldman and Faith Wilson assisted with the statistical analysis. James Anderson, Arnold Cooke, and Gene Likens kindly read an early version of the manuscript and made helpful suggestions. This study was supported by Federal Hatch Funds.

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PRELIMINARY BIOCHEMICAL OBSERVATIONS OF FISHES INHABITING AN ACIDIFIED LAKE IN ONTARIO, CANADA

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ABSTRACT

Blood serum and other tissues of white suckers *(Catostomus commersoni)* and other species of fish have been examined in a preliminary effort to understand losses of fish from acid lakes. Maturing females of highly acid George Lake failed to show the normal degree of increase in serum calcium over males captured in the same location. Elevated serum calcium was always observed in females, relative to males, from non-acid locations when maturation stages were similar. A number of body tissues were examined to determine whether the distributions of calcium or other elements were altered and the only striking change evident in fish from George Lake was their high manganese content. Bone in particular was examined for N, Na, Mg, P, K, and Ca and no evidence of demineralization was found. Other tests such as hemoglobin indicated that an anticipated adaptive response to asphyxia was absent. Our results indicated that potential mechanisms of fish losses such as asphyxia and starvation are unlikely to have been significant. However, they do not firmly establish any alternate mechanism. As a working hypothesis we suggest that calcium dynamics may limit ovarian development and that absorption of this metal at exchange surfaces may be impaired.

INTRODUCTION

The effects of acid upon fishes have been subjects of scientific study for well over half a century, and they nonetheless remain essentially unknown. Early studies attempted to explain the presence or absence of certain fish species on the basis of water chemistry data including pH (Jewell and Brown, 1924; Powers, 1929; Creaser, 1930) with varying degrees of success. Several more recent studies have noted

declines and losses of fish populations coincident with acidification (Harrison, 1958; Beamish and Harvey, 1972; Jensen and Snekvik, 1972). Field observations of fish in a number of lakes in the Sudbury area of Ontario indicated that some species of fish were more sensitive to acidification than others (Beamish and Harvey, 1972; Beamish, 1974a) and further that fish losses were not the result of prior elimination of food organisms (Beamish, 1974b). There seemed little doubt that acid, possibly in combination with other pollutants, acted upon fish to bring about the collapse of populations as a result of failure of mature individuals to spawn (Beamish and Harvey, 1972). Our fundamental assumptions were simply that some abnormality must be present in fish in acidified lakes - particularly those fish of reproductive age - or spawning would not cease and further that it should be possible to identify and measure any such abnormalities.

This report will include some preliminary screening analyses made in our efforts to apply biochemical pathology to fish in George Lake, a lake undergoing acidification some 65 km southwest of Sudbury, Ontario. The analyses are compared with those from fish taken from other locations, and with those in literature reports. The types of analyses to be made were selected partly because previous studies had suggested they might be instructive and partly because we had some experience in their performance. Certain highly desirable analyses such as blood respiratory gases were excluded on the grounds of difficult sampling or storage requirements. Considering the widespread nature of the acidification problem, and the long history of investigation, there is a striking paucity of literature on the mechanisms involved in acid toxicology. An equally striking paucity of literature exists to help the pathologist recognize those values which may be abnormal. With the exceptions of those few species of fish which have enjoyed intensive culture for economic or research purposes little work has been done to understand the biochemistry of freshwater fish. It is hoped that the data presented here will prove useful for comparison with future studies of fish in acidified lakes, and that future work will enable us to interpret these data more rigorously.

MATERIALS AND METHODS

Fish were captured form several sources by various means including trap nets, gill nets, and hand dip nets. In some cases we wished to observe the effect of forced exercise on suckers *(Catostomus commersoni)* and a period of one half hour was devoted to "chasing" the fish with a dip net either in a mesh enclosure in the acid lake or in an aerated laboratory tank.

Blood samples were taken by syringe from caudal vessels except in the case of white suckers for which heart puncture was found to

be more convenient. Blood was allowed to clot at 0°C and serum was decanted either for immediate analyses or more commonly for storage frozen until laboratory examination could be made. After blood was obtained, fish were examined internally to determine sex and maturity and they too were frozen until analyzed. The methods of chemical analyses were, in general, standard procedures of microanalyses (Mattenheimer, 1970) adapted to the small quantities of sample available and they are tabulated below.

Analysis	Procedure
serum sodium	flame emission
serum chloride	microtitration (Schales and Schales, 1941)
serum protein	biuret
serum inorganic phosphate	molybdate
serum glucose	glucose oxidase
serum calcium	atomic absorption
serum cortisol	fluorometric (Mattingly, 1962)
total serum phosphorus	ultraviolet irradiation, then molybdate
whole blood lactate	lactate dehydrogenase
whole blood hemoglobin	cyanmethemoglobin
whole blood hematocrit	centrifugation
whole blood pH	Radiometer combination electrode
metals in bone, skin, gonads and scales	hydrochloric acid digestion and flame emission (Na, K) or atomic absorption (Ca, Mg, Mn)
metals in muscle	nitric acid digestion and flame emission (Na, K) or atomic absorption (Ca, Mg,Mn)
nitrogen in bone	sulfuric acid digestion and micro Kjeldahl procedure
Phosphorus in bone	hydrochloric acid digestion, ultraviolet irradiation, then molybdate

RESULTS AND DISCUSSION

Our earliest hypothesis that fish in an acid lake might suffer asphyxia was based upon several literature reports and upon the simple reasoning that gill surfaces are large and in constant contact with the acid water, hence they may well be expected to function at a reduced capacity. There is no doubt that water pH effects the minimum levels of dissolved oxygen which can be tolerated by silver salmon (Townsend and Cheyne, 1944). A possible mechanism by which acid might limit oxygen transport is the precipitation of mucus on gill filaments with accompanying decreased permeability (Westfall, 1945). Decreased oxygen consumption has been shown to result from acid exposure of brook trout

(Packer and Dunson, 1972). If oxygen transport by fish has been reduced in the acid lake, we might reasonably expect to observe adaptive responses such as increases in hemoglobin and hematocrit, since these have been produced experimentally both by acid exposure (Vaala and Mitchell, 1970; Anthony et al. 1971) and by asphyxia (Phillips, 1947). Hemoglobin levels were determined for five groups of white suckers in 1972 and results are tabulated below.

Hemoglobin levels in white suckers (*Catostomus commersoni*) from an acid Lake (George) and two other lakes

Group and time	Condition	Hemoglobin concentration (g/dl) ±S.D	Range	No. of fish
George Lake Sept. 1972	trap net unexercised	8.67 ± 1.25	5.85-10.24	10
George Lake Sept. 1972	trap net exercised	9.53 ± 0.80	8.38-10.53	12
Georgian Bay Sept. 1972	gill net	8.28 ± 1.44	6.33-11.22	15
Lake Manitoba Dec. 1972	laboratory unexercised	8.84 ± 0.83	7.53-10.01	9
Lake Manitoba Dec. 1972	laboratory exercised	8.22 ± 0.83	6.89-9.32	7

These values are generally quite similar and they indicate that little if any adaptive increase has occurred in George Lake suckers. Black (1955) found mean hemoglobin levels from 8.8 to 11.5 g/dl in the sucker *Catostomus catostomus* from British Columbia and our values are comparable with Black's lower groups. The George Lake pre-exercise values are almost the same as the Lake Manitoba/laboratory pre-exercise group. Vaala and Mitchell (1970) noted a 29 percent increase in hemoglobin concentrations of acid-treated brook trout and certainly changes of that magnitude are absent from these acid lake (pH 5.1) suckers.

Hematocrit measurements were made on George Lake brown bullheads (*Ictalurus nebulosus*) trap netted in August, 1973 and the mean hematocrit (± S.D.) was 28.9% ± 4.6 with a range of 21% to 36%. For comparison, Haws and Goodnight (1962) reported a mean hematocrit of 27.9% ± 6.5 with a range of 15.0% to 40%. Black (1940) found a slightly higher mean value of 32.2%, the range being 20.5% to 39.7%. By comparison with literature values then, brown bullheads in the acid lake exhibited no obvious adaptive increase in hematocrit. Some

however, she exceeded males by only a factor of 1.3, consistent with other failing species. A ratio of serum calcium in females to that in males of about 1.4, then has separated species failing to reproduce in George Lake from species still reproducing in that lake and also from similar species reproducing in other lakes. Assuming the low calcium ratios are more than coincidence, and lacking data from fish inhabiting George Lake prior to acidification, we cannot be certain whether low calcium excesses in females have resulted from acidification, or whether acidification has erected a selective barrier which can be met only by species maintaining higher female:male calcium ratios during maturation.

Sites of uptake of calcium from water have been reviewed by Simmons (1971) and it seems that calcium is exchanged at gills and other body surfaces, particularly those around certain fins. Dietary calcium has been reported to accumulate most readily in skeleton and skin in brown trout (Podoliak and Holden, 1964). As shown earlier, we have found no indication of reductions in calcium content of bone, muscle, or scales and similarily we found no shortage of calcium from skin as shown below.

Skin calcium concentrations in white suckers from George Lake and Lake Manitoba

Source and time	Skin calcium (g/100 g wet skin) ±S.D	Number of Samples	Range
George Lake, Sept. 1972	8.44 ± 0.80	5	7.1 - 9.0
George Lake, Dec. 1972	7.73 ± 1.02	7	6.5 - 9.6
Lake Manitoba Jan. 1973	8.54 ± 1.38	5	6.9 - 10.3

Ovaries developing in two white suckers taken in December, 1972 contained calcium at concentrations of 215 and 193 mg/kg (wet weight) concentrations above muscle concentrations for the same fish (100 and 90 mg/kg respectively). For comparison, suckers maturing in Roddy Lake in March, 1974, had ovarian calcium levels averaging 272 mg/kg (Roddy Lake has an even lower calcium content than George Lake). It is obvious that substantial quantities of calcium are required for ovarian development or such high concentrations could not be achieved in such large organs. Our analyses suggest that calcium was not obtained from internal sources such as muscle, skin, scales, or bone and we agree with the suggestion by Fleming et al. (1964) that at least part of the extra calcium needed by maturing females must be obtained from the environment. It seems probable that the explanation of a calcium matabolism problem in fishes inhabiting an acid lake is more likely to be found in

caution must be exercised with these hematocrit measurements, however, since they and several other measurements tended to change in an orderly manner throughout the sampling sequence. In fact, when hematocrit was plotted against the sequence number of a fish in the sampling order (Fig. 1), a significant ($p \leq 0.01$) correlation ($r = -0.83$) was found to exist. Other authors have not reported this effect and it is presumably some reaction of the fish to the sampling experience or possibly a segment in a diurnal rhythm.

Inorganic phosphate has also been found to increase in fish during asphyxia (Bange, 1962). We obtained a mean inorganic phosphate P level of 8.18 ± 1.65 mg ^{P}/dl in brown bullhead serum in August 1973. McCay (1931) reported a value of 7 mg ^{P}/dl in this species and Hunn (1972) found 18.77 mg PO_4/dl (6.12 mg ^{P}/dl) in the yellow bullhead (*Ictalurus natalis*) from the upper Mississippi river. The values we obtained then are somewhat higher than expected but once again some artifact may be suspected since phosphate decreased ($p \leq 0.01$; $r = -0.73$) throughout the sampling order (Fig. 1). Total serum phosphorus values were not related to sampling sequence (25.2 ± 6.77 mg ^{P}/dl) and it seems likely that high early phosphate values represent storage time. That is, the inorganic phosphate probably increased during blood and serum storage at 0°C at the expense of labile organic phosphorus compounds. The analyses were performed in the field on the evening of collection, and the times between sample collection and phosphate analyses decreased from about 9 hours for the first sample to about 5 hours for the last sample.

Serum glucose has been reported to increase during asphyxia in several fish species (Menton, 1927; Hall et al. 1926; Heath and Pritchard, 1965) including bullheads (Simpson, 1926). The review by Chavin and Young (1970) indicates that mean glucose levels from 22 mg/dl to 59 mg/dl have been reported for brown bullheads. Our values were almost double the previous maximum. For 15 fish from the acid lake in August 1973 (water temperature, 21°C) the mean glucose concentration (± S.D.) was 109.7 ± 46.9 mg/dl and the range was 32.8 to 196 mg/dl. There was a tendency to increase ($p \leq 0.05$; $r = +0.57$) throughout the sampling order (Fig. 1), which may indicate asphyxia or other stress during sampling, however, even initial values were high for bullheads. The first five values, for example, were 80.5, 74.3, 32.8, 102 and 64.5. Silbergeld (1974) has recently indicated the value of blood glucose assays as indicators of stress in fish, and these glucose levels suggest some sub-lethal stress related to life in the acid lake or possibly to the capture experience.

Blood pH also increased systematically as fish were sampled sequentially throughout the afternoon (Fig. 1). We wished to obtain measurements of blood pH because both Lloyd and Jordan (1964) as well as Packer and Dunson (1970) found a fall in blood pH of salmonids exposed to acid, and it has been established that acidosis induced by injection of acids can kill fish (Jonas et al. 1962). We measured blood pH in whole blood (lithium heparin anticoagulant) from 15 brown

bullheads in the acid lake at 21°C in August, 1973, and we obtained a very wide range from 7.112 to 7.816. Two standard buffers recommended by Bates (1973) were used before and after each blood sample, and it seems unlikely that measuring errors would extend beyond the last two decimal points. The upward trend throughout the afternoon of sampling was striking ($p \leq 0.01$; $r = +0.89$), and this direction is contrary to that expected during asphyxia (Caillouet, 1968). The average pH obtained simply as the sum of all readings divided by 15 (the number of samples) was 7.562, and the average obtained by first converting each pH to hydrogen ion concentration was 7.489. It seems that the first averaging procedure is in more common use in fish studies. Fish blood pH measurements have been reviewed by Houston (1971) and a range of means from 7.49 to 7.99 has been reported for *Ictalurus* species; in spite of the relation to sample sequence, then, our mean of 7.56 is within the range of previous means. Our early values are, however, the most acid reported. For example, our first three values were 7.198, 7.112, and 7.332 and our last three were 7.816, 7.806, and 7.763. In spite of low early values the fish showed no indication of distress, and evidently critically acid blood pH is below 7.112 in bullheads. Our early values suggest that acidosis is in fact a problem for bullheads in George Lake, however, the mean and later values argue against this. Garey (1972) found that several captured fish had much lower blood pH values than did the same species catheterized and swimming freely, the respective values for pink salmon (*Oncorhynchus gorbuscha*) being 7.54 and 8.10 at 14°C.

Animals generally turn to anaerobic metabolism when oxygen does not reach tissues rapidly enough to meet the needs of cellular respiration. Under these conditions we might expect an increase in some product of anaerobic metabolism, namely lactic acid. Lactate levels were determined in blood of white suckers captured in the acid lake in September 1972 with and without a period of forced exercise defined by "chasing" the caged fish with a dip net for half an hour. The results are shown below.

Lactate levels in white suckers (*Catostomus commersoni*) from an acid lake (George) and two other lakes

Group and time	Condition	Water temp. °C	Lactate concentration (mg/dl) ±S.D	Range	No. of fish
George Lake Sept. 1972	trap net unexercised	17	44.7 ± 16.5	22.2-69.8	10
George Lake Sept. 1972	trap net exercised	17	96.1 ± 8.63	82.9-110.0	12

Lactate levels in white suckers (*Catostomus commersoni*) from an acid lake (George) and two other lakes

Group and time	Condition	Water temp. °C	Lactate concentration (mg/dl) ±S.D	Range	No. of fish
Georgian Bay Sept. 1972	gill net	-	67.4 ± 24.3	30.7-112	15
Lake Manitoba Sept. 1972	laboratory unexercised	3.5	19.8 ± 3.30	14.9-26.3	15
Lake Manitoba Dec. 1972	laboratory exercised	3.5	35.1 ± 16.5	14.0-68.0	14

Generally the September samples are well above those reported by Black (1955) for *Catostomus catostomus*; Black obtained mean values from 15.4 to 19.1 mg/dl without exercise and from 54.4 to 56.4 mg/dl after 15 minutes exercise at 11.5°C. There is some disagreement in the literature concerning the relation between water temperature and blood lactate in fish. For example, Wendt (1964) observed a large lactate difference between groups of speckled trout (*Salvelinus fontinalis*) exercised at 5°C and 15°C; however, Black (1957) found no difference between groups of Kamloops trout (*Salmo gairdneri*) exercised at 11.5°C and 20°C. The total range for George Lake specimens was 22.2 to 110 mg/dl, almost the same as that for gill netted fish from Georgian Bay (30.7 - 112 mg/dl); however, the effect of gill netting upon lactate levels in the Georgian Bay group may have been large. The important question is whether lactate concentrations before exercise in George Lake suckers were pathologically high, and a definitive answer will have to await comparison with future data. Striking seasonal variations in lactate levels have been observed in exercised rainbow trout (*Salmo gairdneri*) (Lockhart et al. 1975); increases in our values over those reported by Black (1955) may have related to temperature or some other natural variable. The George Lake suckers and those from Lake Manitoba approximately doubled their blood lactate levels as a result of the forced exercise, indicating that life in the acid lake had left the mechanism of glycolysis intact at least qualitatively.

In general, the measurements carried out to detect the presence of asphyxia do not answer the question unequivocally. Adaptive responses such as increases in hematocrit and hemoglobin seem to be absent, but relatively high levels of glucose and lactate in unexercised groups of George Lake fish leave the question in doubt. The four measurements which changed throughout the sampling sequence (Fig. 1)

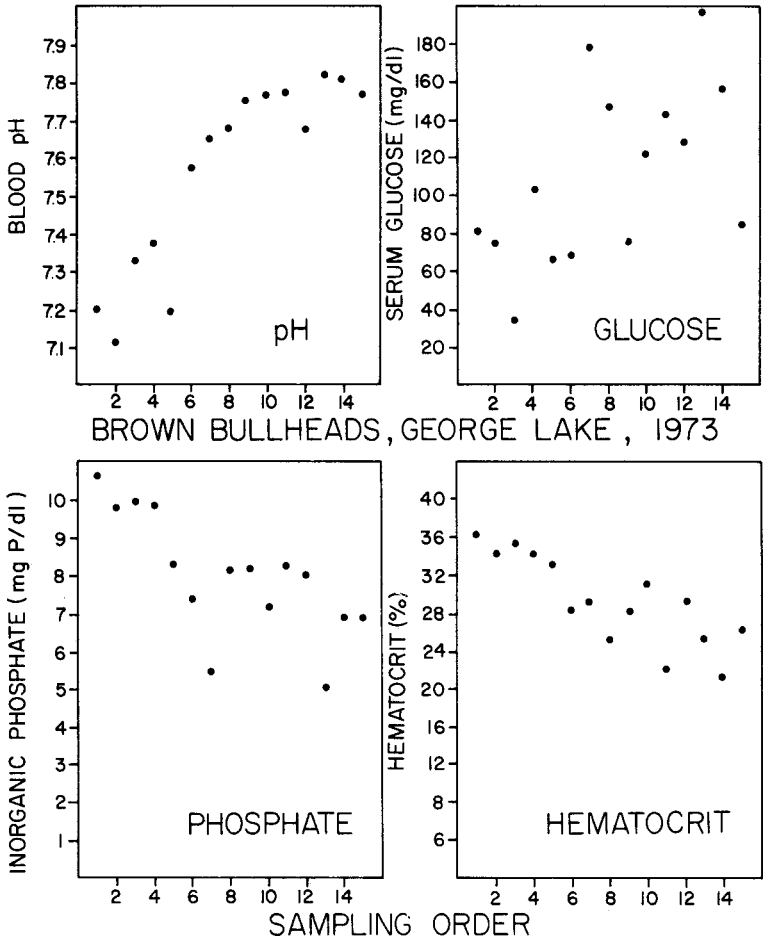

Figure 1. Apparent relationship between position in sampling sequence and four blood measurements for brown bullheads trapped in George Lake in August, 1973. Fish were removed from the water one at a time for collection of blood, thus the first fish removed was number 1 in the sampling order, and the last fish some 4 hours later, was number 15. Correlation co-efficients between these numbers in the sampling order and the four blood measurements shown were: $r = + 0.89$ for pH ($p \leq 0.01$); $r = + 0.57$ for glucose ($p \leq 0.05$); $r = - 0.73$ for phosphate ($p \leq 0.01$); $r = - 0.83$ for hematocrit ($p \leq 0.01$).

do not support the hypothesis that asphyxia was developing progressively during the sampling period since three of the four (hematocrit, inorganic phosphate, and pH) changed in the unexpected direction.

An unusually high frequency of deformities was noted in the white sucker population of George Lake (Beamish et al. 1975). In view of the fall in blood pH demonstrated in acid-treated rainbow trout (Lloyd and Jordan, 1964) and brook trout (Packer and Dunson, 1970), we wished to test the attractive hypothesis that deformities were the result of demineralization of bone as salts were extracted to combat a condition of chronic acidosis. Experimental exposures of fish to acid solutions have resulted in deformities (Beamish, 1972; Mount, 1973); the stoichiometry of skeletal demineralization has been described by White et al. (1968). Unfortunately, suckers were not caught in trap nets during our 1973 sampling efforts and we used brown bullheads instead as the only species available. Measurements of blood pH seemed unlikely to reveal acidosis in this species since early work by Jobes and Jewell (1927) indicated no depletion of the alkali reserve of blood from bullheads in an acid lake in Michigan, and furthermore, deformities have not been observed in this species. The results of pH measurements in bullheads were presented above and they are difficult to interpret in view of the progressive increase throughout the afternoon while samples were collected. It seems that some but certainly not all the bullheads were in a condition of acidosis at the time of sample collection. The second part of a demineralization process seemed more readily detected simply by analyses of bone. We analyzed anterior ribs from suckers captured in the acid lake in 1972 for nitrogen, sodium, magnesium, phosphorus, potassium and calcium (Table 1) for comparison with suckers from Lake Manitoba. The greatest difference between groups of suckers was in rib magnesium content and acid suckers were 107% of non-acid suckers. Biltz and Pellegrino (1969) included one species of fish (*Lutjanus aya*) in their survey of cortical bone from the femora and tibiae of vertebrates and they found Ca, 23.26%; P, 10.85%; Mg, 0.3%; and Na, 0.32%. Komárková and Bilyk (1973) have reported calcium and phosphorus values for several different bones of various fish species, and their rib values were 22.9 to 26.0% for Ca and 10.2 to 11.2% for P. Based on rib analyses then, suckers in the acid lake had not experienced severe demineralization of bone, and other causes of deformities will need consideration. Deformities are easily produced in fish; Rasquin and Rosenbloom (1954) induced severe spinal deformities by simply maintaining fish in darkness and Mehrle and Meyer (1975) induced them by exposing fish to toxaphene.

Very severe loss of one mineral element, namely sodium, has been found to result from experimental acid exposure (Packer and Dunson, 1970). Sera of brown bullheads collected in August 1973 were analysed for both major ions, sodium and chloride, and the results are shown on the next page.

Source		Sodium (mg/dl)	Chloride (mg/dl)
George Lake (trap net)	$\bar{X}$	272.4	377.7
	SD	29.3	16.4
	range	223 - 323	352 - 412
	n	15	15
Georgian Bay (gill net)	$\bar{X}$	295.8	353.8
	SD	43.0	25.3
	range	180 - 380	302 - 387
	n	19	19

Table I

Bone (Rib) Analyses : White Suckers, December 1972

Nitrogen, Sodium, Magnesium, Phosphorus, Potassium, Calcium as Percent Dry Weight of Bone

		N	Na	Mg	P	K	Ca
George Lake		5.1	0.35	0.40	10.0	0.44	22.9
		5.1	0.33	0.39	9.8	0.42	22.3
		4.8	0.37	0.56	10.4	0.46	22.7
		5.0	0.47	0.46	10.6	0.44	22.5
		5.1	0.44	0.47	9.4	0.46	20.8
		5.1	0.35	0.52	10.0	0.41	21.7
		5.1	0.41	0.57	10.4	0.39	22.4
	$\bar{X}$	5.04	0.39	0.48	10.1	0.43	22.2
Lake Manitoba		5.5	0.34	0.37	10.2	0.46	21.5
		5.1	0.39	0.47	10.4	0.45	22.6
		5.1	0.37	0.49	10.8	0.42	24.0
		5.0	0.36	0.45	10.7	0.41	24.4
	$\bar{X}$	5.2	0.37	0.45	10.5	0.44	23.1

Hunn (1972) obtained sodium and chloride values of 134.3 ± 1.4 meq/l (308.9 mg/dl) and 113.3 ± 3.9 meq/l (401.6 mg/dl) respectively. Comparison of mean sodium concentrations (using a transformation to natural logarithms) indicated that bullheads did not differ between George Lake and Georgian Bay ($t = 1.624$, $df = 32$). To the extent that Georgian Bay values are representative of bullheads, the acid-exposed fish have not suffered depletion of major serum ions sodium and chloride. The same may be said of bone sodium in suckers from the data in Table 1. Since the major portion of body weight is composed of muscle tissue, that too was examined in the 1972 white sucker samples, and the

results (Table 2) suggest that neither sodium nor other major metals

Table II

White Muscle Metals, White Suckers. 1972

		Metal Concentrations (mg/kg wet tissue)			
		Sodium	Potassium	Calcium	Magnesium
George Lake					
Sept. 1972	$\bar{X}$	277	4440	98.1	348
Unexercised	SD	18.9	172	6.84	28.9
From Trap	Range	250-300	4200-4700	92-111	296-376
	n	7	7	7	7
George Lake					
Sept. 1972	$\bar{X}$	250	4110	95.3	315
Exercised	SD	28.7	176	7.47	12.6
From Trap	Range	200-300	3900-4300	86-107	292-334
	n	9	9	9	9
George Lake					
Dec 1972	$\bar{X}$	400	3750	130	290
Gill Netted	SD	67.3	206	70.9	17.6
	Range	290-500	3430-3930	90-287	262-309
	n	7	7	7	7
Georgian Bay					
Sept 1972	$\bar{X}$	250	4190	92.1	321
Gill Netted	SD	57.4	183	6.26	21.0
	Range	180-340	3800-4400	79-104	275-349
	n	12	12	12	12

were depleted below Georgian Bay values in September 1972. Thurston et al. (1959) reported sodium and potassium concentrations for fillets of a number of freshwater species and for suckers (*Catostomidae* sp) the mean sodium concentration was 590 mg/kg (range, 460 - 860 mg/kg); for potassium the mean concentration was 3280 mg/kg (range, 3260 - 3330 mg/kg). In comparison with fillets then, all the muscle analyses here are low in sodium and high in potassium. It is of interest that Packer and Dunson (1970) did not observe sodium differences among wild trout inhabiting streams ranging in pH from 6.05 to 7.10.

Serum cortisol has been measured in fish as a response to non-specific stress (Wedemeyer, 1969) although the value of this measurement as an indicator of chronic low-level stress is in doubt (Hill and Fromm, 1968). Little attention has been given to suckers, however, Phillips (1959) reported plasma cortisol concentrations of 44 µg/dl for male suckers and 20 µg/dl for females. Cortisol concentrations were measured in sera of suckers captured in 1972 and the results are tabulated on the next page.

Serum cortisol levels for white suckers (*Catostomus commersoni*) from an acid lake (George) and a non-acid lake (Georgian Bay)

Group and time	Condition	Water Temp. °C	Concentration (µg/dl) ± S.D	Range	No. of fish
George Lake Sept. 1972	trap net unexercised	17	50.0 ± 11.1	28.0-62.0	10
George Lake Sept. 1972	trap net exercised	17	109. ± 34.6	58.0-190.	12
Georgian Bay Sept. 1972	gill net	-	88.6 ± 28.0	35.2-119.	15

Prior to exercise, the George Lake males and females were indistinguishable on the basis of cortisol, but females appeared to respond slightly more to the forced exercise than did males; for the George Lake exercised group males had mean cortisol levels of 92.3 (Range 58 - 120) µg/dl and females 126.5 (Range 95 - 190) µg/dl. Fagerlund (1967) noted that female sockeye salmon also showed a greater response to stress than males. The response to forced exercise in these fish has been to approximately double the pre-exercise cortisol concentrations, and this might be considered a relatively low increase as compared with salmonids, however, the pre-exercise values may not be true resting levels since these fish were trapped in a net and since simple stresses such as holding a handnet in a tank without forcing exercise have caused increases in cortisol (Fagerlund, 1967). The pre-exercise values agree well with male values given by Phillips (1959) but females reported here are more than double those in the earlier report. Gill netted fish from Georgian Bay showed a wide range of values, presumably as a result of the netting. Cortisol increases in George Lake suckers following exercise indicate that the necessary mechanisms of pituitary and interrenal glands were qualitatively intact. Wedemeyer (1969) has suggested that production of 17-hydroxycorticosteroids in response to stress may be a measure of vigor useful in applied genetic studies. A low cortisol response to stress then may be a measure of reduced vigor, however, future data will be needed to define a normal response for this species before we can be certain that the response shown was in fact low.

White suckers in George Lake and acidified lakes in the same region have been shown to grow at an unusually slow annual rate (Beamish, 1974b; Beamish et al. 1975). Acidification has also altered zooplankton communities (Sprules, 1975) giving rise to the hypothesis that reduced productivity at low trophic levels has been a cause of fish losses. Some of the measurements reported here are relevant to this hypothesis and generally they do not support an argument that fish

were grossly starved. For example, anemia has been shown to result from starvation in fish (Kawatsu, 1966) and neither suckers nor bullheads from George Lake were anemic as judged by hemoglobin and hematocrit measurements. Similarly blood sugar has been shown to fall in some chronic starvation experiments (Larsson and Lewander, 1973) and bullheads from George Lake showed elevated rather than reduced sugar values. A number of biochemical changes have been associated with starvation in fish (Love, 1970) including reductions in serum protein in some species (Creach and Bouche, 1969). Serum protein concentrations were measured in white suckers from George Lake and the results below show no apparent reduction.

Serum protein concentrations in white suckers (*Catostomus commersoni*) from George Lake and other sources

Species	Source and time	Sample Number	Condition	Serum Protein (g/dl) ± S.D	Range
White Sucker	George Lake Sept. 1972	10	trap net unexercised	4.61 ± 0.54	3.90-5.40
White Sucker	George Lake Sept. 1972	12	trap net exercised	4.33 ± 0.79	2.90-6.00
White Sucker	Georgian Bay Sept. 1972	11	gill net	4.98 ± 0.85	3.80-6.90
White Sucker	Lake Manitoba Dec. 1972	15	laboratory unexercised	4.43 ± 0.79	3.65-5.70
White Sucker	Lake Manitoba Dec. 1972	13	laboratory exercised	4.36 ± 0.70	3.22-5.43

Another interesting change associated with starvation was noted by Ichikawa (1953) and that change was reabsorption of scales. Scales of white suckers from George Lake were analyzed for calcium content and compared with scales from the same species in Roddy Lake. Calcium content of scales of George Lake suckers ranged from 10.8 to 13.5 percent with a mean of 11.9%; in suckers from Roddy Lake, it ranged from 8.9 to 13.9% with a mean value of 11.7%. These biochemical data do not indicate starvation and they support the argument advanced by Beamish (1974b) that suckers are disappearing from acid lakes "despite the presence of adequate food reserves".

Failure of a number of species in George Lake has been associated with failure of females to release ova (Beamish et al. 1975). Striking elevations in serum calcium concentrations have been observed during

sexual maturation of female fishes (Hess et al. 1928; Fleming et al. 1964; Woodhead and Plack, 1968). Increases in serum calcium have been induced in fish by treatment with estradiol (Bailey, 1957) and the extra calcium has been described as "complex calcium phosphoproteinate" being transported from liver to ovary for deposition of egg yolk (Urist and Schjeide, 1961). There is evidence that fish obtain most of their calcium supply directly from water rather than from food (McCay et al., 1936) and hence the same reasoning which has prompted several studies of oxygen consumption and our own interest in asphyxia can be applied to calcium metabolism - namely that it is an essential element which must be obtained at surfaces in contact with the acid water. The general subject of calcium metabolism in fish has been the subject of several recent reviews (Simmons, 1971; Simkiss, 1973; Fleming, 1967; Urist, 1966) and we have analyzed serum and several other tissues of fish from George Lake and other lakes for calcium.

Serum calcium concentrations for white suckers are shown in Table 3 and for several other species in Table 4. From the serum data there

Table III

Mean Serum Calcium Concentrations (mg/dl) for White Suckers from George Lake and other sources with number of samples.

Source	Date	Calcium in Females	Calcium in Males	Female/Male Ratio
George Lake	Sept '72	11.44(9)	12.47(13)	0.917
	May '73	14.36(16)	11.26(10)	1.275
	Nov '73	14.97(7)	11.07(7)	1.352
Georgian Bay	Sept '72	17.16(7)	11.13(3)	1.541
	May '73	15.65(2)	10.95(2)	1.429
Roddy Lake	Sept '73	12.94(18)	11.00(10)	1.177*
	Jan '74	14.71(10)	8.60(4)	1.710
	Mar '74	14.25(6)	8.43(3)	1.690
Beaver Glen	May '73	10.75(3)	10.54(3)	1.020**
Creek	May '74	11.43(4)	8.65(8)	1.321**
Kakakise	May '73	16.40(1)	12.00(3)	1.367
Lake	Nov '73	15.18(6)	10.00(4)	1.518
Lake Manitoba	Dec '72	22.98(11)	11.57(17)	1.986

* Very early in maturation

** From spawning run

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Table IV

Mean Serum Calcium Concentrations (mg/dl) for various species of fish from George Lake and other sources with numbers of samples.

Species	Source	Date	Calcium Females	Calcium Males	Female/Male Ratio
Brown Bullheads	George Lake	May '73	10.70(4)	8.95(6)	1.196
		Aug '73	12.33(4)	12.70(10)	0.970
		Nov '73	13.18(11)	10.20(7)	1.292
	Georgian Bay	May '73	22.95(2)	9.70(4)	2.366
		Aug '73	20.63(10)	14.38(9)	1.435
Yellow Perch	George Lake	May '73	22.63(10)	12.83(4)	1.765
	Georgian Bay	May '73	32.08(4)	9.90(1)	3.240
	Muriel Lake	May '73	30.34(8)	11.38(8)	2.667
Lake Herring	George Lake	Nov '73	20.64(5)	11.47(6)	1.800
	Kakakise Lake	Nov '73	19.67(12)	11.81(8)	1.665
Northern Pike	George Lake	May '73	25.5(1)	19.15(8)	1.332

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appears to be some depletion in females of failing species in acid lakes. When samples were taken very early in gonadal maturation (Table 3, Roddy Lake, Sept. 1973) or as late as the annual spawning run (Table 3, Beaver Glen Creek, May 1973 and May 1974) then females show little if any excess over males captured at the same time. During periods of ovarian development, however, female suckers exceeded males by a factor of about 1.4 or greater, except in George Lake. The only exception we have noted was based upon four fish from Kakakise Lake in May 1973 when females exceeded males by a factor of only 1.367. Kakakise Lake is very near George Lake, and it is also undergoing acidification, although at a reduced rate (Beamish and Harvey, 1972) and fish losses have not yet been observed. Considering other species (Table 4), a similar phenomenon is present; brown bullheads are failing in George Lake and females did not show a high excess over males. Yellow perch, (*Perca flavescens*) and lake herring (*Coregonus artedii*) are still reproducing successfully in George Lake and in both these species serum calcium in females exceeds that in males by factors greater than 1.4. Unfortunately, only one female northern pike (*Esox lucius*) was captured from George Lake,

however, she exceeded males by only a factor of 1.3, consistent with other failing species. A ratio of serum calcium in females to that in males of about 1.4, then, has separated species failing to reproduce in George Lake from species still reproducing in that lake and also from similar species reproducing in other lakes. Assuming the low calcium ratios are more than coincidence, and lacking data from fish inhabiting George Lake prior to acidification, we cannot be certain whether low calcium excesses in females have resulted from acidification, or whether acidification has erected a selective barrier which can be met only by species maitaining higher female:male calcium ratios during maturation.

Sites of uptake of calcium from water have been reviewed by Simmons (1971) and it seems that calcium is exchanged at gills and other body surfaces, particularly those around certain fins. Dietary calcium has been reported to accumulate most readily in skeleton and skin in brown trout (Podoliak and Holden, 1964). As shown earlier, we have found no indication of reductions in calcium content of bone, muscle, or scales and similarly we found no shortage of calcium from skin as shown below.

Skin calcium concentrations in white suckers from George Lake and Lake Manitoba

Source and time	Skin calcium (g/100 g wet skin) $\pm$ S.D	Number of Samples	Range
George Lake, Sept. 1972	8.44 $\pm$ 0.80	5	7.1 - 9.0
George Lake, Dec. 1972	7.73 $\pm$ 1.02	7	6.5 - 9.6
Lake Manitoba, Jan. 1973	8.54 $\pm$ 1.38	5	6.9 - 10.3

Ovaries developing in two white suckers taken in December, 1972 contained calcium at concentrations of 215 and 193 mg/kg (wet weight), concentrations above muscle concentrations for the same fish (100 and 90 mg/kg respectively). For comparison, suckers maturing in Roddy Lake in March, 1974, have ovarian calcium levels averaging 272 mg/kg (Roddy Lake has an even lower calcium content than George Lake). It is obvious that substantial quantities of calcium are required for ovarian development or such high concentration could not be achieved in such large organs. Our analyses suggest that calcium was not obtained from internal sources such as muscle, skin, scales, or bone and we agree with the suggestion by Fleming et al (1964) that at least part of the extra calcium needed by maturing females must be obtained from the environment. It seems probable that the explanation of a calcium metabolism problem in fishes inhabiting and acid lake is more likely to be found in

studies that measure rates of calcium exchanges and neuroendocine mechanisms controlling those exchanges than in static concentrations reported here.

High levels of manganese were found in tissues of George Lake fish (below).

Manganese concentrations in tissues of white suckers captured from acid George Lake and other sources

Source and time	Tissue	Manganese concentration (mg/kg) wet tissue ± S.D	Number of Samples	Range
George Lake Dec. 1972	scales	551 ± 96.9	7	414 - 654
Roddy Lake March 1974	scales	160 ± 39.8	8	107 - 221
George Lake Sept. 1972	skin	356 ± 103.	5	244 - 464
George Lake Dec. 1972	skin	305 ± 53.9	7	236 - 396
Lake Manitoba Apr. 1973	skin	7.20 ± 1.50	5	5.7 - 9.1
George Lake Sept. 1972	muscle	1.00 ± 0.52	7	0.24 - 1.96

Comparing scale analyses between George Lake and Roddy Lake suckers, we find a three-fold increase in George Lake; comparing skin levels we find a striking increase of some 40-fold over skin concentrations from Lake Manitoba. When calcium is accumulated from water by areas near fins it must pass through skin and we may speculate that high fluxes of manganese in skin, or even high static concentrations here, could compete with or otherwise impair calcium uptake. This situation appears to apply to uptake of magnesium by pine seedlings (Safford, 1975). The mechanism of manganese poisoning in humans includes disturbances in calcium metabolism since manganese poisoning is accompanied by abnormally high serum calcium concentrations (Chandra et al., 1974). The behavior of manganese in acidified lakes seems to merit additional research effort.

SUMMARY

Several biochemical properties of fish inhabiting an acidified lake near Sudbury, Ontario, are reported. Values for hemoglobin indicated that an anticipated adaptive response to asphyxia was absent. Apparent sampling artifacts were noted in brown bullheads with respect to hematocrit, blood pH, sugar and inorganic phosphate analyses. It was thought that deformities observed in white suckers in the acid lake might be explained by demineralization of the skeleton, however, no biochemical deficiencies were found in rib analyses. No indication of starvation was found when several measurements reported to change during starvation were made, and it appears that reduced growth shown by acid lake suckers was not caused by starvation. Female white suckers and other species undergoing reproductive failure did not achieve as great an excess in serum calcium values over males in the acid lake as they did in non-acid locations. Females of species still reproducing successfully in the acid lake did achieve the expected calcium excesses over males. It is suggested that calcium dynamics are altered in fish from the acid lake. High levels of manganese, particularly in skin, were found in acid lake suckers.

The subject of calcium metabolism in fish seems to deserve increased attention in attempts to understand the pathology of acid pollution.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of the following people: R. J. Beamish, D. Metner, A. Dwilow, R. Wickstrom, R. Hanson, R. Hunt, K. Tam, B. Thompson, A. Yakimischak, G. McFarlane, J. Drolet, G. Decterow and L. Allard. Dr. P. M. Mehrle (Fish-Pesticide Research Laboratory, Bureau of Sport Fisheries and Wildlife, Columbia, Missouri) kindly carried out the cortisol analyses and Dr. J. F. Klaverkamp reviewed the manuscript.

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EFFECTS OF ACID-MINE WASTES ON AQUATIC ECOSYSTEMS*

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ABSTRACT

The Cedar Creek Basin (39th N parallel 92nd W meridian) was studied for the period June 1952 through August 1954 to observe the effects of both continuous and periodic acid effluent flows on aquatic communities. The acid strip-mine effluent contained ferric and ferrous iron, copper, lead, zinc, aluminum, magnesium, titratable acid, and elevated hydrogen ion concentration, and was toxic to many of the aquatic organisms. In the areas of Cedar Creek, subjected to continuous acid flow, planktonic and benthic species had become adapted to the severe conditions and varied in abundance and diversity. No fishes were observed in the area with continuous acid effluents. Downstream, where periodic mineral acid conditions changed drastically during an excessive effluent flow, planktonic and benthic communities had high diversity but low density. The populations of fishes were variable in this stream reach. The chemical basis of water quality variability was shown to be time related, and statistically related to the aquatic communities.

Physical, chemical and biological conditions of acid lakes formed by surface mining were reviewed. In addition to apparent physical and chemical differences in lakes, due in part to variable solar absorbance due to suspended oxides of iron, chemical variability related to organic composition was reviewed. It is quite probable that degradation of such lakes can be reversed.

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*Contribution from the Missouri Cooperative Wildlife Research Unit: U.S. Fish and Wildlife Service, Wildlife Management Institute, Missouri Conservation Commission, Edward K. Love Foundation and University of Missouri cooperating.

INTRODUCTION

Acid precipitation, its chemistry and its effects, is not a new problem nor is it a problem restricted to a specific geographical area. Highly polluted precipitation has fallen over Scandinavia since the late 1800's, in the Sudbury Basin of Canada since the mid-1920's, and in the eastern United States since the late 1940's and early 1950's.

Acid precipitation contains large amounts of hydrogen ion, sulfate, and nitrate, with a variety of heavy metals, e.g., copper, lead and zinc, that have been produced mainly from manufacturing activities using highly sulfated fossil fuels. The result has been a wide range of deleterious effects on the environment.

The decline in the quality of aquatic ecosystems in Norway, first reported in the 1920's, has become a national disaster with the loss of much of the sport fisheries and the commercial salmon fisheries. Similar decline in the quality of aquatic habitat due to acid precipitation is now affecting other waters with the subsequent loss of fish populations. Notably, the 'smelter belt' region of Canada and the Adirondack Mountain region of the northeastern United States have recently been affected.

An older body of information, which lends itself to the prediction of the outcome of acidification of aquatic ecosystems by the sulfate ion and its myriad possible cations is, at least in part, available in the numerous studies concerning acid-mine wastes and the environment.

The literature* on coal strip-mine effluents is now voluminous, treating both the effects on natural waters and the chemical and biological succession in man-made acid sulfate waters. While a thorough literature search was conducted this paper does not incorporate a comprehensive literature review. With an understanding of the stream ecosystem in normal flux, its response to acid-mine wastes, and the recovery of man-made acid lakes, the general effects of acid precipitation on aquatic ecosystems should be predictable, though not necessarily completely abatable at this time.

The stream ecosystem from origin to confluences has been characterized in numerous ways: by a current in one direction, by an increase in volume, by changes in substrate structure, by the longitudinal change in the two major habitats, i.e., riffle to riffle-pool to pool communities, and by an increase both in temperature and in the dissolved oxygen supply.

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*Mine Drainage Abstracts, A Bibliography. 1964. With Supplements 1965 through 1974. Bituminous Coal Research, Inc. Pittsburgh, Pennsylvania.

These physiographic changes are accompanied by longitudinal biotic colonization, through specialized structures, physiological response, and by simply taking advantage of the physical environment afforded. This colonization results in a myriad of longitudinal communities of aufwuchs, plankton, benthos, and fishes. The populations within each group increase in diversity with the continual development of the ecosystem.

The open stream ecosystem is dependent upon the watershed -- terrestrial, as well as ponds, lakes and backwaters -- for its basic energy supply, and upon drift as the major mechanism in the distribution of that energy supply.

THE STREAM ECOSYSTEM IN NATURAL FLUX

During the annual seasonal cycle, animal populations will vary in numbers naturally. Zooplankton, though seldom reaching the predominance of benthos or fishes, fluctuates widely in numbers, primarily as a function of stream volume and flow. Warm spring rains bring on the first of the plankton which by June reach a relatively stable population. The small amount of rain during the 'dog days' of August heralds the onset of low volume and low flow with a marked increase in the number of individuals per taxon. Continued low volume and flow, plus the major introductions of allochthonous materials, contributed during September and October in northern temperate forested regions, bring about a series of nearly separate leaf-choked temporary ponds. These factors contribute to the drastic change in the species composition and the size of populations which takes place. With November rains and full stream volume and flow, a small population pulse occurs in December, only to be followed by the disappearance of zooplankton from January through March until the spring rains.

The more stable benthic populations give way to emerging, maturing, breeding adults, which repopulate the stream during the short period of time in June and July. The first sampling of new larvae begins in August. The apparent increase in numbers, the innate lag time, variables in reproduction, the dispersal and hatching of eggs, and the growth of larvae which occur through September, October, and November are all factors in determining population size. During the period of limited rainfall, low stream flow severely hampers the complete colonization of the riffle areas. As the various species grow to catchable size and continue to mature through the winter months, the size of the populations remains rather constant. The biomass, however, increases markedly through March, April, and May, reaching a maximum again at the time of emergence.

As the dominant life form, the fishes are also the most restricted in distribution. The high waters in the spring bring about feverish

upstream migration of many species. The low stream flow of late summer forces the riffle species to seek the nearest pool. The populations are under the great stress of near oxygen depletion. Fall rains bring an increased inflow and usually a redistribution of the fishes. The fish populations then remain stable until the spring rains bring about an increase in the volume of flow and the upstream migration of the fishes.

THE STREAM ECOSYSTEM AND ACID WASTES

When strip-mining* activities are in the upper reaches of a stream, two aquatic ecosystems become directly associated with acid wastes: 1) the natural stream or stream drainage system and 2) a variety of man-made lakes. The watershed associated with the lakes 1) has a greatly increased surface area, 2) is an exposed source of toxic materials, and 3) is the source of acid waste run-off for both lake and stream.

The chemical breakdown of iron sulfide, the sulfuritic material associated with strip-mine areas, is due to both chemical and biological oxidation (Parsons, 1957). The oxidation products of this material are primarily sulfuric acid and iron sulfate (Parsons, 1957; Stumm and Morgan, 1970). The occurrence of various other sulfate salts depends upon the nature of the mineral content of the associated strata.

Apparently, oxidation of iron sulfide is nearly complete before the products enter the lake. Therefore, the strip-mine lakes serve as holding areas and have little to do with the formation of mine effluents. The major role of the lake is the hydrolysis of ferric sulfate (Parsons, 1955, 1957, 1964). Though this reaction produces another molecule of sulfuric acid, it also forms basic ferric sulfate, which is readily oxidized.

Acid-mine wastes consist chiefly of the sulfates of ferrous iron, ferric iron, aluminum, calcium, and magnesium, together with traces of a wide variety of other ions including at times several heavy metals (Braley, 1951; Parsons, 1955).

The effects of acid wastes on a stream are often modified by natural events, such as the emergence or migration or both of animal populations and the amount and distribution of rainfall. The latter affects stream flow and thus, the dilution factor. Further, a flow of acid wastes disrupts the abiotic environment, i.e., 1) the increase in the number of toxic ions and their concentrations, 2) the precipitation of the normal silt load, 3) the dissipation of the bicarbonate buffer system, and 4) destruction of dissolved oxygen, with the ultimate

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*The mining of coal at the surface. "Open-cast-mining" is the term familiar to international readers.

destruction of the biotic populations of the ecosystem.

As an example of the effects of acidification, the studies on Cedar Creek and the ecological ramifications of sulfate and related cations (Parsons, 1955, 1956, 1968) will be used as a basis for the discussion of acid precipitation. Researches on the effects of acid-mine wastes on aquatic ecosystems show a number of reactions which are quite similar to the effects of acid precipitation. These acid-mine waste effects are often more abrupt, but not necessarily more calamitous. A second aquatic ecosystem, ponds or lakes, created by the extraction of coal, their chemical characteristics, a chemical aging to normalcy (Parsons, 1955, 1964; Campbell et al. 1965a, 1965b; Campbell and Lind, 1969), and the reverse process of the effects of acid precipitation on fresh waters, will be the basis for additional elaboration.

The Cedar Creek Study was neither the first nor will it be the last study on the effects of acid effluents on the ecology of streams. The study was, however, definitive in covering the acid chemistry and the plankton, benthic, and fishes populations. In an earlier singular study of the hydrogen ion, Trax (1910) lamented that the Youghiogheny River was more acid than the Allegheny River. In a more recent comprehensive work, Cairns et al. (1971) found, in six case histories, that stream communities exhibited various degrees of recovery after reclamation. Recovery was found to be ". . .a function of physical, chemical, and biological characteristics of the receiving stream, the severity and duration of the stress, and the availability of undamaged areas to serve as sources for recolonizing organisms" (Cairns et al. 1971).

DESCRIPTION OF STUDY AREA

The Cedar Creek Basin (Figure 1) is located in Boone and Callaway counties (39th N parallel 92nd W meridian) in central Missouri north of the Missouri River, on the southern edge of the easternmost projection of the Western Interior Coal Province (Campbell, 1922; Parsons, 1955).

Cedar Creek is 44.4 miles (71.5 kilometers) long, flowing north-south with a gradient of 6.7 feet per mile (1.3 meters per kilometer), a mean velocity of one-third foot (0.1 meter) per second, and a traversal time of approximately eight days. Cedar creek drains a narrow valley of approximately 1.28×10^5 acres (5.18×10^4 hectares), an average of 2.9×10^3 acres of watershed for each linear mile of stream (7.2×10^3 hectares per kilometer). The general appearance of the strip-mine areas of this study is shown in Figure 2. The physical relationship of the disturbed areas to Cedar Creek and its tributaries is shown in Figure 3, with source areas of acid waters designated numerically.

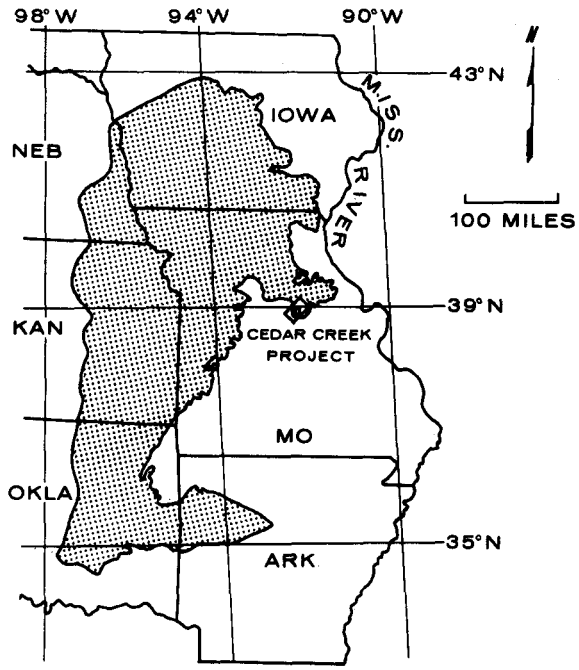

Figure 1. Location of the Cedar Creek Studies - Missouri, U.S.A.

The upstream area of the watershed was disturbed by surface mining operations. A total of 33% of the headwater region consisted of overburden materials with numerous strip pits. The assay of these materials has been reported to be 78% toxic, i.e., areas with more than 75% of the surface material having a pH of 4.4 or less (Rogers, 1951). This area also contained several lakes formed by mining operations. Watershed physiographic conditions varied significantly from highly disturbed areas with toxic overburden to narrow valley with rock outcrops and high bluffs. Stations 1-5 were representative of the upper watershed conditions, Stations 6-9 of the middle watershed, and Stations 10 and 11 of the lower watershed (Figure 4).

METHODS AND MATERIALS

Studies on Cedar Creek were begun June 1952 and continued through August 1954. Monthly samples were supplemented with intensive sampling to describe major events on the watershed.

Figure 2. General strip-mine area with typical chevron basin red lake.

Chemical

Standard methods (APHA, 1947) of chemical analysis were used to determine oxygen (sample-blank modification of the Winkler method), alkalinity, acidity, and pH (glass electrode) of water samples (Ellis et al. 1946). The titrametric benzidine method was used to determine the sulfate content of the samples following the procedure of Ellis et al. (1946). This method was modified due to the interference of ferric iron in accordance with Theroux et al. (1943). To determine the amount of the remaining sulfur(ous) compounds, the above procedure was used for the assay of sulfides, sulfites, and other non-sulfate sulfur(ous) forms following an oxidative procedure.

The remainder of the ions were assayed by colorimetric methods designed for trace analysis, using a Hellige-Diller photoelectric colorimeter, Model 400. The procedures as given by Ellis et al. (1946) were used to determine the concentration of both ferric iron (thiocyanate

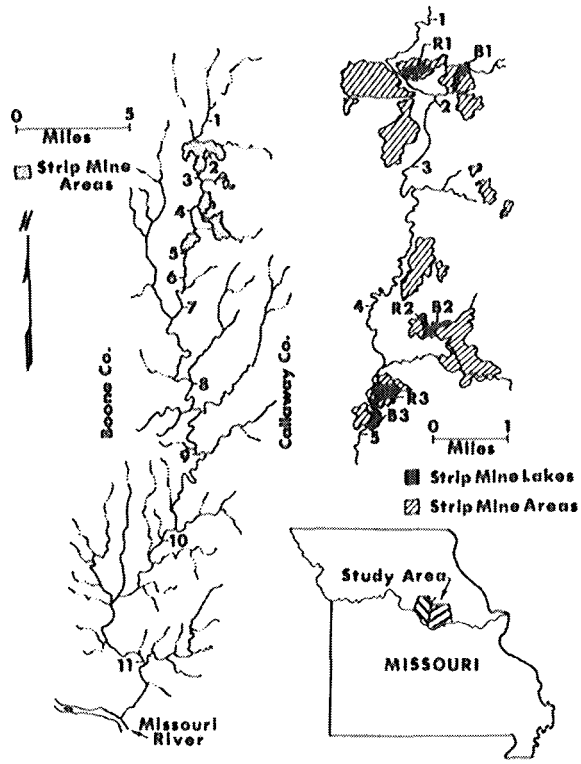

Figure 3. Cedar Creek with permament sampling stations and related lakes with color notation.

method) and copper (sodium diethyldithiocarbamate method). Ferrous iron (2,2' dipyridyl method), zinc and lead (diphenylthiocarbazone mixed-color method), aluminum (aurintricarboxylate method), and calcium (oleate method), were assayed following the procedures of Sandell (1950). Magnesium was determined by thiazole yellow method, a procedure adapted from Graham (1950).

Biological

Standard methods (Parsons, 1955, 1968) were used in collecting, preserving and counting both planktonic and benthic samples.

During the study of the populations of fishes, samples were taken once a month with an electric seine. The seine was modeled after Funk (1947), modified by Larimore et al. (1950), and further modified by Parsons (1955).

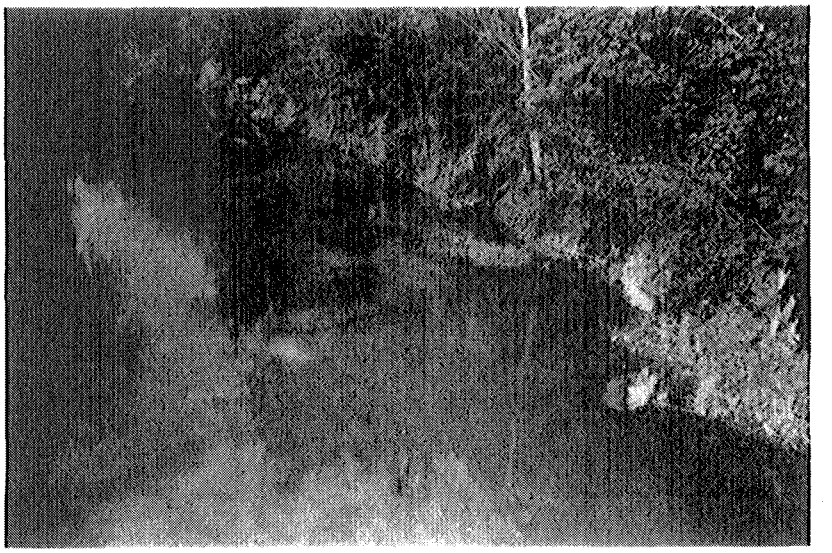

Figure 4. Station 10, typical of the mid and lower stream.

Physical

Physical measurements were taken employing the Secchi disc and platinum wire techniques for turbidity, a Foxboro thermophone for water temperatures at one-foot (0.3 meter) intervals in depth of both types of acid lakes, and a Taylor pocket thermometer for stream temperatures.

Data Processing

Statistical analyses, modeling, and the prediction of the best line of fit are the result of multiple linear regressional analysis -- Program Linear (McNeil et al. 1973). Discriminatory program BMDO5M and parameter accountability program BMDO3M were used for further data analyses.

RESULTS

Acid Waste Delivery

There were two different aspects of acid-mine pollution in Cedar Creek. The upstream area, Stations 2 through 7, was continuously polluted by acid-mine effluents originating in the strip-mine areas above Station 5 (Figure 3). The downstream area, Stations 8 through 11 was considered unpolluted (Figure 3). However, during excessive flows of acid-mine effluents, part or all of the downstream area was polluted.

The initiation of an excessive acid flow occurs in the Cedar Creek Valley immediately above Station 5. A sizable portion of this area drains, in terms of strip-mine run-off, directly into Cedar Creek. Here, as on the other strip-mine lands of this general area, salts produced by the breakdown of iron sulfide are concentrated by evaporation at the surface of the spill piles. Large amounts of the various sulfate salts accumulate during the warmer months of the year under the high temperatures and prolonged dry periods. It appears that rainfall initiates excessive acid flows by dissolving the various sulfate salts from the spill piles and carrying the resultant effluent ions into the stream (Parsons, 1956).

The maintenance of an excessive acid flow, to the extent that the downstream unpolluted area is affected, depends primarily upon the addition of effluent ions from the overflow of strip-mine lakes. Thus, the level of the strip-mine lakes is important, for if maintained at a high level the effluent overflow during a rain increases the distance which the acid flow will travel.

The Natural Ecosystem

The usual distinct longitudinal succession associated with a stream of this type has been modified to a more or less recognizable degree (Parsons, 1968). The modified biotic succession has been in response to the continuous atypical aquatic phase of the environment. The greatest deviation from the expected pattern was found in the most susceptible group, the fishes, and the least in the benthos with its great dependency upon the character of the abiotic substrate phase of the environment, with an intermediate response in the zooplankton with both inhabitable volume as well as quality of the water phase being a factor.

Abiotic

The visual indicators of an acid flow entering the unpolluted area of the stream were the formation of a milky suspension, followed by suds formation at the surface from the "saponification" of the natural occurring suspended solids (Figure 5), and the precipitation of these solids as a white flock (Figure 6). The reaction with the most dramatic results is shown in Figure 7, as the pH drops abruptly during an acid flow, with the loss of bicarbonate ion and thus the loss of the buffer-capacity of the stream. Of near equal importance was the oxygen-ferrous iron relationship. As noted in Figure 8, the oxygen concentration also drops abruptly and as much as 2 mg/liter, but does not become a critical factor in the survival of stream communities.

Within 2 months, the effects of the mineral acid have all but dissipated. The hydrogen ion concentration reached a peak in 48 hours with a gradual dissipation after the first week (Figure 9). Bicarbonate ion, on the other hand, did not recover until about 3 1/2 months

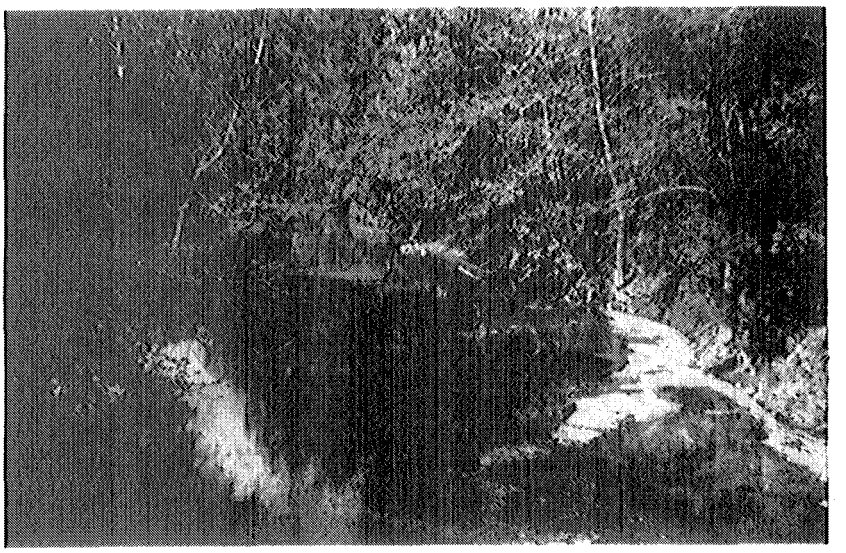

Figure 5. Sudsing action during an acid effluent flow.

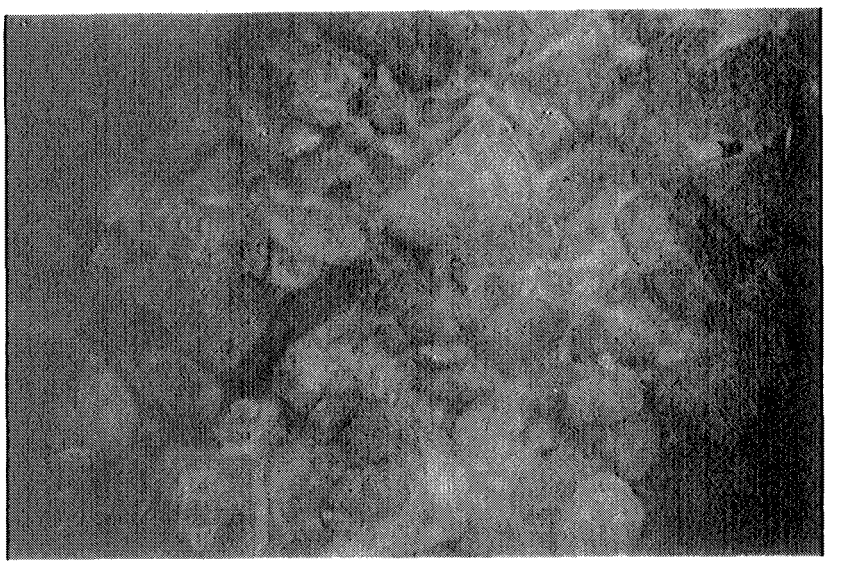

Figure 6. Precipitated flock - the end-product of acid water reaction with normal turbidity.

following the onset of an acid flow, due to the lack of runoff from the watershed. Concentrations of dissolved oxygen fell to their lowest in 48 hours and gradually increased to near normal readings in 2 months (Figure 10). Neither ferric nor ferrous iron concentrations were such as to affect the normal biotic communities.

Titratable acid reached its highest concentration in 48 hours and though it dropped rapidly (Figure 11), the concentration was sufficient

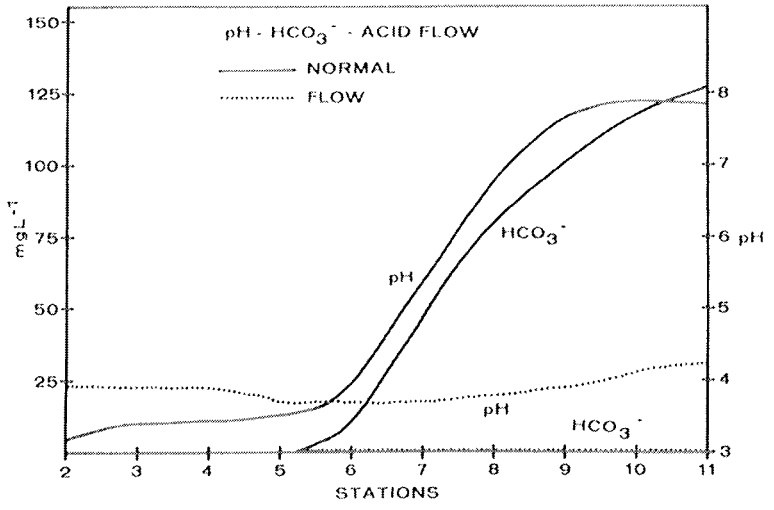

Figure 7. Linear reaction of pH and bicarbonate ion - onset of flow.

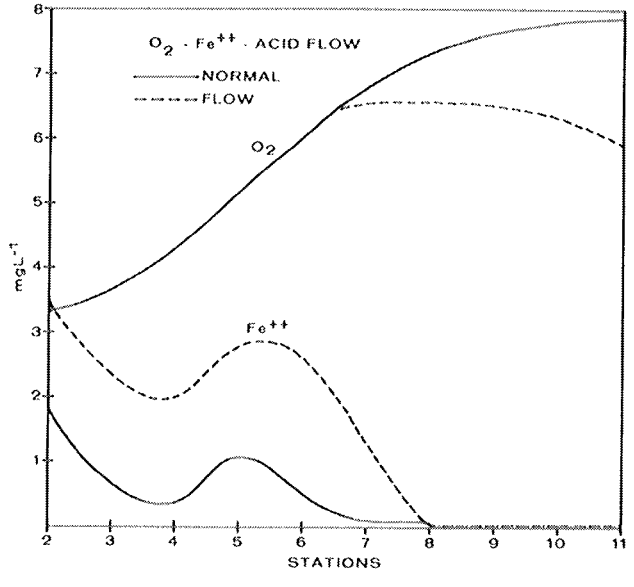

Figure 8. Linear reaction of oxygen and ferrous iron - onset of flow.

at 30 mg/liter mineral acid to completely control the recovery of the buffer system.

The calcium-magnesium ratio for flowing waters of the area was approximately 20:1 mg/liter and in the acid-mine affected streams about 1:2 mg/liter. Concentrations of both remained high until mid-winter (Figure 12).

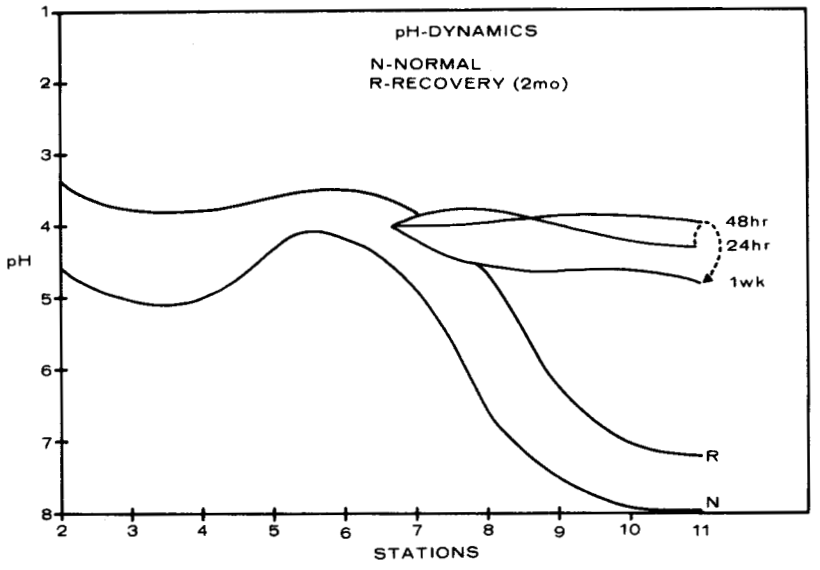

Figure 9. Time and linear reaction - pH with acid flow.

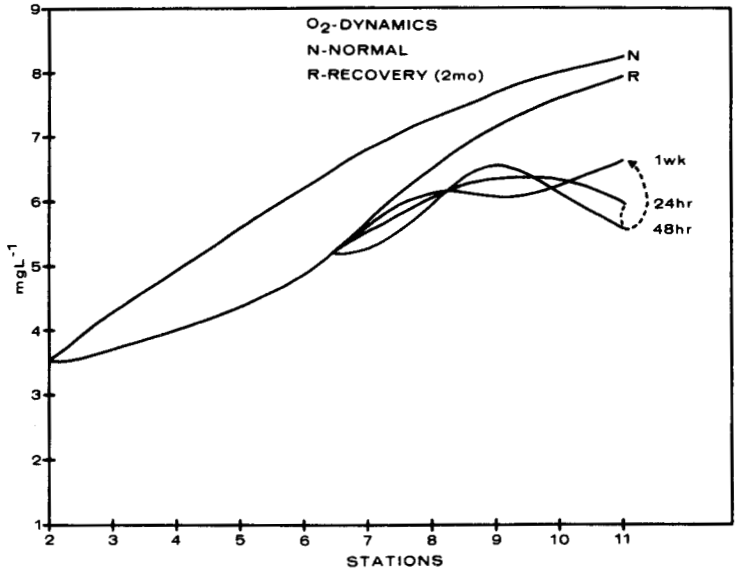

Figure 10. Time and linear reaction - oxygen with acid flow.

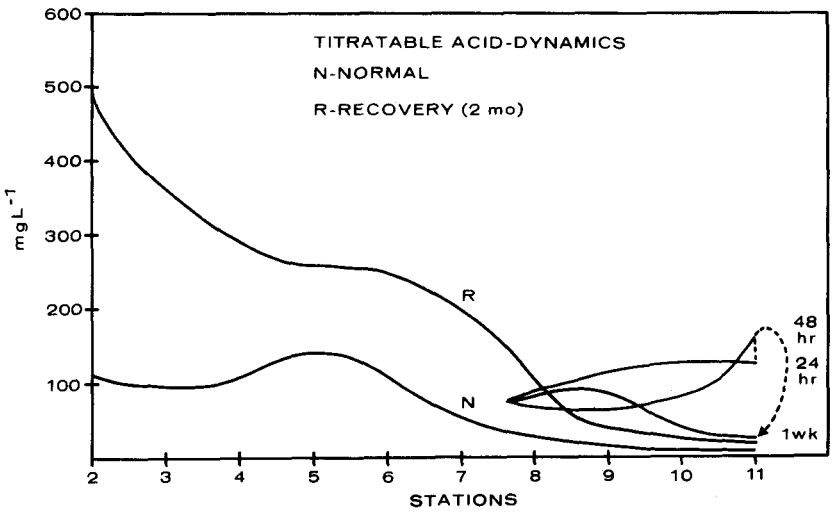

Figure 11. Time and linear reaction - titratable acid with acid flow.

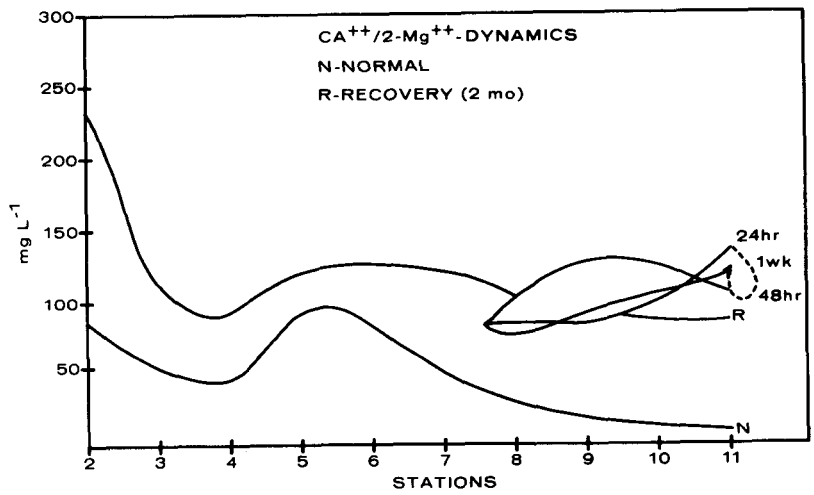

Figure 12. Time and linear reaction - calcium, magnesium with acid flow.

Sulfate as the predominant anion was always present in normal waters from the continuous seepage flow from the upstream mine areas. Although sulfate, aluminum, and zinc were found in a 30:6:1.5 relationship, the ions responded similarly during an acid flow (Figure 13). The concentrations of aluminum and zinc dropped to zero by mid-winter.

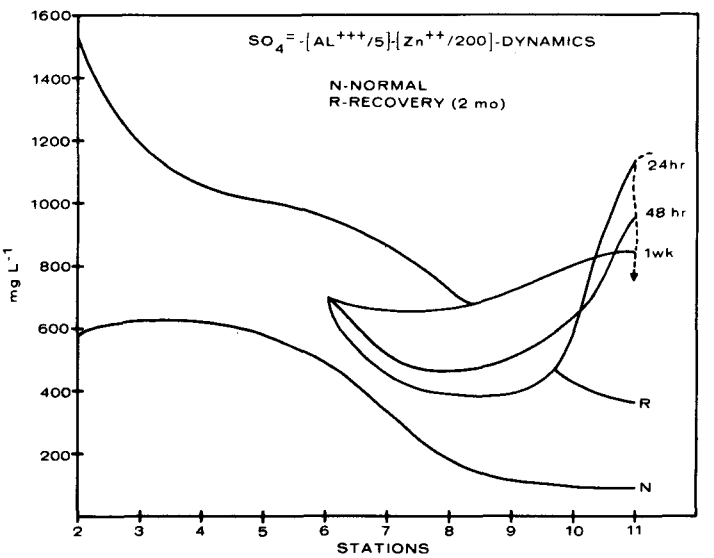

Figure 13. Time and linear reaction - sulfate, aluminum, zinc with acid

Neither lead nor copper concentrations were high enough to play a significant role in water quality of the ecosystem during an acid flow.

Biotic

To illustrate quantitatively the effects of acid-mine effluents upon stable stream populations, the total number of individuals are plotted against decreasing acid toxicity under stable water flow conditions. These 'normal' populations are compared with 'flow' populations and referenced to the previous year's populations for both the planktonic and benthic communities (Figures 14, 15).

The large increase in zooplankton individuals was typical of acid flows. Qualitatively, the upstream populations were comprised of four to six species of test rotifers which were the residents of the polluted region. Downstream, the original populations were destroyed. Drift rotifer populations made up the plankton communities. Zooplankton populations were for the most part non-existent during the winter months. Once these populations were destroyed, full recovery was not complete until the following spring. Fluctuations in these populations

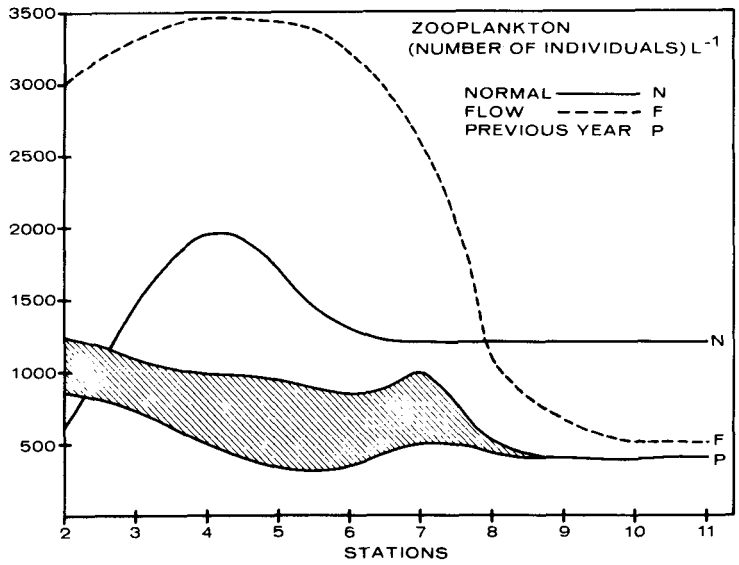

Figure 14. Zooplankton response to acid effluent stress.

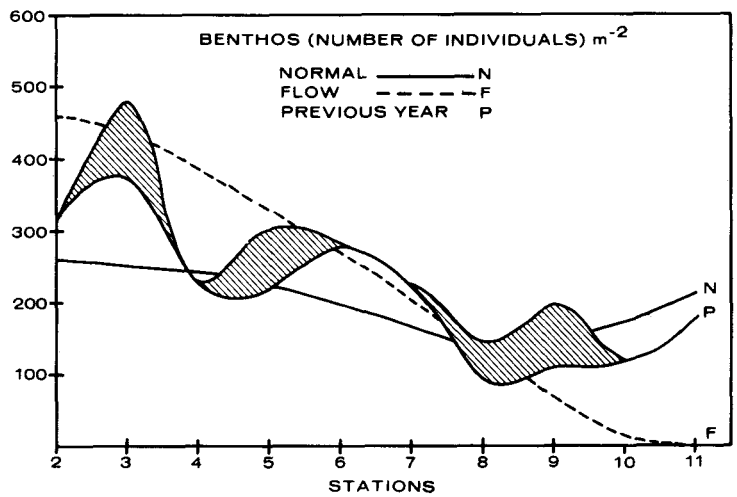

Figure 15. Benthos response to acid effluent stress.

during the previous years were very likely due to fluctuations in volume of flow rather than water quality.

The increase in benthic populations during and following an acid flow were due to the development of a second generation by several species, especially Procladius spp. (Figure 16). The effects of acid water on the populations in the transition zone (Stations 7 through 9)

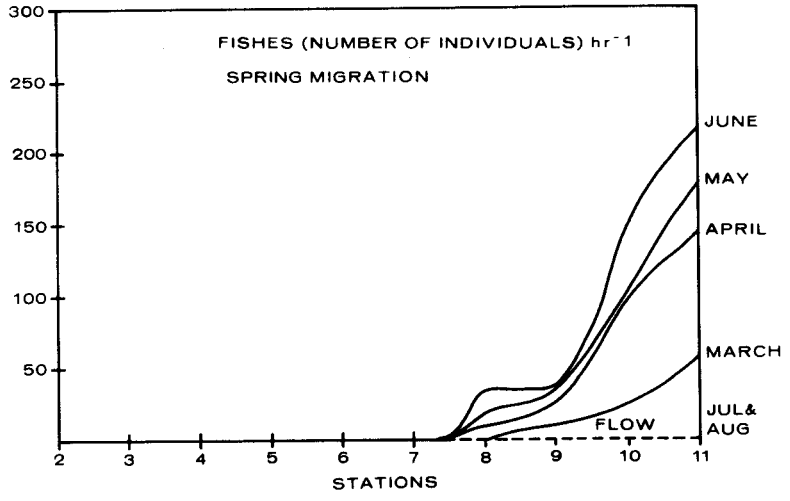

Figure 16. Fishes response to acid effluent stress.

range from moderate to heavy. The benthic communities at Stations 10 and 11 were all but destroyed. The fluctuations during the previous year were due, again, to second generation populations. Repopulation by benthic species proceeded in a normal manner by adults from the polluted region and tributaries of Cedar Creek.

The periodic migration of fishes up a tributary stream is initiated with increased spring flow (Figure 16). Populations of fishes were observed above the permanent sampling Station 8, and the populations appeared to stabilize in Stations 8 through 11 by mid-June. The effects of a late acid flow in June are shown in Figure 16. Recovery of the populations was not complete until the following spring. Observations of the previous year indicated that rather low populations were carried over the winter season. It appears that fish population dynamics were approximately the same from year to year, i.e., high spring populations with migration from the Missouri River, followed by a low or wanting winter population, depending upon normally low fall flow or summer acid flow, respectively.

Analyses

Utilizing Program Linear and the community approach to analyze the effects of acid-mine effluents on the ecology of a stream (Parsons, 1968), the following results were obtained: 1) the R^2 for zooplankton populations (criterion) and the abiotic and biotic environment as predictors was 0.9987 and highly significant; 2) the R^2 for benthic populations (criterion) and the abiotic and biotic environment as predictors was 0.9991 and highly significant; and 3) the R^2 for fishes (criterion) and the abiotic and biotic environment as predictors was 0.9964 and, again, highly significant.

Analysis of the stream data by station in both time and the linear dimension revealed that R^2's were seldom above 0.50. Thus there was as much or more variance within each station's measured parameters as there was among the stations' environments. This statement holds true regardless of the choice of criterion or the numerous restrictive codings placed on the acid effluent parameters as predictors.

The use of the discriminatory program BMDO5M was quite useful, for its use 1) confirmed the validity of the community approach above and 2) showed a definite transitional zone alluded to by Parsons (1955). Program BMDO3M was used to determine the parameters factored out and accountable for the variance. Parameter accountability, in order, within each stream area, was as follows: 1) titratable acid, sulfate, calcium and magnesium ions (polluted zone), 2) titratable acid, calcium, magnesium and aluminum ions (transitional zone), and 3) bicarbonate ion, temperature, calcium and magnesium ions (normal zone).

The Man-Made Ecosystem

One of 25 hectares in the United States is covered with water and one in 50 of these may some day become useful as water supplies for domestic, industrial and recreational activities. There are, to date, any number of impressive sites of reclaimed lands and lakes; however, these are woefully small in number compared to the hundreds of thousands of hectares now in need of reclamation.

Two types of lake basins were formed during surface mining of the Cedar Creek Area. In the chevron basin 90-95% of the resultant water mass was in contact with the surrounding spoil banks, whereas the parallel lake basin, when filled, was 50% or less continuous with the disturbed watershed. The chevron lakes had the potential of becoming a holding basin for near 100% of the acid run-off from the immediate spoils without additional earth moving. Parallel basins could receive and hold less than 1% of the potential acid water from adjacent strip lands.

In this study, of the three red lakes, two were chevron and one parallel; of the three blue lakes, two were modified chevron (chevron diggings off a parallel high wall) and one parallel. The physical and chemical characteristics of both red and blue lakes have been presented in some detail by Parsons (1955, 1964).

Physical

Turbidity caused by the reddish-black oxides of ferric iron in the red lakes played a major role in thermal stratification during the summer months and contributed to a heat budget which was 65% less per unit volume than that of blue lakes. This held true regardless of any of the above morphometric characteristics. Conversely, the blue lakes,

of approximately the same water quality, minus the iron oxides, were homothermous throughout the year.

Chemical

The chemical breakdown of the sulfuritic materials occurred on the strip-mine spoil banks and was complete or nearly so before the run-off entered the lakes. This was based on the fact that no forms of sulfur other than sulfate were found in lake waters. A vast variety of cations may be associated as sulfates and are a function in both quality and quantity of the strata adjacent to the coal seam, above and below.

In the case of the Cedar Creek Studies, strip-mine lakes were in part responsible for the duration of toxic flows. The water quality of the six study lakes was assayed and the following chemicals were found to be present in varying quantities: ferric iron, ferrous iron, aluminum, copper, lead, zinc, calcium, magnesium, sulfates, hydrogen ion, and titratable acidity.

Other measures of the chemical and physical qualities of strip-mine lakes have been reported by early works of Crawford (1942) and Heaton (1951) and more recently the excellent works of Campbell et al. (1965a, 1965b) and Campbell and Lind (1969).

DISCUSSION

Researchers studying acid precipitation will continue to be faced with events similar to those presented above, as some aquatic ecosystems become slightly polluted with acids and heavy metals, while others are subjected to heavy effluent concentration triggered by sporadic rains, rapid thaw, and the like.

Various types of acid flows were described by Parsons (1955, 1956) indicating the complexity of factors which were responsible for the initiation and maintenance of a toxic flow. The biotic communities which were continually polluted, with their adaptive populations, were not adversely affected by the additional acid present during a toxic flow. The subtle adaptive responses of taxa to the continuous stress of acid-mine effluents were reported by Parsons (1968) and Dambach and Olive (1969).

Acid flows into relatively undisturbed areas are an entirely different matter. Large fish kills are, by far, the most visually dramatic result and receive the most attention in the news media. In the more severe cases, nearly all of the animal populations are decimated. Recovery of these populations, as in the case of the initiation and maintenance of acid flows, hinges on a number of interdependent factors.

Typically, recovering plankton populations will be pioneered by euglenoid forms within a few weeks, benthic populations may arise from acid-resistant eggs and invaders from the adaptive populations, and the fishes may repopulate the upstream communities at the next high water nontoxic flow. (Parsons, 1955, 1968)

The obvious effect of acid-mine effluent upon the biota of a stream, especially the fishes, following the destruction of the bicarbonate buffering system, is very likely acidaemia in fishes (Powers, 1922; Lloyd and Jordan, 1964; Reppert, 1964), and this appears to be true in the invertebrates (Parsons, 1955, 1968; Warner, 1971).

From a quantitative measure of both plankton and benthic populations, it would be difficult to assess the effect of the change in water quality during an acid flow. A qualitative assessment of the community structure and species diversity (Parsons, 1955, 1968) was necessary to complete the analysis of acid-mine effluents on a stream ecosystem. Stream communities subjected to acid-mine effluents declined in species diversity (Parsons, 1968; Dambach and Olive, 1969). The presence of metal ions appeared to accentuate this effect in some areas (Dills and Rogers, 1972).

With the recovery of the buffer system, the fishes repopulated Cedar Creek. However, the recovery of the original invertebrates depends upon the complete restriction of acid flow and its metals into the stream from the mine area. The restriction of run-off of acid water into streams coupled with natural stream characteristics has been shown to be closely related to the successful recolonization of animal communities (Cairns et al. 1971; Dieffenbach, 1974).

The mechanism in the streams would be similar to that in lakes in that the successful colonization of bottom habitat does not necessarily mean the re-establishment of the original species in complete life cycle (Harp and Campbell, 1967). Now three major parameters may be useful in establishing the influence of acid water, regardless of its origin, on aquatic ecosystems: 1) quantitative analysis of populations, 2) community structure, and 3) the establishment of a complete life cycle.

Cedar Creek Area strip-mine lakes of the study have not been researched in detail since the original work. However, 10 years later, a cursory series of aerial and ground observations were made.* Of particular note was the fact that chevron red lakes were still reddish-black and acid, while the single parallel lake was natural in appearance and supported submergent vegetation.

Early attempts to classify strip-mine lakes by previously established systems of lake classification have been reported by Crawford (1942) and Heaton (1951). However, it remained for Parsons (1955, 1964),

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*Parsons, J. D. 1965. Unpublished data.

using both chemical and physical parameters, to establish a means of physiocochemical aging as the foundation of acid lake classification.

That chemical recovery and biological colonization of lakes occur naturally in time has been shown by early works of Crawford (1942) and Heaton (1951), and the more recent works of Riley (1960), Campbell et al. (1965a, 1965b), Harp and Campbell (1967), Campbell and Lind (1969), Smith and Frey (1971), and Stickney and Campbell (1972). The mechanism of chemical recovery in such lakes, experimental evidence on accelerated recovery, and the use of organic waste matter as a precursor to such recovery have been well-researched by Decker (1971), Ogg (1972), Simmler (1973), King and Simmler (1973), and King et al. (1974). These works might well be used by acid precipitation researchers in an attempt to recover already acidified waters, in view of the 170 billion metric tons net primary production (dry weight) produced by the biosphere (Whittaker and Likens 1975) and the disproportionate distribution by man's activities.

In comparing strip-mine lakes to natural lakes, Campbell and Lind (1969) mentioned "the initial successional stage is acid rather than classically oligotrophic, . . .". Oligotrophication as a self-accelerating phenomenon in natural lakes subjected to an excessive supply of acid materials (Grahn et al. 1974) is now recognized in both Norway and Sweden as a feedback mechanism to further accelerate the process of acidification.

Must the recovery of the ecosystem, through the recovery of its various populations, emulate those of the original communities in terms of the number of individuals, represented by the same species and carrying on a complete life cycle, or should we be satisfied with some usable measure of biomass per unit of time or space? It has already been shown that in spite of 1) the wide variety of taxa present from lake to lake (Lind and Campbell, 1970) and 2) the remarkably distinctive limnochemistry from lake to lake (Campbell et al. 1965a, 1965b; Campbell and Lind, 1969), the rates of community metabolism in strip-mine lakes were surprisingly similar.

It would appear that we should now relate levels of community metabolism to levels of quality and quantity of the causative biomass in order to establish an acceptable set of standards by which to assess the success of rehabilitation programs used in the reclamation of acid ecosystems.

ACKNOWLEDGMENTS

The author wishes to acknowledge the contributions of the Division of Academic Computing and the Central Photography Shop, Southern Illinois University at Carbondale. Special thanks are due Dr. Benjamin Shepherd for his criticisms of the original manuscript.

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SEASONAL PATTERNS IN ACIDITY OF PRECIPITATION AND THEIR IMPLICATIONS FOR FOREST STREAM ECOSYSTEMS

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ABSTRACT

Data collected since 1965 at a network of 9 stations in the northeastern United States show that precipitation is most acid in the growing season (May-September) and least acid in winter (December-February). For the Hubbard Brook station in New Hampshire, where the mean hydrogen ion content of precipitation ranges between 46 μeq/l in winter and 102 μeq/l in summer, the seasonal pattern in acidity correlates closely with seasonal differences in sulfur deposition from the atmosphere. As summer precipitation passes through the forest canopy, hydrogen ion concentrations are lowered by an average of 90 percent, primarily as a result of exchange with other cations. In winter the hydrogen ion content of incident precipitation is lowered from a mean of 50 μeq/l to a mean of 25 μeq/l during storage in the snowpack.

Information about the chemistry of precipitation in the northeastern United States has accumulated in recent years to the point where it is now possible to look for trends or patterns. By coupling any discovered patterns with current knowledge of the forest-stream ecosystem, we can more accurately evaluate the ecologic role of precipitation chemistry. In this study, we have attempted to determine seasonal patterns in the acidity of precipitation in the Northeast, and to discuss their implications for the forest-stream ecosystem.

If we assume that the chemistry and acidity of precipitation are the result of in-cloud scavenging and of washout, some reasons for expecting seasonal patterns are obvious. For example, the origins and tracks of major storms often differ by seasons. In turn, the sources of chemicals and the amounts of them that occur in precipitation may be expected to vary with season.

Also, chemicals entering the atmosphere as a result of industrial emissions, residential heating, combustion engines, and other activities may be related to the season. Dusts and organic materials may have greater impacts on the chemistry of precipitation at certain times of the year because of seasonal activities such as farming and construction or the presence of wind-borne pollen or snow cover. And seasonal temperature patterns may have an effect simply by determining whether precipitation occurs as rain or as snow.

The receiving surface also has seasonal patterns that are important to the chemistry of precipitation. For example, growth activities take place in spring and summer, so the potential of precipitation chemistry for stimulation or damage may be greatest during these seasons. Also, the intercepting surface of forests, especially deciduous hardwoods, changes with the seasons and affects the chemistry of precipitation reaching the forest floor. Soil moisture patterns are seasonal and can affect the length of time that precipitation is stored in the soil and the extent to which its original chemical composition is changed before it becomes streamflow. Nutrient ions in the forest canopy, forest floor, and soil may be more susceptible to exchange or leaching during certain seasons, depending on biologic activity.

METHODS

We analyzed data from nine stations in the Northeast for seasonal patterns in acidity of precipitation. Eight of the stations are part of a U.S. Geological Survey (USGS) network located in New York and Pennsylvania (Pearson and Fisher 1971); the ninth station is at the Hubbard Brook Experimental Forest in central New Hampshire and is operated by the U.S. Forest Service in cooperation with Cornell and Yale Universities. The USGS locations were used only to determine the existence and extent of seasonal patterns in acidity; Hubbard Brook was studied in greater detail for causes and implications of seasonal patterns.

The USGS network began operating in the autumn of 1965, and our study includes data collected through December 1973 (U.S. Department of Interior, 1965-1974). Precipitation samples are composites for monthly periods from collectors which are continuously open to the atmosphere. The collectors were described by Gambell and Fisher (1966); they consist of a straight-sided glass funnel through which precipitation drains into a polyethylene reservoir. A fritted glass disc is attached at the bottom of the funnel for filtration, and the funnel and reservoir are housed in an insulated chest. Techniques for the chemical analysis of precipitation samples are described in Pearson and Fisher (1971).

We began determining the chemistry of precipitation at Hubbard Brook in 1963, but we include here only the data collected from

June 1965 through June 1974, the period comparable to available USGS data. Precipitation samples are collected weekly from a polyethylene collector consisting of an uncovered funnel, tubing, and reservoir in summer and plastic trash cans in winter (Likens et al. 1967). The entire system is meticulously cleaned and re-installed each week. In addition to the precipitation data, our paper incorporates information from other Hubbard Brook studies concerning the chemistry of throughfall and stemflow (Eaton et al. 1973), the snowpack (Hornbeck and Likens 1974a and b), and streamflow. The analytical procedures for all samples collected at Hubbard Brook are those given by Likens et al. (1967) and Fisher et al. (1968) with the exception that automated colorimetric analysis has been used for anion and ammonium determination since 1972 (Likens 1972). Hydrogen ion concentrations for both Hubbard Brook and the USGS stations are calculated from measured pH values determined with glass electrodes and electronic pH meters.

We have based much of this paper on the means of monthly values that have been weighted proportionally for amount of precipitation. We determined coefficients of variation together with the means and found that Hubbard Brook consistently had lower coefficients of variation than the USGS stations. For example, the monthly coefficients of variation for hydrogen ion concentration in Hubbard Brook precipitation ranged from a low of 23 percent for July to a maximum of 58 percent for October. As examples from the USGS data, monthly coefficients of variation ranged from 75 to 163 percent for Albany, N. Y.,; 31 to 100 percent for Rock Hill, N. Y.; and 37 to 74 percent for Athens, Pa.

There are several possible explanations for the differences in coefficients of variation between Hubbard Brook and the USGS stations. Samples are collected at weekly intervals at Hubbard Brook as opposed to monthly intervals at USGS stations. Variations caused by contamination and aging should be less over the shorter sampling interval used at Hubbard Brook. Higher variations in the USGS data might also be a result of the glass funnels and filters used in the collectors. Glass is known to be more active chemically than polyethylene, so variation may be greater for those collectors than for samples collected in a system made completely of polyethylene. These factors would tend to raise the pH values of the USGS samples, thus giving a conservative estimate of precipitation acidity.

SEASONAL PATTERNS IN ACIDITY OF PRECIPITATION

A comparison of monthly means for each of the nine stations suggests some patterns in acidity of precipitation. With the exceptions of Albany, Hinckley, and Mays Point stations, acidity in terms of hydrogen ion concentration is generally maximal in summer months, intermediate in spring and fall, and minimal in winter (fig. 1). Maximum hydrogen ion concentrations most often occurred in June, July, or

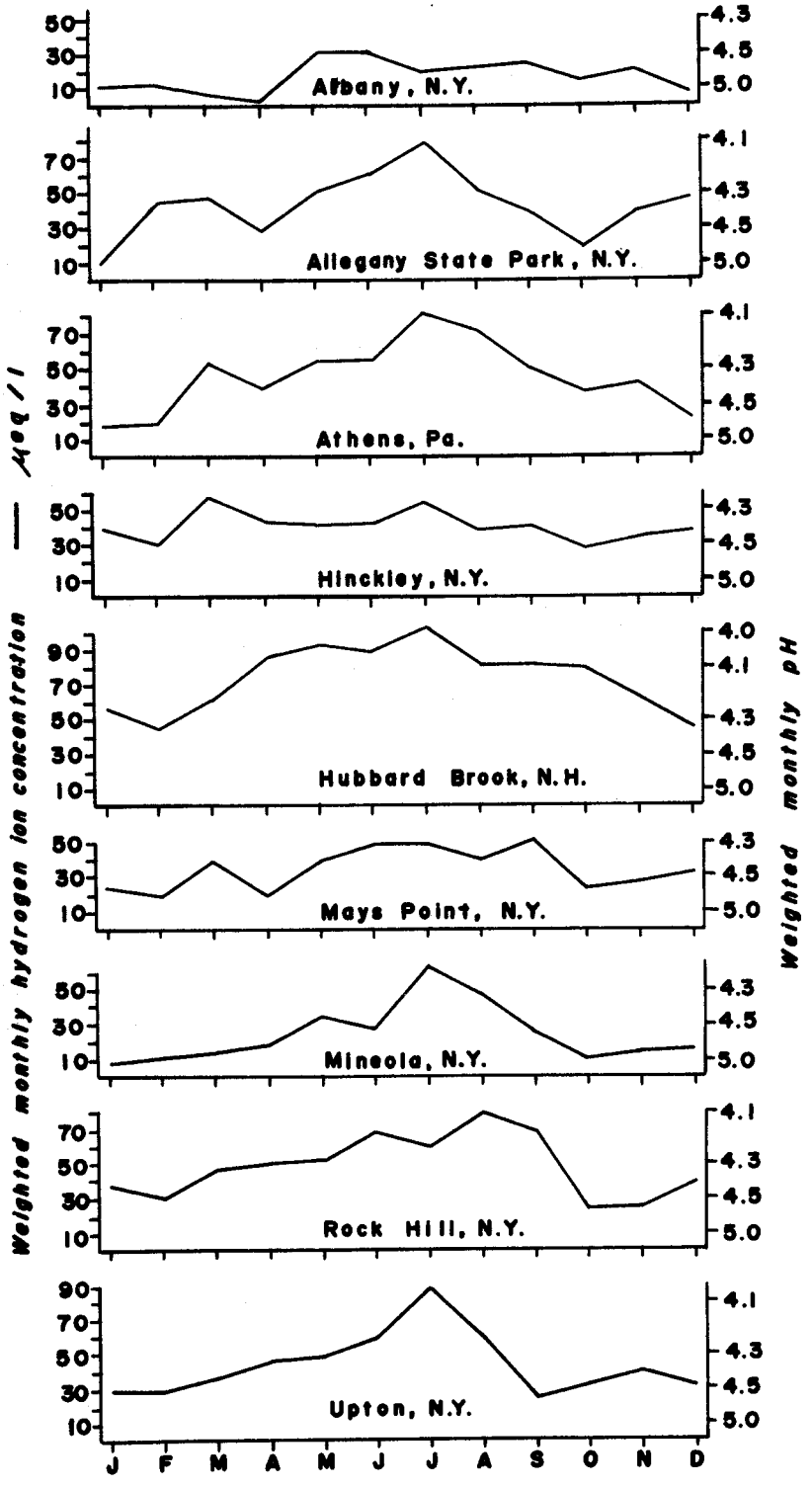

Figure 1.--Weighted hydrogen ion concentration and pH of precipitation. The curves are based on 8 or more years of data for each location.

August. Minimum values most often occurred in January or February.

The levels and ranges of acidity varied considerably among stations (fig. 2). Albany, N. Y., had the lowest hydrogen ion concentration,

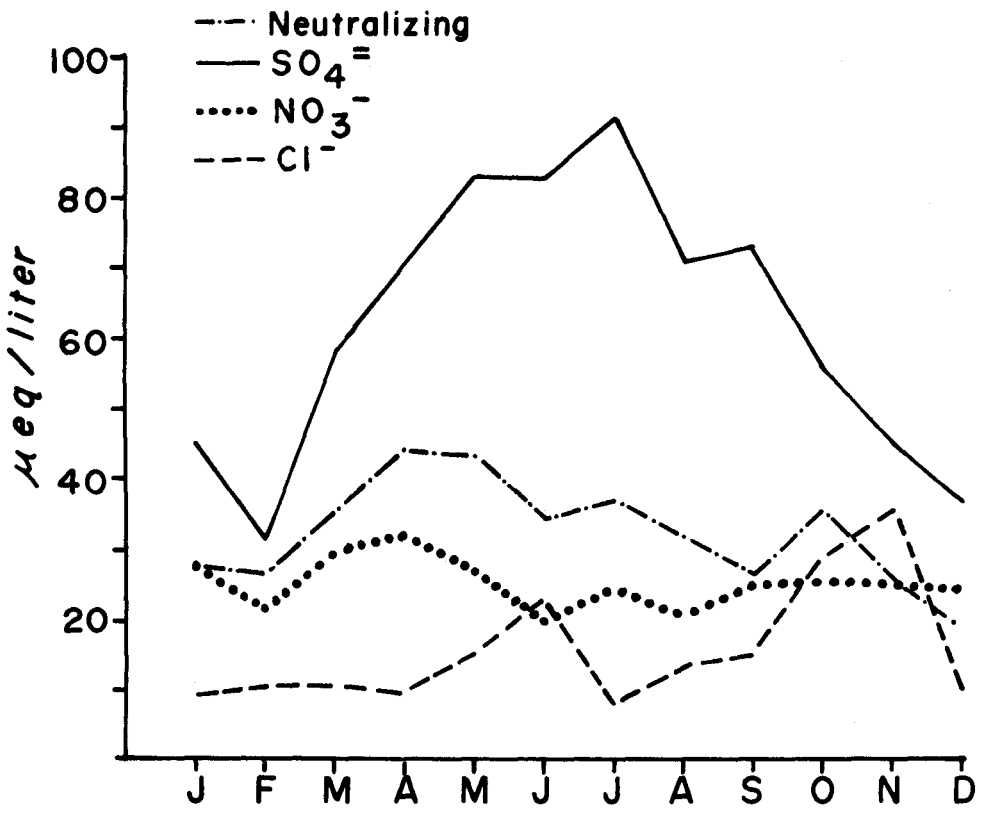

Figure 2. Neutralization and acid-forming components in Hubbard Brook precipitation. These data are weighted means for 9 years of record.

with average monthly values ranging from 2 to 30 μeq/l. Hubbard Brook had the highest levels, ranging from an average of 45 μeq/l in February to over 100 μeq/l in July. Four stations - Allegany State Park, Athens, Hubbard Brook, and Upton - had maximum and minimum values that were separated by at least 55 μeq/l.

The differences in levels and ranges between stations may be due in part to location. Hubbard Brook is the most isolated and is surrounded by vast areas of forest, while the USGS stations are located closer to agricultural, urban, and industrial activities. Thus the chances of neutralization by dusts and other materials may be least at Hubbard Brook, and quite variable at the other stations.

The apparent seasonal patterns in acidity of precipitation at most of the stations suggest that a sine curve is a useful first approximation for modeling the acidity of precipitation over the course of a year. The phase constant appears to be similar for most of the stations, but the amplitude is variable. Testing potential biologic impacts by using different phases and amplitudes for the curve could be an interesting experiment to perform with such a model.

EXPLANATION OF SEASONAL PATTERNS

Chemical data for precipitation at Hubbard Brook were analyzed in greater detail for possible explanations of seasonal patterns in acidity. Total neutralization and acid-forming components found in Hubbard Brook precipitation were calculated on an equivalent basis and plotted as monthly means for a 9-year period (fig. 2). The total neutralization component includes the sum of calcium, magnesium, potassium, sodium, and ammonium ions.

The chloride, nitrate, and neutralization components show some month-to-month variation, but no strong seasonal patterns. In contrast, the sulfate component shows a strong seasonal pattern practically identical to that for hydrogen ion concentration (fig. 1). This close relationship between hydrogen and sulfate is strong evidence that the seasonal pattern in acidity is almost solely the result of seasonal differences in sulfur deposition from the atmosphere.

The primary sources for sulfur found in precipitation are combustion of fossil fuels and natural processes such as forest fires, volcanic eruptions, and biologic reduction of sulfate. The combustion of fossil fuels is considered to be a particularly important source in the northeastern United States (Likens 1972; Likens and Bormann 1974; Pearson and Fisher 1971). The seasonal pattern is puzzling in this regard. Because of their use in heating, it would seem that maximum combustion of fossil fuels would be in winter. Yet the maximum sulfur in precipitation occurs in midsummer. As one possible explanation, Fisher et al. (1968) have suggested that snow may be less efficient than rain in capturing sulfur compounds from the atmosphere. Another possibility may be that greater electric power generation in summer more than compensates for the reduced heating. In any case, the apparent importance of sulfur on a seasonal basis and in the overall chemical composition and acidity of precipitation suggest that future research should further quantify its sources and explain its seasonal patterns.

IMPLICATIONS FOR THE FOREST-STREAM ECOSYSTEM

The seasonal patterns in acidity have some obvious implications for the forest-stream ecosystem. For example, maximum acidity occurs during the season when plants are actively growing and the potential for biologic impacts may be at a maximum. An important concern is the impact that higher summer acidities may have on the leaching of nutrients from foliage and soils.

A study showing the importance of hydrogen ion exchange as a mechanism for leaching cations from above-ground vegetation was conducted at Hubbard Brook during June through October 1969 (Eaton et al. 1973). For the study period, the precipitation had a weighted mean hydrogen ion concentration of 87 μeq/l (table 1). On the other hand, throughfall or

Table 1.--Hydrogen ion content of precipitation above and below the forest canopy at Hubbard Brook Experimental Forest. Mean monthly values for June to October 1969

Month	Above canopy			Below canopy		
	pH	Concentration	Total content	pH	Concentration	Total content
		μeq/l	meq/ha x 10^{-5}		μeq/l	meq/ha x 10^{-5}
June	4.12	76	0.71	4.85	14	0.11
July	3.93	117	2.37	4.89	13	.23
August	4.16	69	1.01	5.52	3	.04
September	4.15	71	.34	4.72	19	.07
October	4.18	66	.42	5.70	2	.01
Weighted mean	4.06	87	.97	5.01	10	.09
Total	--	--	4.85	--	--	0.46

precipitation that passed through the canopy had a weighted mean hydrogen ion concentration of 10 μeq/l. Thus about 90 percent of the hydrogen ions were left in the forest canopy as the precipitation passed through on the way to the forest floor.

Budgetary information showed that hydrogen ions made up 4.85×10^{-5} meq/ha or 74 percent of the total cation input in precipitation

and only 0.46×10^{-5} meq/ha or 2 percent of the cation loss in throughfall and stemflow (table 1). The net cation loss from the canopy for this same period was 16.28×10^{-5} meq/ha. It was therefore concluded that as much as 27 percent of the leaching which occurred from the forest canopy can be accounted for by hydrogen exchange from the rain (Eaton et al. 1973).

The removal of hydrogen ions by exchange in the canopy lessens the potential impact of acidic precipitation on forest soils at Hubbard Brook. Also, exchange in the canopy increases the nutrient content of rainfall reaching the forest floor, and most of the added nutrients are probably in a form directly available for plant use. These advantageous effects of the forest canopy coincide with the season of maximum acidity. However, these effects should not at this point be construed as lessening the potential problems of precipitation acidity. The sources and biologic significance of the leached ions and the ultimate fate of hydrogen ions remaining in the canopy must be determined, as well as the impact of the large quantities of sulfur that are associated with the higher summer acidities.

The important chemical changes that occur as precipitation passes through the summer canopy raise the question of what may happen when the forest canopy is removed. In an earlier study at Hubbard Brook, in which a previously forested watershed was devegetated for a 3-year period, the stream water pH decreased from 5.1 to 4.3 (Likens et al. 1970). This change represents about a fivefold increase in hydrogen ion content of stream water. There were many complex changes in the chemical composition of the stream as a result of devegetation. However, the absence of hydrogen ion exchange in the canopy may have contributed to the increased acidity of stream water after vegetation was eliminated.

During the dormant season the leafless hardwood canopy has less impact on precipitation passing through it. However, in places where a snowpack develops, there are opportunities for further changes in the acidity of precipitation before it infiltrates the soil. We have been studying the chemistry of the snowpack for the past three winters at the Hubbard Brook Experimental Forest (Hornbeck and Likens 1974a and b). The annual snowpack reaches a maximum accumulation of 1 to 2 meters and has a water equivalent of 20 to 40 cm, about 30 percent of annual precipitation.

Our findings show that the snowpack is generally less acid than the incident precipitation (fig. 3). Hydrogen ion concentrations in the snowpack seldom exceed 25 μeq/l, whereas in incoming precipitation they average more than 50 μeq/l and their maximum values exceed 100 μeq/l. These findings are similar to those of an earlier study in Wyoming (Clement 1966), which showed that as snow ages it becomes less acid.

Most of our chemical data for the snowpack were determined from all the meltwater from weekly snowpack samples. However, for seven

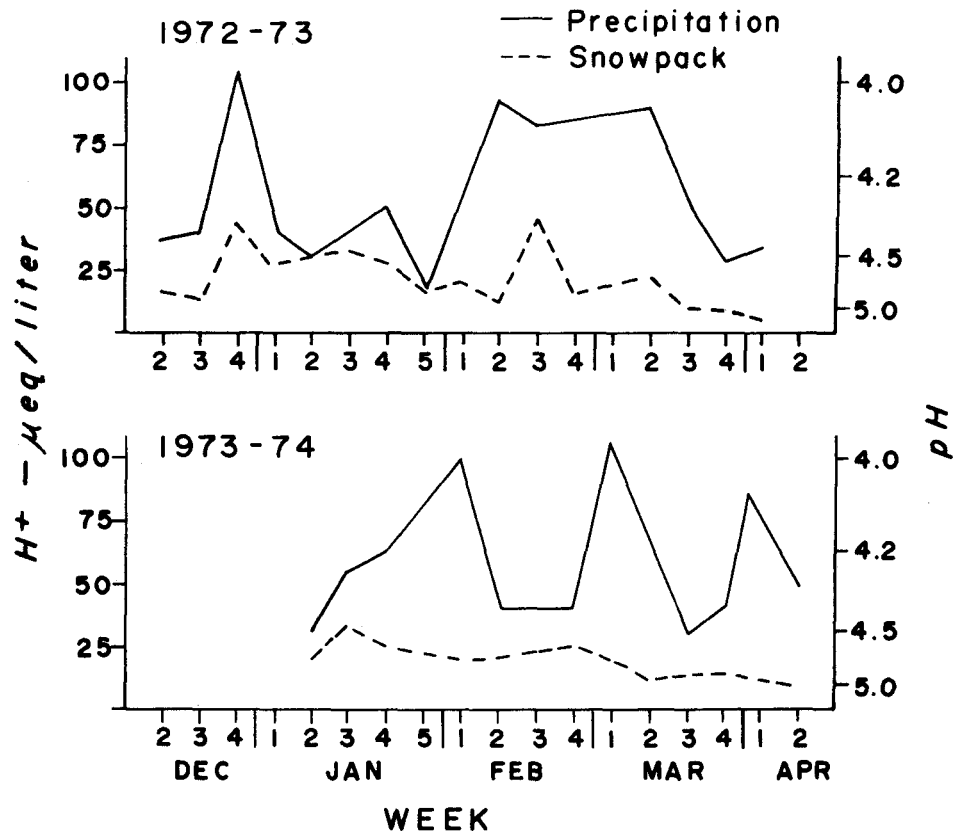

Figure 3. Hydrogen ion concentration and pH for incident precipitation and snowpack at Hubbard Brook.

dates during the first 2 years of our study, we also compared the first 20 percent of the meltwater from a sample with the final 80 percent of the meltwater. The average hydrogen ion concentration in the first 20 percent of the meltwater was 33 μeq/l, compared to 21 μeq/l in the final 80 percent. Most other ions showed a similar pattern; greater concentration in the first 20 percent of the meltwater. Thus part of the decline in acidity while precipitation is stored as snow can be explained by a differential contribution of ions from the snowpack.

The decline in acidity may also be partly the result of hydrogen ion exchange with cations from organic material. Organic material, in the form of birch cone scales and seeds, leaves, twigs, and bark fragments, is transported to the snowpack by wind or precipitation in surprisingly large quantities. Hydrogen may exchange with several different cations in the organic materials, but potassium seems to be one of the most important. Our data showed that potassium content was about four times as great in the snowpack as in the incident precipitation.

EFFECTS OF PRECIPITATION ACIDITY ON STREAMFLOW

We have discussed seasonal patterns in acidity that would seemingly affect stream water. However, there are other variables that must be considered in discussing the acidity of streams. For example, as precipitation infiltrates the soil at Hubbard Brook and moves toward stream channels, it encounters a variety of conditions of soil acidity and chemistry. The organic and A_2 horizons are extremely acid, having pH values of 3 to 4. The upper B horizons have pH's between 4 and 5, and the lower B and the C horizons usually have pH's greater than 5. The cation exchange capacity and degree of base saturation also vary greatly between horizons.

In addition to the variety of acidities encountered, soil water may also be subject to varying residence times, depending on season. For example, in summer when evapotranspiration is maximal, soil water deficits occur and movement of water is slowed.

Despite the seasonal patterns in acidity of precipitation, the varying conditions of acidity encountered in the soil, and variations in residence time, the streamflow acidity at Hubbard Brook is remarkably uniform (fig. 4). For 9 years of record, the mean hydrogen ion concentration for the 12 individual months ranged between 10 and 17 μeq/l. In contrast, precipitation for the same period had a range from 46 to 102 μeq/l. The variation in streamflow acidity is usually low, as attested to by small standard deviations (fig. 4) and coefficients of variation that never exceeded 40 percent.

The stability of stream water acidity at Hubbard Brook indicates a uniform buffering action by forest vegetation and soils that reduces the hydrogen ion content of precipitation by a factor of between 5 and 10. The fact that streamflow retains some acidity (hydrogen ion concentrations of 10 to 17 μeq/l) suggests that the weathering reaction in soils is incomplete. The reasons for this are unclear, but Johnson et al. (1972) have suggested that it may be the result of microscopic coatings of alumina and clay on rock surfaces and mineral grains. Incomplete weathering means a slower rate of cationic denudation with one tradeoff being more acidic streamflow.

CONCLUSION

To sum up our conclusions we have prepared an illustration of the acidity conditions at Hubbard Brook in summer and in winter (fig. 5). Precipitation is decidedly more acid in the summer, entering the canopy

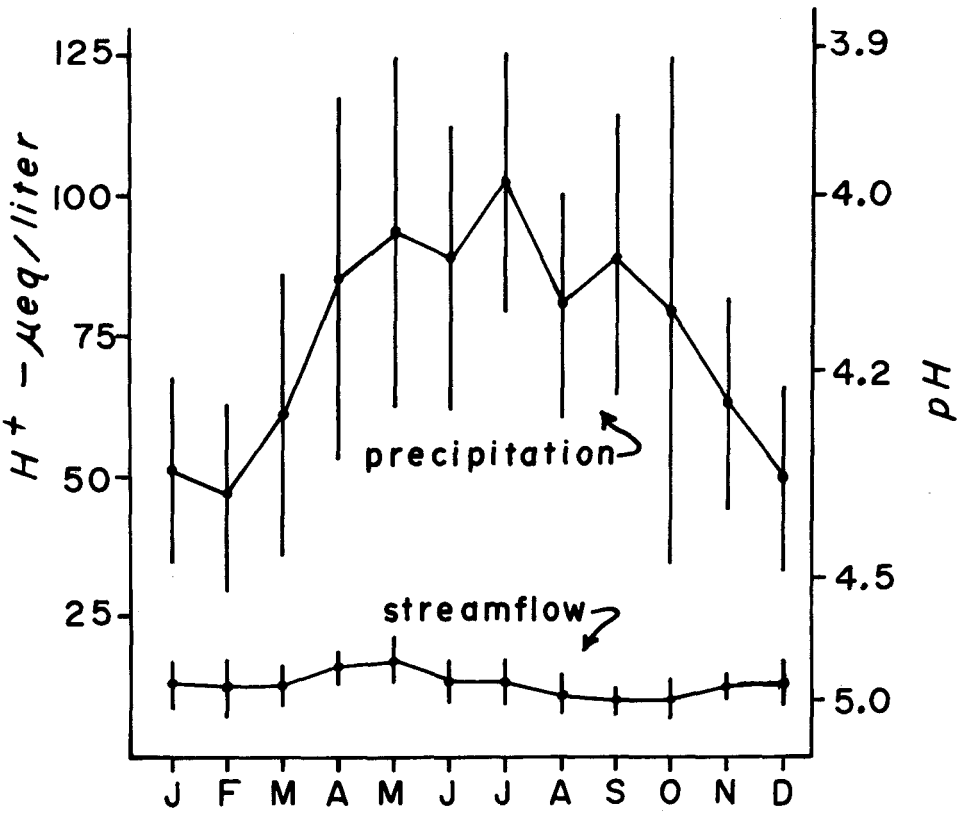

Figure 4. Weighted monthly hydrogen ion concentration and pH of precipitation and streamflow at Hubbard Brook from 1965 to 1974. The vertical lines for each month represent one standard deviation.

with a hydrogen ion concentration of 85 to 100 μeq/l. As precipitation passes through the canopy, the hydrogen ion concentration is lowered to 10 to 20 μeq/l. The precipitation that infiltrates and becomes soil water passes through soil horizons with widely different acidities, before emerging as streamflow with a hydrogen ion concentration of 10 to 15 μeq/l.

The less acid winter precipitation has hydrogen ion concentrations in the range of 50 to 60 μeq/l. While it is stored in the snowpack, its acidity declines to around 25 μeq/l. Meltwater leaves the snowpack at varying acidities to pass through the soil and becomes streamflow with hydrogen ion concentrations of 10 to 15 μeq/l (fig. 5).

The acidity of precipitation in spring and autumn is intermediate between summer and winter values. In the absence of a leaf canopy or snowpack, the acidity of precipitation entering the soil during spring and autumn may be higher. However, the streamflow acidity shows little effect, remaining fairly constant year-round at 10 to 15 μeq/l.

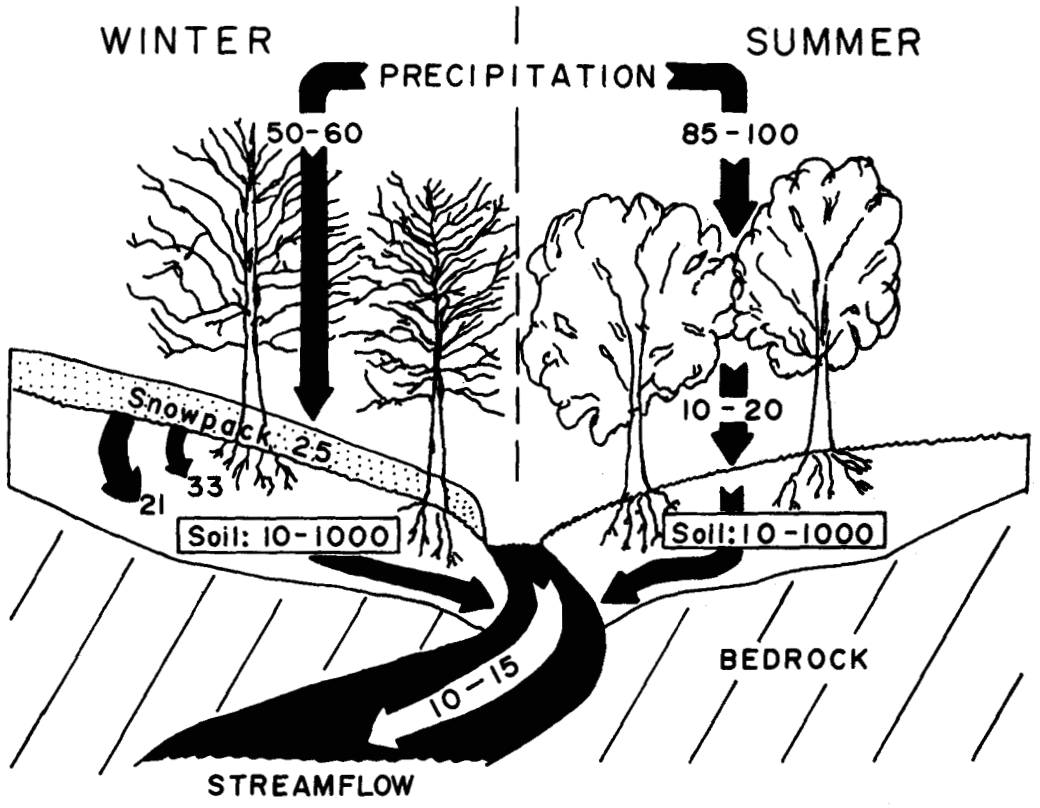

Figure 5. Acidity of water at two seasons at Hubbard Brook. The values are hydrogen ion concentrations in μeq/l.

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GEOCHEMICAL AND LITHOLOGICAL FACTORS IN ACID PRECIPITATION

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ABSTRACT

Acid precipitation is altered by interaction with rocks, sediment and soil. A calcareous region buffers even the most intense loading at pH ∿8; an alumino silicate region with unconsolidated sediment buffers acid loadings at pH ∿6.5; alumino silicate outcrops are generally acidified. Either FeOOH or alumino silicates are probable H^+ ion sinks in non-calcareous sediments. Glacially derived sediment is more important than bedrock in assimilation of acid precipitation in Shield areas. Toxic metal concentrations are dependent upon sediment metal concentrations and the pH of water.

INTRODUCTION

The pH of precipitation has been measured as low as 3.5 over various parts of the world and commonly approaches 4 (Cogbill and Likens, 1974; Granat, 1972; Oden, 1971), whereas the expected pH of unpolluted atmospheres from the CO_2-H_2O equilibria is about 5.7. Low pH appears to be the most common toxic factor for biomass, although Cd and Cu concentrations are commonly significant factors. A pH of 5-5.5, Cd concentration of 0.01-1 mg/l and Cu concentration of 0.1-0.5 mg/l are considered threshold conditions for toxicity to fish and invertebrates, although combinations of metals and pH may lower the threshold value by an order of magnitude (Arthur D. Little, 1971).

Precipitation may have metal and pH values which infer toxic conditions, but there is always a tendency for increase in pH and decrease in soluble metal concentrations when precipitation reacts with the lithology. It is the purpose of this paper to define interactions of soils and rocks with acid precipitation and associated metals in order to predict the resulting water quality.

1. pH - ALKALINITY

The main variables in the system are H^+ ion, alkalinity, and soluble metal ions. Alkalinity is the concentration measure of any possible sink for H^+ and includes carbonate alkalinity, sorption on colloidal metal oxides including FeOOH, alumino silicates, $Al(OH)_3$ and ionizable organic acids. Figure 1 is a typical pH-alkalinity curve obtained for

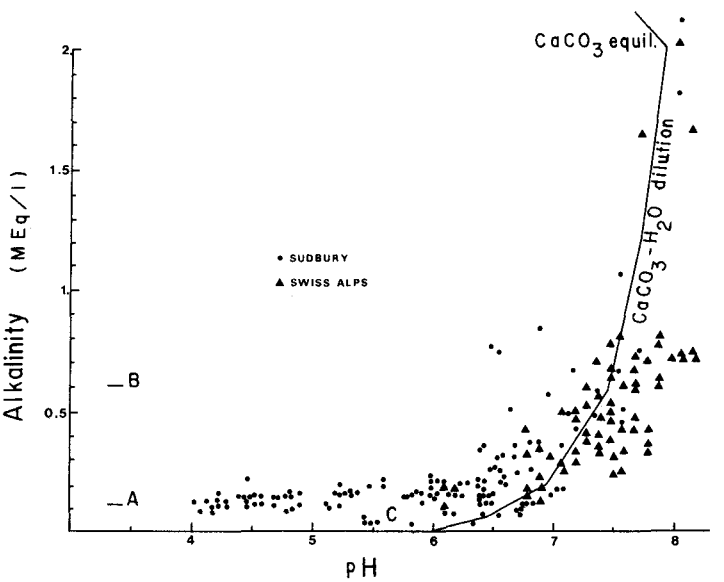

Figure 1. pH-alkalinity relationship for lakes in the Canadian Shield and Swiss Alps. The solid line represents the dilution of water equilibrated with $CaCO_3$ at 2 meq/l carbonate alkalinity. A and B represent pH boundary values for alumino silicate control whereas C represents the alkalinity pH obtained from $FeOOH-H_2O-CO_2$ (atm) equilibrium.

lakes in Canada and Switzerland. (See also Oden, 1973; Figure 12.) The general shape of the curve is apparently universal. An alkalinity of about 2 meq/l and a pH of 8 is indicative of a calcareous sediment. The pH-alkalinity relationship is defined by the equilibrium of $CaCO_3$ and/or $CaMg(CO_3)_2$:

$$CaCO_3 + H^+ = Ca^{+2} + HCO_3^-$$

or

$$CaMg(CO_3)_2 + 2H^+ = Ca^{+2} + Mg^{+2} + 2HCO_3^-$$

In this case, the alkalinity is entirely carbonate alkalinity. Furthermore, this system has an almost infinite H^+ ion assimilation capacity if the carbonate mineral content is large. Lower alkalinity waters are found which represent a simple dilution of the equilibrium $CaCO_3$-H_2O system as shown in Figure 1. Carbonate alkalinity is less than 0.01 meq/l at a pH of about 6, yet measured alkalinities between pH 4-6 are almost constant, ranging between 0.1-0.2 meq/l. This alkalinity can be due to interactions of cation alumino silicates such as

$$1.5\ H_2O + KAl_3Si_3O_{10}(OH)_2 + H^+ = 1.5\ Al_2Si_2O_5(OH)_4 + K^+$$

OR

$$4.5\ H_2O + KAlSi_3O_8 + H^+ = 0.5\ Al_2Si_2O_5(OH)_4 + K^+ + 2\ H_4SiO_4$$

which are noted on Figure 1 by A and B. There are numerous other alumino silicate reactions that give results between A and B.

Fe commonly occurs in oxidized portions of the earth's crust as colloidal FeOOH as small as 100Å (Lengweiler et al., 1961), and these particles can impart a large H^+ ion buffering capacity. FeOOH gives a pH of about 5.7, which is analagous to the CO_2-H_2O system.

Alumino-silicates and FeOOH are singled out as H^+ ion sinks, only because they represent the most abundant oxides on the surface of the earth. There are other less abundant metal oxides that can act as H^+ sinks. FeOOH is probably a more common buffer because it tends to occur in very fine particle sizes, allowing a large specific surface for reaction. Alumino-silicates tend to occur in larger sizes and they tend to equilibrate very rapidly in water (Houston, 1972; Wollast, 1967).

In addition to metal oxides, it is possible that soluble organic acids that have a dissociation constant of about 10^{-4} to 10^{-5} can assimilate H^+ ion at low pH and account for the alkalinity noted. Although there are many organic acids with the proper dissociation constant, few natural waters of pH 4-6 have high enough soluble organic carbon concentrations to exhibit the pH control.

More knowledge on the nature of the alkalinity of a water body below 6.5 is required in order to assess the H^+ ion assimilation capacity of acid rain. Particularly, the detailed knowledge of detritus is required. Commonly lakes of low pH are very transparent (Secchi depth $\sim$20m) and this transparency may be due to the total dissolution of the fine colloidal buffer; or the transparency may be due to the lack of organic detritus caused by negligible biological production.

In summary, a classification of H^+ ion assimilation of sediment

and rock in decreasing order is:

Kind	Alkalinity	pH	Capacity re: acid rain
Calcareous rock and soil	2 meq/l	8	Very large
Fine-grained non-calcareous soil and sediment	0.2-1 meq/l	6-7	Can be altered
Non-calcareous rock outcrop	0.1 meq/l	4-7	Is altered by acid rain

The detailed mineralogy of the unconsolidated post-glacial cover is the most important parameter in assessing the H^+ ion assimilation of acid precipitation in non-calcareous terrain, and this information cannot be obtained from general geological maps. Furthermore, knowledge of the complete surficial and subsurface hydrology is required as lower soil horizons may be calcareous, whereas surface deposits may be non-calcareous. This situation exists quite commonly on the Canadian Shield.

A useful indicator of the pH-alkalinity relationship can be expressed by the calcite saturation index (CSI), which is the logarithm of the degree of saturation of a water body with respect to $CaCO_3$ (Conroy et al., 1974).

The CSI is defined by:

$$CSI = p(Ca^{+2}) + p(Alk) - p(H) + pK$$

where $p(X) = -\log_{10}(X)$, $pK = +2$, (Ca^{+2}) = mol/l, (Alk) = eq/l, and (H^+) = eq/l.

If a body of water is saturated, with respect to $CaCO_3$, the CSI = 0; if supersaturated, the CSI < 0, and if undersaturated, the CSI > 0. A body of water with a CSI $\leq$ 3 is generally stable relative to acid precipitation. Bodies of water with a CSI from 4-6 are unstable relative to acid loading and are typically non-productive (Conroy et al., 1974).

2. METAL SORPTION

Assume that soluble metals are sorbed onto surfaces of bonding of the type either Me-O or Me-OH. One can derive an exchange reaction of the form:

$$\log_{10}Me(aq) = \log_{10}Me(sed) + pK - pH$$

where $\log_{10}Me(aq)$ is the soluble metal concentration (µg/l), Me(sed) is

the detrital sediment metal concentration (ppm) and pK = 2.6, 3.9, 4.75, 4.5 for Fe(+3), Cu(+2), Ni(+2) and Zn(+2) respectively. The values of pK have been calculated from lake data for the Canadian Shield with pH ranges 4-8 and metal concentrations varying over 3 orders of magnitude.

Using the above sorption relationship, values of trace metals in igneous and calcareous rocks for the earth's crust (Horn and Adams, 1966), and corrections for OH, HCO_3 and CO_3 ligands, the soluble trace metal concentration can be calculated. Table 1 gives the estimates from

Table 1. Predicted soluble metals in an average crustal rock for calcareous, igneous and acidified water bodies. Metal values are in µg/l.

Total Soluble Metal	pH 8.1 calcareous	pH 6.4 igneous	pH 4.5 acidified
Fe(+3)	.03	7	500
Cu(+2)	.0003	.3	25
Ni(+2)	.006	2	170
Zn(+2)	.004	1	80

the calculation for Fe(+3), Cu(+2), Ni(+2) and Zn(+2) in calcareous terrain (pH $\sim$ 8.1), igneous rock terrain (pH $\sim$ 6.4) and acid lake environments (pH $\sim$ 4.5), using average values of metals for the earth's crust. The effect of going from pH 8.1 to 4.5 and from calcareous to non-calcareous sediment is very large on soluble trace metal concentrations. The change in trace metal concentrations and resultant concentrations in acidified lakes, due primarily to the decrease in pH, compares with estimates of threshold concentrations for toxicity effects. Therefore, one should expect not only toxicity effects due to a decrease in pH, but also toxicity effects from increased soluble metal concentrations. In a buffered calcareous terrain, however, there would be very little chance of large soluble trace metals concentrations.

3. SUDBURY LAKES REGION

There exist calcareous and non-calcareous lakes to the NE of the Sudbury, Ontario, smelting operations. Lakes vary from a pH of 4-8, with total soluble Ni, Cu, Fe and Zn varying from <0.1 to 200 µg/l. The area is generally covered by igneous and metamorphic rocks typical of Precambrian Shield areas, but there is also an ample cover of post-glacial sediment.

The unconsolidated sediment is the key factor regarding the acidity and resultant production of lakes in the region, and the lithological control completely overshadows the acid precipitation loading. Acid precipitation contours (as well as SO_4, Fe, Cu and Ni) decrease NE-SW away from Sudbury, paralleling major wind directions (Figure 2). But

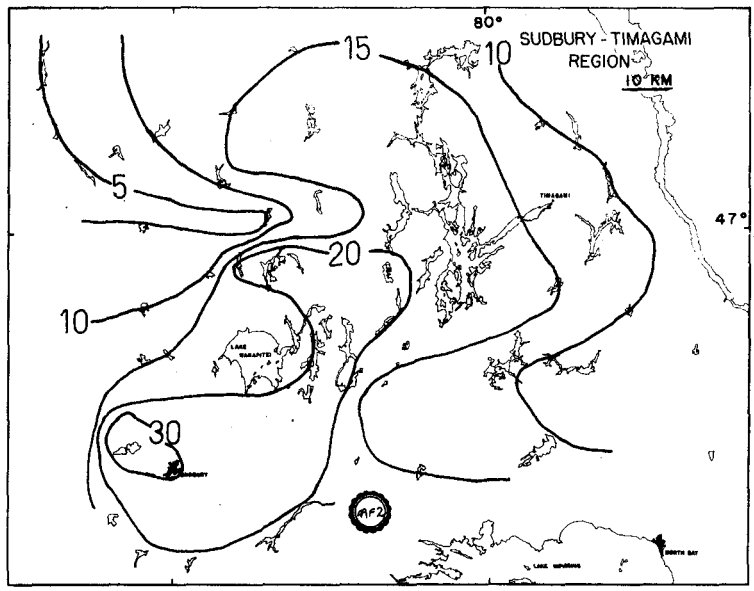

Figure 2. Concentrations of SO_4 (mg/l) in lake waters derived from smelter emissions in the Sudbury, Ontario region. Natural background is about 2 mg/l SO_4. Lakes outlined are those sampled.

acid lakes lie in quartzite rocks which have little or no unconsolidated sediment (Beamish and Harvey, 1972). The NE-SW trend of the calcite saturation index (CSI) parallels the glacial movement direction (Figure 3). Thus glacial scouring eroded some regions in a NE-SW direction and filled other regions with fine sediment. The CSI value of 0, reflecting a calcareous regime in the middle of igneous and metamorphic rocks, occurs in lakes that have a large subsurface flow, suggesting that unconsolidated sediments at depth are calcareous.

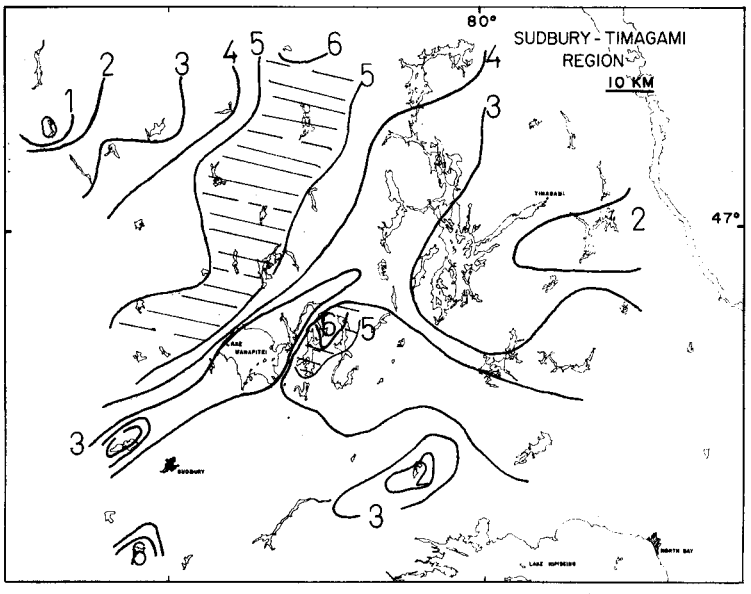

Figure 3. The calcite saturation index (see text) calculated for lakes in the Sudbury area. Those lakes below pH 5 are in the area hatched. Compare with loadings as shown by SO_4 in Figure 2.

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ACID PRECIPITATION AND ITS EFFECTS ON FRESHWATER ECOSYSTEMS: AN ANNOTATED BIBLIOGRAPHY[1,2]

RICHARD F. WRIGHT,[3] The SNSF-project (Acid Precipitation - Effects on Forest and Fish), 1432 Aas-NLH, Norway.

INTRODUCTION

It is especially difficult to obtain an overview of the literature on acid precipitation and its effects on freshwater ecosystems because this research covers disciplines in meteorology, chemistry, biology, geology, and hydrology. In addition, much of the work done in Scandinavia is not published in international journals and thus not included by major abstract services. Furthermore, many of these reports are written in Swedish and Norwegian and are, therefore, of little use to non-Scandinavian scientists.

The aim of this annotated bibliography is to provide a ready access to the literature by gathering together pertinent articles from the diverse sources and by supplying a brief description in English of the contents of each article.

DESCRIPTION OF LITERATURE COVERAGE

This bibliography contains literature on two topics:

1) Atmospheric and precipitation chemistry, and
2) The chemical and biological effects on aquatic ecosystems.

Included in this bibliography is literature available prior to the First International Symposium on Acid Precipitation and the Forest Ecosystem, held 12-15 May 1975 at The Ohio State University, Columbus, Ohio, USA.

The early literature on atmospheric and precipitation chemistry was thoroughly reviewed by Eriksson (1952a, 1952b) and more recently by

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[1] Published as a supplement to the Symposium Proceedings for the purpose of enhancing their usefulness as a reference source on acid precipitation research. The editors are indebted to Dr. Wright for this contribution.

[2] SNSF-contribution FA 3/75.

[3] Norwegian Institute for Water Research, P. O. Box 333, Oslo 3, Norway.

Gorham (1961). Since then research has been more or less confined to one of the several areas where the phenomenon of acid precipitation has been recognized. Recent overviews of precipitation chemistry for these areas are given by Summers and Whelpdale (1975, Proc. 1st Intl. Symp. Acid Precipitation and the Forest Ecosystem, Ohio State University) for Canada, Cogbill and Likens (1975) for the northeastern U.S., Oden (1972) for Scandinavia, and Bolin et al. (1971) for Sweden.

Adverse effects of acid precipitation on aquatic ecosystems in these areas have been investigated. Recent overviews published in English in international journals include Canada (Stokes et al. 1973, Jeffries et al. 1974, Beamish et al. 1975), northeastern U.S. (Schofield 1975, Proc. 1st Intl. Symp. Acid Precipitation and the Forest Ecosystem, Ohio State University), Sweden (Almer et al. 1974, Grahn et al. 1974), Norway (Jensen and Snekvik 1972, Wright et al. 1975, Proc. 1st Intl. Symp. Acid Precipitation and the Forest Ecosystem, Ohio State University), and Great Britain (Sutcliffe and Carrick 1973a, 1973b, 1973c). This bibliography probably includes nearly all articles that specifically deal with the effects of acid precipitation on aquatic ecosystems.

Another part of the literature that is pertinent to studies on aquatic ecosystems deals with physiological responses of aquatic organisms to acidity, sulfate, heavy metals, and other chemicals associated with acid precipitation. Here, although a number of relevant articles have been included, an exhaustive literature search was not attempted.

Finally a few references on the effects of acid mine drainage have been included, merely as an introduction to the extensive literature on this related subject (cf. Katz 1968, Packer and Dunson 1972).

CLASSIFICATION BY GEOGRAPHIC AREA

Following the bibliography is a list of articles grouped by geographic area. The areas are: world, Europe, Scandinavia, Norway, Sweden, Finland, British Isles, North America, Canada, United States, Antarctic/Arctic, and miscellaneous (theoretical articles etc.).

ABBREVIATIONS AND SOURCE NOTES

Following the short description of each article is a capital letter denoting the language in which the article is written. These letters stand for English (E), French (F), Finnish (Fi), German (G), Japanese (J), Norwegian (N), and Swedish (S).

Some of the Scandinavian articles are available from the institutes listed below:

NORWAY:

Direktoratet for vilt og ferskvannsfisk, Freshwater Fisheries Research Institute, Directorate of Fish and Wildlife, 1432 Ås.

IHD-Norden, International Hydrological Decade, P.O. Box 5091, Oslo 3.

Landbrukshøgskole, Norwegian Agricultural College, 1432 Ås.

Miljøverndepartementet, The Ministry of Environment, Oslo 1.

NILU, Norwegian Institute for Air Research, P.O. Box 15, N-2007 Kjeller.

NIVA, Norwegian Institute for Water Research, P.O. Box 333, Oslo 3.

*Norges Vassdrags- og Elektrisitetsvesen,*Norwegian Water and Electricity Board, Middelthunsgate 29, Oslo 3.

SNSF, The SNSF-project, NISK, 1432 Ås-NLH.

SWEDEN:

Agricultural College, 75007 Uppsala.

Institute of Meteorology and International Meteorological Institute, University of Stockholm, P.O. Box 19111, 10432 Stockholm 19.

Royal College of Forestry, 10405 Stockholm 20.

Statens Naturvårdsverk, National Swedish Environment Protection Board, Fack, 17102 Solna 1.

Swedish Water and Air Pollution Research Laboratory, Box 5207, 40224 Gothenburg.

Sötvattenslaboratoriet, Drottningholm, Institute of Freshwater Research, Drottningholm, Fack, 17011 Drottningholm.

EUROPE:

EIFAC, European Inland Fisheries Advisory Committee, Dept. of Fisheries, FAO, Via delle Terme di Caracella, 00100 Rome, Italy.

ACKNOWLEDGEMENTS

This bibliography would not have been possible without the cooperation of many individuals who kindly supplied copies of their published and unpublished reports. B. Bøhmer took much of the responsibility for procuring, cataloging, and classifying the articles.

Financial support came in part from the Royal Norwegian Council for Scientific and Industrial Research.

Ahl, T., and S. Oden. 1972. Nya undersökningar ger besked Åkrarnas Kväve gödslar vattnet. Forskning og Framsteg 7: 23-26.

Data from the synoptic study of Scandinavian rivers (1965 and 1970) and from monthly samples from several Swedish rivers (1965-1972) indicate that the NO_3-N content of these waters is strongly affected by variations in weather. About 70% of NO_3-N comes from precipitation and 30% from agricultural fertilizers. S.

Allen, S. E., A. Carlisle, E. T. White, and C. C. Evans. 1968. Plant nutrient content of rainwater. J. Ecology 56: 497-504.

The deposition of Na, K, Ca, Mg, P, and N was measured at 5 sites for 3 years. The amounts of these elements contained in precipitation are related to rainfall volume and to agricultural and marine influences. E.

Almer, B. 1972a. Ragnarök och fiskdöd. Svenskt Fiske. No. 12: 40-44.

This is a general discussion of the increasing acidification of Swedish lakes and rivers and the effects on fish, especially the phenomenon of large, old fish that survive in acid lakes. S.

Almer, B. 1972b. Försurningens inverkan på fiskbestånd i västkustsjöar. Information från Sötvattens-Laboraotiret, Drottningholm, No. 12. 47 p.

Test fishing and other investigations in 50 lakes in western Sweden showed that the increasing acidification of lakes causes a discoloration of water, decrease in plankton abundance and drastic alterations in fish fauna. The roach is affected at pH less than

5.5. Many acid lakes contain only old and large fish due to the inhibition of reproduction. Perch is similarily affected. S(E summary).

Almer, B., W. Dickson, C. Ekström, E. Hörnström, and U. Miller. 1974. Effects of acidification on Swedish lakes. Ambio 3: 330-336.

An investigation of 400 lakes on the Swedish west coast during 1970-72 revealed that about 25% of the lakes in the area are adversely affected by acid precipitation (pH less than 5.0), and that the pH in some lakes has declined 1.8 units over the last 20-30 years. Sulfate increased also. Biologic effects such as changes in phytoplankton species composition, zooplankton and fish populations are reported. E.

Andersen, C. 1966. Vannets kjemiske forhold. Norg. Jeg. og Fiskeforb. Tidsskr.: 174-175.

This is a general discussion of pH and hardness in natural waters. N.

Andersson, Gun, and P. Grennfelt. 1974. The concentration of some trace elements in fuel oils and an estimation of the atmospheric emission of these elements from oil combustion in Sweden. Swedish Water and Air Pollution Research Laboratory, Gothenburg, Publ. B204. 6 p.

Emissions of 13 trace elements from fuel combustion in Sweden were estimated from the analysis of commercial fuel oils. E.

Andersson, Gunnar. 1971. Vattenkemi och långtidsmässiga förändringar i Anebodaområdets sjöar. Limnol. Inst. Lund, Sweden. Unpubl. report. 37 p.

The chemistry of 30 small lakes in the south Swedish highlands was studied during 1967-69, and the results were compared with data from the 1930's. In 6 forest lakes the pH has declined, while in lakes influenced by cultural activities the pH has risen. Specific conductance has risen by 10-30 micromhos/cm in 28 of the lakes to about 50 micromhos/cm. Sulfate concentrations have also increased. The chemistry of these lakes is strongly influenced by inputs from the atmosphere. S.

Andersson, G., K. J. Gustafson, and T. Lindström. 1971. Rödingen i Rösjöarna på Fulufjäll. Information från Sötvattenslaboratoriet, Drottningholm No. 8. 9 p.

Fish surveys and test fishing in several small acid lakes in Sweden show that acidification has altered the fish populations during the past 50 years. S.

Ångström, A., and L. Högberg. 1952a. On the content of nitrogen (NH_4-N and NO_3-N) in atmospheric precipitation. Tellus 4: 31-42.

NH_4-N and NO_3-N concentrations in precipitation depend on the amount of precipitation previously fallen and the type of air mass (tropical versus polar). The constant ratio of 2:1 (NH_4-N/NO_3-N) suggests a common origin. E.

Ångström, A., and L. Högberg. 1952b. On the content of nitrogen in atmospheric precipitation in Sweden II. Tellus 4: 271-279.

Deposition maps of NH_4-N for Sweden show lower amounts at higher latitudes, probably due to lower contents of NH_4-N in the atmosphere at these latitudes. The constant ratio of NH_4-N to NO_3-N in precipitation may be due to a common photochemical reaction. E.

Anon. 1972. Sulphur pollution across national boundaries. Ambio 1: 15-20.

This article briefly summarizes the results from "Sweden's case study" (Bolin et al. 1971). E.

Anon. 1974a. Sur nedbør-problemet, status idag. Miljøverndepartementet, Oslo, Informasjon, Nr. 12: 2-4.

This is a brief report of the December 1974 meeting in Oslo on the European monitoring of air pollutants. N.

Anon. 1974b. Miljövårds forskning 1972-75. Swedish National Nature Conservancy Office.

This document is a description of all Swedish research projects that have been funded by the Nature Conservancy Office for 1972-75. S.

Askne, C. 1973. Method of determining strong acid in precipitation based on coulometric titration with application of Gran's plot. Swedish Water and Air Pollution Research Laboratory, Gothenburg, Publ. B152. 41 p.

The construction and design of a function generator is described. It is used for electronic evaluation of Gran's plot titrations. E.

Askne, C., and C. Brosset. 1972. Determination of strong acid in precipitation, lake-water and air-borne matter. Atmospheric Environ. 6: 695-696.

Titration of CO_2-free samples with NaOH allows calculation of the strong acid content. E.

Aston, S. R., D. Bruty, R. Chester, and R. C. Padgham. 1973. Mercury in lake sediments: a possible indicator of technical growth. Nature 241: 450-451.

The Hg concentrations in the sediments of Lake Windermere, England, increased about 10-fold from 1400 AD to the present, due to both anthropogenic Hg that is initially released into the atmosphere and to local pollution sources. E.

Barrett, E., and G. Brodin. 1955. The acidity of Scandinavian precipitation. Tellus 7: 251-257.

Beamish, R. J. 1972. Lethal pH for the white sucker *Catostomus commersoni (Lacepede)* T. Am. Fish. S. 101: 355-358.

Experiments with white sucker show that feeding stops below pH 4.5. Weight-loss, activity patterns and other physiological effects were observed at low and lethal pH levels (3.0-3.8), perhaps due to loss of calcium. E.

Beamish, R. J. 1974. Loss of fish populations from unexploited remote lakes in Ontario, Canada, as a consequence of atmospheric fallout of acid. Wat. Res. 8: 85-95.

Beamish, R. J., and H. H. Harvey. 1972. Acidification of the La Cloche Mountain Lakes, Ontario, and resulting fish mortalities. J. Fish. Res. Bd. Canada 29: 1131-1143.

Loss of fish populations from lakes SW of the Sudbury, Ontario, smelter is attributed to increasing acidification of the lakes due to large loadings of sulfuric acid from the atmosphere. E.

Beamish, R. J., W. L. Lockhart, J. C. Van Loon and H. H. Harvey. 1975.

Longterm acidification of a lake and resulting effects on fishes. Ambio 4: 98-102.

Acidification of a lake in Ontario (pH decreased 0.13 units/yr) resulted in various physiological responses by fish, including failure to spawn, low serum calcium in adult females, appearance of spinal deformities, changes in the average size of age classes, reduction in the population sizes, and disappearance of species. The results suggest that increased acidity interferes with Ca metabolism. E.

Bell, H. L. 1971. Effect of low pH on the survival and emergence of aquatic insects. Water Res. 5: 313-319.

Experiments with mature larvae and nymphs of 9 species at pH 1.0 to 7.0 showed that the pH at which 50% of the individuals died after 30 days of exposure ranges from 2.45 to 5.38 depending on the species, and that all species are more acid-sensitive during the period of emergence. E.

Bell, H. L., and A. V. Nebeker. 1969. Preliminary studies on the tolerance of aquatic insects to low pH. J. of Kansas Entomol. Soc. 42: 230-237.

Laboratory tests on mature larvae of 10 species of aquatic insects showed that the acid-tolerance is species dependent. The lethal pH (50% of individuals die after 96 hours) varied from 4.65 to 1.5. E.

Bertine, K. K., and E. D. Goldberg. 1971. Fossil fuel combustion and the major sedimentary cycle. Science 173: 233-235.

The combustion of fossil-fuel injects many elements into the atmosphere at rates comparable to the rate of weathering. Since most fossil-fuel consumption is in the Northern Hemisphere, the changes in atmospheric- and water-chemistry will be most evident there. E.

Berzins, B. 1966. Kalkning av sjöar. Södra Sveriges Fiskeriförening 1959-1966: 28-35.

Addition of chalk to several acid lakes in southern Sweden resulted in increased pH-levels, increased growth of phytoplankton and survival of salmonoid fishes. S.

Biesinger, K. E., and G. M. Christensen. 1972. Effects of various metals in survival, growth, reproduction, and metabolism of

Daphnia magna. J. Fish. Res. Bd. Canada 29: 1691-1700.

The toxicity of 21 major and trace metals was measured and correlated with the solubility product constant of the metal sulfide, electronegativity, and equilibrium constant of the metal-ATP complex. E.

Bischof, W. 1973. Carbon dioxide concentration in the upper troposphere and lower stratosphere III. Report Al-24, Institute of Meteorology, University of Stockholm, 11 p.

Air samples collected by airplane during 1962-71 show that the CO_2 content of the atmosphere (N Hemisphere) is increasing by 0.09 ppm^2/yr. E.

Bjor, K., R. Horntvedt, and E. Joranger. 1974. Nedbørens fordeling og kjemiske innhold i en skogbestand på Sørlandet (Juli-Desember 1972). SNSF FR 1/74. 28 p.

The chemistry of rainfall, throughfall, and stemflow at Birkenes, Norway, is discussed. N.

Block, C., and R. Dams. 1975. Inorganic composition of Belgian coals and coal ashes. Environ. Sci. & Technol. 9: 146-150.

The concentrations of 44 elements in coals were measured by neutron activation analysis. During combustion of coal the halogens, Hg, As, Se, and Sb are emitted preferentially while the other elements are present in fly-ash in the same concentrations as in bulk coal. E.

Bolin, B., and L. Granat. 1973. Local Fallout and long-distance transport of sulfur. Ambio 2: 87-91.

This article compares Högström's (1973) findings with other studies of the long-distance transport of sulfur, including a discussion of dry-fallout versus washout in precipitation. E.

Bolin, B., L. Granat, L. Ingelstam, M. Johannesson, E. Mattson, S. Odén, S. Rohde, and C. O. Tamm. 1971. Air pollution across national boundaries.

The impact on the environment of sulfur in air and precipitation. Sweden's case study for the United Nations conference on the human environment. 96 p.

More than 75% of the atmospheric sulfur in NW Europe is of anthropogenic origin, and following conversion to sulfate, long-distance transport deposits large amounts of sulfuric acid in Sweden. This "excess" acid causes damage to arable land, forests and lakes and rivers. An economic analysis of the costs of this pollution and of possible remedies is presented. E.

Bolin, B., C. Persson. 1974. Regional dispersion and deposition of atmospheric pollutants with particular application to sulfur pollution over Western Europe. Inst. of Meteorology, Univ. Stockholm, Report AC-28. 60 p.

Assuming a statistical independence of some physical and chemical processes in the atmosphere, a model of sources, sinks and transformations of atmospheric pollutants is constructed. As an example the model is used to describe the sulfur emission, transport and deposition in NW Europe. E.

Börjeson, H., and A. Aldberg. 1974. Buffertkapacitet och pH i mjölke från två övingsstammar. Information från Sötvattenslaboratoriet, Drottningholm No. 3. 6 p.

Trout from lakes in the Kloten area, Sweden, live near the lower pH-tolerance limit. No chemical difference in the milk from this stock and a reference stock could be found. S (E summary).

Borman, F. H. 1974. Acid rain and the environmental future. Environmental conservation 1: 270.

The realization that acid precipitation falls over large areas of the northeastern US raises the concern that serious changes in terrestrial ecosystems might result. E.

Bornefeld, T., and W. Simonis. 1974. Effects of light, temperature, pH, and inhibitors on the ATP level of the blue-green alga *Anacystis nidulans*. Planta 115: 309-318.

Various experiments conducted at pH 6.5-9.0 are described. E.

Borneff, J. 1974. Die Verunreinigung von Grund-und Oberflächenwasser durch organische Substanzen des Luftaerosols, p. 33-45. In H. E. Vogel (ed.) European Fed. Protection Waters, Zürich, Info. Bull. 21.

The concentrations of polycyclic aromatics, pesticides, and polychloric biphenyls may reach harmful levels in surface and ground

waters in central Germany. Many of these compounds are introduced into the atmosphere by man and subsequently find their way into freshwaters. G (E, F summary).

Braarud, T., and O. J. Aalen. 1939. Undersøkelser over makrovegetasjonen i en del Aust-Agder-vatn. Nytt Mag. f. Naturv. B. 79: 1-48.

The macrophytes of 40 lakes were studied and the distribution and abundance of individual species were related to geological and geomorphological chemical, climatic, and cultural factors. N (G summary).

Braekke, F. (ed.). 1974a. Hydrokjemiske og hydrobiologiske rapporter fra NIVA. SNSF-project. IR 3/74. 39 p.

This is a collection of interim reports on 1) hydrochemical results from several gauged watersheds in southern Norway, 2) the effect of pH on microbiological decomposition of organic matter, 3) development of a method for measuring primary productivity and results from acidification experiments, and 4) survival of several species of salmonoid fish in water from an acid watercourse. N.

Braekke, F. (ed.). 1974b. Faginnlegg på Kontaktmøte i SNSF-prosjektet 8. Februar 1974. SNSF-project. IR 2/74. 90 p.

This is a collection of reports on the early research conducted by the SNSF-project.

Braekke, F. 1975. Hydrokjemiske myrundersøkelser. SNSF-project. TN 5/75. 28 p.

Studies on the effect of acid precipitation on bog ecosystems include field experiments on bog water-chemistry and laboratory experiments using peat sections and lysimeters. N.

Brandt, N. 1971. Sur Nedbør - Redusert tilvekst i våre skoger? NILU OR 28/71. 16 p.

Based on a limited amount of tree-ring data from pine and spruce forests in eastern Norway, it is concluded that there has apparently been no significant reduction in growth due to acid precipitation. N.

Brosset, C. 1973a. Air-borne acid. Ambio 2: 2-9.

During the combustion of fossil-fuel the sulfur is converted to SO_2 which is oxidized to H_2SO_4 either in the stack or in the atmosphere. This H_2SO_4 is washed out of the atmosphere both in the vicinity of the stack and at long-distances from the stack. Some of the sulfuric acid is deposited as particles, which may present a serious human health-hazard. E.

Brosset, C. 1973b. Danger of water pollution through air. In Proc. Symp. Eur. Fed. Protection Wat., Finland. 11 p.

This general discussion of atmospheric chemistry and long-distance transport of pollutants in Europe focuses on the uncertainties concerning the impact of particulate deposition on aquatic ecosystems. E.

Brosset, C. 1973c. Problems involved in choosing a suitable method of determining hazardous acidity on particles. Swedish Water and Air Pollution Research Laboratory, Gothenburg, Publ. B148. 9 p.

Because there are several types of acid particles, the choice of a suitable measuring technique for particles cannot be made until the hazards to human health presented by each of these particles types are known. E.

Brosset, C. 1974. Introductory comments on sulphur dioxide and acidification made at the IVL-Conf. Stockholm on 11th December, 1973. Swedish Water and Air Pollution Research Laboratory, Gothenburg, Publ. B186. 3 p.

There are 4 processes by which acidification of water by sulfur dioxide is possible, 1) dry deposition of gaseous SO_2, 2) dry deposition of acidic particles, 3) washout of SO_2 gas, and 4) washout of H_2SO_4. E.

Brosset, C. 1975. Acid particulate pollutants in Sweden. Swedish Water and Air Pollution Research Laboratory, Gothenburg, Publ. B222. 20 p.

Under certain weather conditions aerosols of acid ammonium sulfate are transported from distant sources to Sweden, where the deposition of such particles in human respiratory tracts represents a possible health hazard. E.

Brosset, C. and Å. Åkerström. 1972. Long distance transport of air pollutants - measurements of black air-borne particulate matter (soot) and particle-borne sulphur in Sweden during the period of Sept.-Dec. 1969. Atmos. Environm. 6: 661-673.

An extensive description of the sampling and analytical procedures involved in collecting particulate matter from air is accompanied by data for southern Sweden that point to regional rather than local sources for particulates in the air. E.

Brosset, C., K. Andreasson, and M. Ferm. 1974. The nature and possible origin of acid particles observed at the Swedish west coast. Swedish Water and Air Pollution Research Laboratory, Gothenburg. Report B 189. 19 p.

Two types of acid particles exist in air collected from a rural area on the Swedish west coast. The first type is perhaps $(NH_4)_3H(SO_4)_2$, generated by catalytical oxidation of SO_2 absorbed in the water droplets round the particles. The second type is perhaps NH_4HSO_4 (i.e. more acid) and the particles may have been formed by photochemical oxidation of SO_2 in the presence of NO_2. E.

Brownscombe, J. L. 1972. Sulphur in rainwater and air at some relatively clean sites in the British Isles from 1959 to 1970. Journ. Food and Agriculture 23: 1146-1147.

Monthly measurements of sulfate in air and precipitation at 3 sites in England conducted as part of the European precipitation network give sulfur deposition rates of 1-3 kg/ha/month. These rates have not significantly increased during the measuring period. E.

Bua, B., and E. Snekvik. 1972. Klekkeforsøk med rogn av laksefisk 1966-1971. Virkning av surhet og saltinnhold i klekkevannet. Direktoratet for vilt og ferskvannsfisk, Norway. Vann 7: 86-93.

Hatching experiments show that the critical pH-limit for salmon is 5.0-5.5, for sea trout 4.5-5.0 and for lake trout 4.5. The hatching success at a given pH is increased by adding neutral salts to the water. N.

Cambray, R. S., D. F. Jefferies, and G. Topping. 1975. An estimate of the input of atmospheric trace elements into the North Sea and the Clyde Sea (1972-3). Environmental and Medical Sciences Division, AERE Harwell, UK, Report R7733. 25 p.

Samples of airborne dust, rainwater and dry deposit were collected at 7 stations in and adjacent to the UK and analyzed for 23 trace

elements. The results show that the atmosphere is an important source of heavy metals for the Clyde Sea. An enhancement of trace elements in the surface microlayer of the sea is responsible for high concentrations in rainwater collected in the presence of sea-spray. E.

Carter, L. 1964. Effects of acidic and alkaline effluents on fish in seawater. Effl. & Wat. T. Journ. 484-486.

Experiments with various marine fish indicate that at pH 5.5-9.0 fish mortalities in seawater are unlikely. E.

Cawse, P. A. 1974. A survey of atmospheric trace elements in the UK. Environmental and Medical Sciences Division, AERE Harwell, UK, Report R7669. 84 p.

Samples of airborne dust, rainwater and dry deposition collected at 7 rural sites in the UK were analyzed for 30 trace elements. The results allow a grouping of the elements according to their principal source - soil, industrial emissions, or sea spray. The raw data and details for Peirson et al. (1974) are given. E.

Cawse, P. A., and D. H. Peirson. 1972. An analytical study of trace elements in the atmospheric environment. Atomic Energy Research Establishment, Harwell, England, Report R7134. 25 p.

The levels of 30 trace elements were measured in airborne dust, rainwater and dry deposition at a rural site in NW England using neutron activation analysis. Various experimental difficulties are discussed. The results indicate that the elements can be assigned to either maritime, soil-derived or anthropogenic sources. E.

Chapin, J., and P. D. Uttormark. 1973. Atmospheric contributions of nitrogen and phosphorus. Tech. Rept. 2. Univ. Wisconsin, Water Resources Center. 35 p.

This is a compilation of published data on the amounts of N and P in precipitation and a discussion of the sources, seasonal variations, and regional patterns of these elements in atmospheric precipitation. E.

Chester, R., and J. H. Stoner. 1973a. Pb in particulates from the lower atmosphere of the eastern Atlantic. Nature 245: 27-28.

The Pb concentrations in atmospheric particulate matter show

enrichment factors of 10-113 relative to crustal composition with greater enrichment in air streams associated with industrial Europe. E.

Chester, R., and T. H. Stoner. 1973b. Average trace element composition of low level marine atmospheric particulates. Nature 246: 138-139.

The concentrations of other trace elements are also enriched but not as much as for Pb. (See Chester and Stoner 1973a). E.

Cogbill, C. V., and G. E. Likens. 1975. Acid precipitation in the northeastern United States. Wat. Res. Res. (In press).

Precipitation in the northeastern US has a pH less than 4.4, with 65% of the acidity due to H_2SO_4, 30% to HNO_3, and less than 5% to HCl. The acidity has increased since about 1950-55, especially that due to HNO_3. The source region is the industrial Midwest. E.

Conroy, N., D. S. Jeffries, and J. R. Kramer. 1974. Acid shield lakes in the Sudbury Ontario Region. Proc. 9th Canadian Symp. Water Poll. Res. (in press).

A survey of water chemistry of 50 lakes near the Sudbury smelter showed that lakes vary in their susceptibility to inputs of sulfuric acid depending on the geology of the watershed and proximity to the stack. E.

Conroy, N., and L. Maki. 1974. Extensive and intensive lake studies in the Sudbury area, p. 138-143. In Ontario Industrial Wastes Conferences 1974.

The principal factors affecting the pH and heavy-metal concentrations in lakes of the Sudbury, Ontario, region are 1) distance and direction from the smelter stack and 2) geology of the watershed. As the pH declines the biological activity is reduced and heavy metals become more abundant until the fisheries are eliminated. E.

Cook, J. R. 1971. Influence of culture pH and phosphate on synchrony of *Euglerea gracilis*. Experimental Cell Research 69: 207-211.

This alga divides synchronously when exposed to a repetitive light-dark cycle and high phosphate levels in the medium. The pH-dependence of synchronous cell-division may be related to changes in cell transport mechanisms. E.

Costa, H. H. 1966. Responses of *Gammarus Pulex* (L) to modified environment. 1. Reactions to toxic solutions. Crustaceana 11: 245-256.

Experiments on the toxicity of several heavy-metals are described. E.

Costa, H. H. 1967. Responses of *Gammarus pulex* (L) to modified environment. II. Reactions to abnormal hydrogen ion concentrations. Crustaceana 13: 1-10.

Experiments on the effects of various acid and alkaline solutions are described. E.

Dahl, E. 1972. Kostnader ved utslipp av svoveloksyder i atmosfæren. Tekn. Ukeblad 119 (22): 3-5.

This article continues a debate between Dahl, Aksel Lydersen and N. A. Sørensen about the cost to society of SO_2 emissions into the atmosphere, both from local and distant sources. N.

Dahl, E., O. Gjems, and J. Kielland-Lund Jr. 1967. On the vegetation types of Norwegian conifer forests in relation to the chemical properties of the humus layer. Meddr. Norske Skogfors. Ves. 24: 503-531.

The cation supply to forests depends on primary factors (weathering and leaching) and external factors (precipitation inputs). The supply of organic matter and also N depends largely on processes within the forest ecosystem. The types of forest in Norway depend on these various processes. E (N summary).

Dahl, E., and O. Skre. 1971. En undersøkelse av virkningen av sur nedbør på produktiviteten i landbruket. Nordforsk, Miljøvårdssekretariatet No. 1: 27-40.

The acidity of precipitation in southern Scandinavia can potentially affect forest growth by causing decreases in the availability of plant nutrients (especially cations) in the soil. Data from Finland show that the availability of these cations is positively correlated to forest growth. N.

Dahl, K. 1920. Undersøkelser over ørretens utdøen i det sydvestlige Norges fjeldvand. Norsk Jæger- & Fisk. For. Tidsskr. 49: 249-267.

The extensive fish-kills reported in 1916 in southernmost Norway are apparently due to disease. Dahl also remarks on the decrease (14-68%) in salmon-catches from 8 rivers during the period 1903-1919. N.

Dahl, K. 1922. Supplerende bemerkninger til undersøkelser over ørretens utdøen i sydvestlige Norges fjeldvand. Norges Jæger- & Fisk. For. Tidsskr. 51: 64-66.

Additional comments on the fish-kills of 1916 (see Dahl 1920). N.

Dahl, K. 1923. Massedød blant ørret ved forgiftning med avløpsvand fra myrer. Norges Jæger- & Fisk. for. Tidsskr. 52: 1-5.

Chemical analyses show that at the time of the 1920 fish-kills in southern Norway the concentration of sulfuric and nitric acids in the streams was unusually high. The kills are ascribed to accumulation of these acids in bogs during the dry summer followed by flushing during subsequent heavy rains. N.

Dahl, K. 1926. Vandets surhetsgrad og deres virkninger på ørretyngel. Tidsskr. norske Landbr.: 232-242.

The effect of acidity on trout-spawning success is discussed, and a series of pH measurements from lakes and streams in southern Norway is reported. N.

Dale, T., A. Henriksen, E. Joranger, and S. Krog. 1974. Vann- og nedbörkjemiske studier i Birkenesfeltet for perioden 20. juli 1972 til 30. april 1973. SNSF-project TN 1/74. 44 p. + appendix.

The small, forested, gauged watershed at Birkenes, southern Norway is described, and some preliminary precipitation- and streamwater chemistry data reported. N.

Dannevig, A. 1959. Nedbørens innflytelse på vassdragenes surhet og på fiskebestanden. Jeger og Fisker No. 3: 116-118.

This is perhaps the first report linking acid rain to acidity of fresh-waters and thence to fish kills. N.

Dannevig, G. 1966. Auren og det sure vannet på Sørlandet. Norg. Jeg. og Fiskerforb. Tidsskr.: 388-393.

Dannevig reports that some strains of trout are apparently more

resistant to acid-stress than others, and these resistant strains can perhaps be used for stocking low-pH lakes in southern Norway. The seasonal and downstream changes in pH for several rivers are discussed. N.

Dannevig, G. 1968. Surt vann og dødelighet på ørret. Zoologisk Revy (Sverige) 30: 53-60.

The disappearance of trout from many lakes and rivers in southernmost Norway is due to increasing acidity of the waters. At low pH breeding, hatching of eggs, and survival of fry are inhibited. Some local stocks are more acid resistant, however. N (E summary).

Dannevig, G. 1970. Auren på Sørlandet dør ut på grunn av forurenset og sterkt sur nedbør. Unpubl. report. 8 p.

Although some fish kills are due to local pollution, the widespread disappearance of fish from lakes and rivers in Sørlandet is due to increasing acidity, as, for example, is the case in Tovdalselva. N.

Dannevig, G., B. Kjos-Hansen, K. W. Jensen, and E. Snekvik. 1971. Fiskebestand og forsurning av vassdrag. Jakt, fiske, friluftsliv 100: 149-151, 198-201.

The increase in acidity of precipitation in southernmost Norway during the last 20 years has caused drastic increases in the acidity of thousands of lakes and rivers and the consequent loss of fisheries. N.

Davis, P., and G. W. Ozburn. 1969. The pH tolerance of *Daphnia pulex* (Leydig, emend., Richard) Can. J. Zool. 47: 1173-1175.

D. pulex is able to survive for 32 hours at pH 4.3 to 10.4, but reproduction was observed only at pH 7.0 to 8.7. E.

DeBary, E., and C. Junge. 1963. Distribution of sulfur and chlorine over Europe. Tellus 15: 370-381.

Using European precipitation-chemistry data for 1954-59, maps of SO_4, Cl, and excess-SO_4 (corrected for sea-water sulfate using Cl) are constructed. Seasonal and geographic patterns are discussed. E.

Delany, A. C., W. H. Pollock, and J. P. Shedlovsky. 1973. Tropospheric aerosol: The relative contribution of marine and continental components. J. Geophys. Res. 78: 6249-6265.

Vertical profiles of the Na, Cl, K, Mn, Br, and Si concentrations in the lower 9 km of the atmosphere (western Pacific, southern California, Nebraska) showed that the middle and upper troposphere has a uniform aerosol composed of 90-95% continental material and 5-10% marine materials. The marine salt, being hydrophilic, is apparently preferentially washed out of the lower layers. E.

Descroix, P. 1974. L'influence de la pollution atmosphérique sur la pollution des eaux en France, p. 93-96. In H. E. Vogel (ed.), European Fed. Protection Waters, Zürich, Info. Bull. 21.

Precipitation falling in the Paris basin has become more acidic during the period 1956-1968. Since the soils and waters of the area are highly buffered, however, this acid precipitation is readily neutralized. Other atmospheric pollutants such as fluorine present greater potential threat to water bodies. F (E, G summary).

Dickson, W. 1971. pH-situationen i Västkustsjöar november-desember 1970. Drottningholm Freshwater Research Laboratory. Unpubl. report. 56 p.

This is a preliminary report on the water chemistry of 314 lakes on the Swedish west coast. Most of these lakes have low buffer capacities and have been greatly affected by atmospheric precipitation. Over 60 of the lakes have pH less than 5, and the pH in some has declined 2 units since the 1930's. S.

Dondoroff, P., and M. Katz. 1950. Critical review of literature on the toxicity of industrial wastes and their compounds to fish. I. Alkalics, acids and inorganic gases. Sewage Ind. Wastes 22: 1432-1458.

This review discusses literature on pH and fish up to about 1950. E.

Dovland, H. 1975. Tidsvariasjonen for noen kjemiske komponenter i elvevann under snøsmeltingen våren 1974. SNSF-project, TN 9/75. 34 p.

The chemistry of several lakes and streams in southwestern and southeastern Norway changed during snowmelt in 1974. These changes are related to the pollutant load in the snowpack and to the buffer capacity of the surface waters, which in turn is related to watershed geology and soils. N.

Dovland, H., T. Dale, and E. Joranger. 1974. Undersøkelse av

elvevannets kjemiske sammensetning under snøsmelting. SNSF-project TN 2/74. 61 p.

The chemistry of three rivers was measured during snowmelt in 1973. Although there were indications of a pulse of pollutants during the first phases of snowmelt, major changes in the rivers were not recorded because 1) the pollutant load in the snowpack of 1973 was unusually low, and 2) the chemistry of these rivers is influenced by base flow from the soils. N.

Dovland, H., and A. Semb. 1975. Tilførsel og avrenning av sure komponenter i Tovdalsvassdraget. SNSF-project. TN 6/75. 22 p.

Using the available data from several precipitation chemistry stations and river chemistry data the H^+ balance for a river in southern Norway was computed for 1973. N.

Dugstad, I. 1972. Målinger av luftforurensninger i Bergen 1969-1972. Foreløpige resultater. Geofysisk institutt, Universitetet i Bergen avd. B. Meteorologi Rapport nr. 2. 26 p.

SO_2 and particulate-matter concentrations in air are reported and related to several meteorological parameters. N.

Dunson, W. A., and R. R. Martin. 1973. Survival of brook trout in a bog-derived acidity gradient. Ecology 54: 1370-1376.

The occurrence of fish in a Pennsylvania stream with low pH due to humic acids is related to pH. Only brook trout survive at low pH (4.7), although some insects tolerate lower levels. E.

Dybdahl, K. 1973. Skadevirkningene av sur nedbør dokumenteres. Tekn. Ukeblad 120 (20): 42, 48.

In this interview with parliament member Per Hysing-Dahl the setting-up of the SNSF-project is explained. N.

Eaton, J. S., G. E. Likens, and F. H. Bormann. 1973. Throughfall and stemflow in a northern hardwood forest. J. Ecol. 61: 495-508.

At Hubbard Brook, New Hampshire, the input of hydrogen ions by acid precipitation probably accelerates the removal of cations from the forest canopy, thus facilitating nutrient cycling. E.

Egnér, H. 1955-1960. Current data on the chemical composition of air

and precipitation. Tellus 7: 134-139, 266-271, 395-400, 522-527; 8: 112-113, 283-285, 411-412, 513-517; 9: 140-143, 250-253, 423-426, 464-468; 10: 170-175, 281-286, 401-406, 500-505, 508; 11: 139-144, 259-264, 366-372; 12: 112-118.

These are the raw data from the European precipitation network 1954-1960. E.

EIFAC. 1969. Kriterium på vattenkvalitet för europeiske insjöfisker. Om extreme pH-värden och sötvattensfisket. T. B. Hasselrot, Trans. Information från sötvattenslaboratoriet Drottningholm nr. 2.

This is a Swedish translation of the original English review of the literature on pH and fish. S.

Elgmork, K., A. Hagen, and A. Langeland. 1973. Polluted snow in southern Norway during the winters 1968-71. Environ. Pollut. 4: 41-52.

Chemical analysis of snow samples (pH, conductivity, hardness, SO_4, Na, K, Cl, total N, Fe, Mn, Pb, Zn, and total C) document the widespread distribution of airborne pollution. E.

Emanuelsson, A., E. Eriksson, and H. Egner. 1954. Composition of atmospheric precipitation in Sweden. Tellus 6: 261-267.

Isopleth maps for the deposition of Na, Cl, K, Ca, NH_3-N and NO_3-N based on Swedish precipitation data for 1948-50 show that seawater is the major source for Na and Cl (although the Cl/Na ratio varies in an unexplained manner), the soil is the major source for Ca, and agricultural activities are the major source for NH_3-N. E.

Eriksson, E. 1952a. Composition of atmospheric precipitation. 1. Nitrogen compounds. Tellus 4: 215-232.

This paper discusses all measurements of nitrogen compounds in atmospheric precipitation from the 1750's to 1950. The sources for N-compounds are seawater, biologic activity, cyclic dust, anthropogenic sources, and lightning fixation. E.

Eriksson, E. 1952b. Composition of atmospheric precipitation. II. Sulfur, chloride, iodine compounds. Bibliography. Tellus 4: 280-303.

This paper continues from (19) and discusses the literature on S, Sl, and I compounds. The importance of fossil-fuel combustion for

the release of S to the atmosphere is stressed, using Cl to estimate "excess sulfur". Some data for Ca and Mg are also presented. E.

Eriksson, E. 1954. Report on an informal conference in atmospheric chemistry held at the Meteorological Institute, University of Stockholm, May 24-26, 1954. Tellus 6: 302-307.

At this meeting of scientists interested in air and precipitation chemistry and geochemical cycling, current research was reported. In addition plans were laid for the establishment of a European precipitation network. E.

Eriksson, E. 1955. Air borne salts and the chemical composition of river waters. Tellus 7: 243-250.

The Cl content of rivers in Scandinavia and in the eastern US points to a marine origin and atmospheric cycling of Cl. The chemical composition of rivers indicates that the atmosphere is a major source for other elements as well, and that chemical denudation rates cannot be inferred directly from the chemistry of groundwater. E.

Eriksson, E. 1959. The yearly circulation of chloride and sulfur in nature; Meteorological, geochemical and pedological implications. Part 1. Tellus 11: 375-403.

The circulation of sea salt via the atmosphere is characterized by fractionation of elements or groups of elements relative to Cl due to differential rates of incorporation from sea spray, reactions in the atmosphere, formation of gaseous and particulate phases, and differential deposition rates in rain and dry-fallout. All of these processes, and the importance of other sources for many elements, result in complicated relationships between various elements. These relationships, however, can be used to follow various meteorological, geological, and pedological processes. E.

Eriksson, E. 1960. The yearly circulation of chloride and sulfur in nature; Meteorological, geochemical and pedological implications. Part II. Tellus 12: 63-109.

See Eriksson (1959). E.

Eriksson, E. 1969. Svoveldioxiden och nederbördens försurning - fakta och spekulationer. Swedish Water and Air Pollution Research Laboratory. Publ. A 28: 86-96.

It is the net acidity (acidic minus basic components) of precipitation that causes damage to forests and freshwater. Isopleth maps of the deposition of net acid from Scandinavian precipitation show changing patterns over the period 1955-66. S.

Fleetwood, Å. 1969. The chemical composition of the precipitation and surface water and its relation to evaporation on Bjørnøya island, Norway. Tellus 21: 113-126.

Precipitation chemistry (for 1965) and water chemistry for 45 lakes on an arctic island north of Norway are interpreted with respect to geology, vegetation, and meteorology (esp. evaporation). E.

Førland, E. J. 1973. A study of the acidity in the precipitation in Southwestern Norway. Tellus 25: 291-299.

Precipitation samples collected every 6 hours during 1970 were analyzed for acidity, and these data were correlated with various meteorological parameters. Analysis of the data shows that precipitation from air masses that have passed over central Europe or Great Britain have pH values of 4.0-5.0, while unpolluted air masses from the Norwegian Sea have pH values of 5.1-6.6. E.

Førland, E. J., and Y. T. Gjessing. 1975. Snow contamination from washout/rainout and dry deposition. Atmospheric Environm. 9: 339-352. By comparison, the chemistry of snow sampled just after snowfall and 3-4 days later, the relative contributions of washout/rainout, dry-deposition and filtering were estimated. E.

Førland, E. J., E. Meisingseth, A. Skartveit, and I. Wefring. 1975. Hydrokjemiske data fra Nordhordland/Ytre Sogn. SNSF TN 8/75.

The frequency distribution of storms, their directions, and associated precipitation chemistry is reported from western Norway for the period 1/1 1973 to 30/6 1974. These observations are used to interpret chemical data from several streams. The raw data are included. N.

Fredriksen, H. 1973. Utslipp av svoveldioksyd fra norsk industri. Norges Industri nr. 20: 22-25.

Norway's SO_2 emissions are only 46 kg/person versus 360 kg/person for East Germany. A listing of SO_2 emission by the industrial and private sectors is presented. N.

Furmyr, S. (ed.). 1973a. Hydrological data - Norden. Representative basins Romerike Norway. Data 1965-1971. Norweg. Nat. Commit. for the Internat. Hydrol. Decade, Oslo. 77 p.

This report describes the Romerike site (southeastern region), gives the sampling and analytical procedures for hydrologic and meteorologic parameters, and lists the raw data for 1968-71. E.

Furmyr, S. (ed.). 1973b. Hydrological data - Norden. Filefjell, Norway. Data 1966-1971. Norwegian Nat. Commit. for the Internat. Hydrological Decade, Oslo. 69 p.

This report describes the Filefjell site (central mountain region) and gives the precipitation, surface-water and meteorological data for 1966-71. E.

Gambell, A. W. 1962. Indirect evidence of the importance of water-soluble continentally derived aerosols. Tellus 14: 91-95.

Based on Junge and Werby's (1958) precipitation chemistry data for the US, the Ca/Cl ratio is proposed as a logical index of the predominence of continental or marine water-soluble aerosols. Except in near-coastal areas, the continental sources dominate the composition of precipitation. E.

Gambell, A. W., and D. W. Fisher. 1964. Occurrence of sulfate and nitrate in rainfall. J. Geophys. Res. 69: 4203-4211.

Data from 6 individual storms in Virginia show that much of sulfate in rainfall is formed from the oxidation of SO_2 in cloud droplets, perhaps with NO_2 as a catalyst. Sulfate, nitrate, and ammonia in rainfall are primarily derived from gaseous components. E.

Gilbert, O. L. 1970. Further studies on the effect of sulphur dioxide on lichens and bryophytes. New Phytol. 69: 605-627.

Six years of data on lichens and bryophytes around Newcastle upon Tyne, England, are reported. Survival depends on shelter, pH and buffer capacity of the substratum, and nutrient flushing. E.

Gjems, O. 1970. Jordbunnen og forurensningsproblemer. Tidsskr. Skogbr. No. 2: 272-277.

The nutrient status, weathering processes, and atmospheric deposition influences on various Norwegian soil-types are discussed with particular reference to acid precipitation. N (E summary).

Gjessing, E. T. 1974. Effects of polluted precipitation on water quality In Proc. 7th Int. Conf. Water Poll. Research, Paris. 5 p.

Preliminary precipitation- and runoff-chemistry results from Birkenes, Norway, are discussed. E.

Gjessing, Y. T., and E. Gjessing. 1973. Chemical composition of an antarctic snow profile. Vatten 6: 233-237.

The concentration increase with depth in a 10 m snow profile is probably the result of filtering of aerosols. The decrease in sulfate, however, is related to a general increase in atmospheric sulfur. E.

Gjessing, Y., and E. Gjessing. 1975. Sneenskjemiske sammensetning som indikator på luftforurensninger. SNSF-project. TN 7/75. 18 p.

The pumping of air through snow colomns showed that snow is an effective filter of atmospheric contaminants. The chemistry of a 10-m snow/ice core from the Hardanger glacier, southern Norway, indicates that contaminants are lost preferentially during melting and may be found in high concentrations in ice layers. N.

Goffeng, G. (ed.). 1973. Hydrological Data - Norden. IHD stations Basic Data 1970-71. Nat. Commit. for the Internat. Hydrolog. Decade in Denmark, Finland, Iceland, Norway and Sweden. 110 p.

This report presents basic physiological, meteorological and geological data for the IHD stations in Scandinavia and also gives hydrologic and chemical data for 1970-71. E.

Gore, A. J. P. 1968. The supply of six elements by rain to an upland peat area. J. Ecology 56: 483-495.

The annual deposition of Na, K, Ca, Mg, N and P was measured over a 6-year period. Various experimental difficulties are discussed. E.

Gorham, E. 1955. On the acidity and salinity of rain. Geochim. et Cosmochim. Acta 7: 231-239.

The chemical composition of 42 rainwater samples collected in 1954 at the English Lake District results from seawater inputs of Na and Cl, and inputs SO_4 and H^+ from industrial sources (soot). E.

Gorham, E. 1958. The influence and importance of daily weather conditions in the supply of chloride, sulphate and other ions to fresh waters from atmospheric precipitation. Phil. Trans. Roy. Soc. B. 241: 147-178.

Chemical analyses of daily precipitation samples collected in the English Lake District during 1955 and data on amount of precipitation, wind direction, wind velocity and temperature showed that sulfate is supplied principally from atmospheric pollution, that Na and Cl are of marine origin, and that atmospheric precipitation is a major source of major ions to fresh waters. E.

Gorham, E. 1961. Factors influencing supply of major ions to inland waters, with special reference to the atmosphere. Geol. Soc. Amer. Bull. 72: 795-840.

The chemistry of inland waters is determined by chemical inputs from the atmosphere (rain, dry fallout, snow, gases) and from soil and rock weathering. The atmosphere, in turn, receives its chemicals from the sea, soil, air pollution, volcanoes and organic matter. This paper includes an extensive literature review. E.

Grahn, O., and H. Hultberg. 1974. Försurningens effekter på oligotrofa sjöars ekosystem - integrerade förandringar i artssammensätning och dynamik. Meddelanden nr. 2. Swedish Water and Air Pollution Research Laboratory, Gothenburg. Report, 17 p.

Grahn, O., H. Hultberg, and L. Landner. 1974. Oligotrophication - a self-accelerating process in lakes subjected to excessive supply of acid substances. Ambio 3: 93-94.

Intensive studies, including whole-lake manipulations are described for 6 lakes in a very acid region of western Sweden. The long-term effects of acidification cause lakes to decrease in productivity and thereby move towards a more oligotrophic state. Alterations in macrophytes, invertebrates and fish populations are discussed. E.

Granat, L. 1972. On the relation between pH and the chemical composition in atmospheric precipitation. Tellus 24: 550-560.

Using chemistry data from 2000 precipitation samples collected on the European Atmospheric Chemistry Network, the relationship between pH and acidity was explored. Since pH is the net result of several acid and basic compounds of different origins, pH and sulfate are not highly correlated. E.

Granat, L. 1974. On the deposition of chemical substances by precipitation (as observed with the aid of the atmospheric chemistry network in Scandinavia). WMO Special Environm. Report No. 3: 71-78.

The problems in the calculation of areal deposition rates from precipitation chemistry data are discussed, and the 20-year record from the European Atmospheric Precipitation Network is used as an illustration. E.

Grande, M. 1966. Vannets pH og dens betydning for ferskvannsfiske. En orientering om norske undersøkelser og erfaringer. NIVA O-139/64. 13 p.

This is a summary of Norwegian information on the effect of acid-waters on fish. N.

Griffiths, D. 1973a. The structure of an acid moorland pond community. J. Animal Ecol. 42: 263-284.

The spatial relations of plants and animals in a small acid (pH 4.4) pond in S.W. England are described, and species abundances and distributions are discussed. E.

Griffiths, D. 1973b. The food of animals in an acid moorland pond community. J. Animal Ecol. 42: 285-294.

By examining the gut contents of animals, the factors affecting food sources were evaluated. E.

Grøterud, O. 1972a. Zooplankton and fish in relation to acid melt water and anaerobic deep water in a lake. Vatten 28: 329-332.

The distribution of a copepod and the fish in an acid lake near Oslo appears to be controlled by the pH in the surface waters and H_2S content of the hypolimnetic waters. E.

Grøterud, O. 1972b. Ice-analyses. Data from three Norwegian lakes. Hydrobiologia 40: 371-391.

Ice analyses indicate that freeze-out concentrates nutrients (N, P) in ice layers. These nutrients are then released during spring-melt. E.

Grøterud, O. 1972c. Hydrographical data from two soft water lakes with

special reference to precipitation (melt water). Arch. Hydrobiol. 70: 277-324.

Two acid lakes just west of Oslo were studied in detail, and the chemistry of these lakes explained in terms of precipitation chemistry, melt-water chemistry, and biological activity in the lakes themselves. E (G summary).

Grøterud, O. 1973. Noen sure innsjøer i Norge. Vatten 2: 153-158.

Chemistry of 8 small lakes just west of Oslo is discussed. These lakes are characterized by low pH, low-conductivity and declining fish-populations. N.

Gunnerød, T. B. 1973. Forsøk med utsetting av lakseunger i Siravass-draget med Moisåna i 1972 og 1973. Direktoratet for jakt, vilt-stell og ferskvannsfiske, Norway. Unpubl. report. 10 p.

Attempts to stock salmon fry in several rivers of southern Norway were unsuccessful, probably because the water was too acid. N.

Haapala, K. 1972. The quality of rainwater in Finland according to observations made during 1971. National Board of Waters, Helsinki Finland.

Precipitation chemistry data from the 42-station network in Finland for 1971 show that northern Finland receives less dissolved solids than southern Finland due to the greater distance from the sea, the greater distance from industrial pollution sources, and the lesser amount of precipitation. Fi (E summary).

Haapala, K. 1974. Undersökningar av nedfallets sammansättning i Finland 1971-73, p. 344-358. In Nordisk Hydrologisk Konference, Copenhagen.

Precipitation chemistry data from the 42-station network in Finland show that precipitation in southernmost Finland has high concentrations of sulfate, nitrate and hydrogen-ion. S.

Hagen, A., and A. Langeland. 1973. Polluted snow in southern Norway and the effect of the meltwater on freshwater and aquatic organisms. Environ. Poll.: 5: 45-57.

Polluted snow and surface ice considerably alter the lake-water chemistry during spring-melt with possible adverse affects on fish and invertebrates due to low pH and high Zn concentrations. E.

Hagen, O., G. Norby. 1967. Noen undersøkelser i forbindelse med problemet surt vann og dets betydning for lakse- og ørretbestanden på Sørlandet. Norg. Jeg. og Fiskeforb. Tidsskr.: 250-255.

The relationship between acid precipitation and acid lakes and rivers is discussed, and the salmon-catch data from 1951-1964 from several rivers in Southern Norway are presented and explained on the basis of pH. N.

Hales, J. M., and S. L. Sutter. 1973. Solubility of sulfur dioxide in water at low concentrations. Atmos. Environm. 7: 997-1001.

Experiments were conducted using SO_2-concentrations at levels commonly found in nature, and the results agree well with theoretical values. E.

Hallsworth, E. G., and W. A. Adams. 1973. The heavy metal content of rainfall in the East Midlands. Environ. Poll. 4: 231-236.

The concentrations of 16 trace elements in rainfall and fly-ash collected during 1963-64 were measured. Particulate emissions from nearby power plants account for only part of the deposition. E.

Hanson, M. 1974. Zooplankton i Fulufjällsjöar med lågt pH. Information från Sötvattenslaboratoriet, Drottningholm No. 5. 17 p.

The zooplankton in 2 alpine lakes with low pH (less than 5) has been affected by the acid conditions with several species (*Daphnia*) absent. S (E summary).

Harrison, A. D. 1958. The effects of sulphuric acid pollution on the biology of streams in the Transvaal, South Africa. Verh. internat. Ver. Limnol. 13: 603-610.

Several streams polluted by acid mine drainage have low pH (as low as 2.9). At pH less than 5 specialized flora and fauna develop, and only these species survive at pH less than 4. E.

Haugbotn, O. 1973. Nedbørundersøkelser i Sarpsborgdistriktet, og undersøkelser over virkninger av forsurende egensskaper. Unpubl. report. Norges Landbrukshøgskole. 151 p.

The local deposition of S in the vicinity of the Norwegian industrial center of Sarpsborg is measured, and the effects on soil chemistry investigated. N (E summary).

Henriksen, A. 1972a. Regresjonsanalyse av pH- og hårdhetsobservasjoner i Sørlandselver. Vann 1: 1-9.

Snekvik's pH and hardness data from 19 rivers in southernwest Norway during the period 1965-70 are treated with various statistical techniques. A decline in pH, increase in hardness, and cyclic periodicity of the data are demonstrated. N.

Henriksen, A. 1972b. Quantitative chemical analysis of snow. Vatten 5: 409-412.

Complete analysis of 1 snow profile from Norway. N.

Henriksen, A., T. Dale, and S. Haugen. 1974. Smelting av forurenset snø i termostatert lysimeter. SNSF IR 1/74. 18 p.

The fractionation and concentration processes during snow-melt were investigated in the laboratory. Eleven chemical components were measured. N.

Henriksen, A., and M. Johannessen. 1975. Avsyring av sure vann. En litteraturoversikt og generell vurdering. SNSF-project. IR 5/75. 44 p.

Based on published and unpublished reports the use of limestone, calcium hydroxide and other alkaline compounds to counteract the acidification of lakes and rivers is evaluated. Experience in Norway indicates that such practice is reasonable only for small streams and ponds. N.

Herman, F. A., and E. Gorham. 1957. Total mineral material, acidity, sulphur and nitrogen in rain and snow at Kentville, Nova Scotia. Tellus 9: 180-183.

Monthly samples of precipitation collected 1952-54 in rural eastern Canada had on average pH of 5.7, and acidic samples also had higher concentrations of nitrate and sulfate. Snow samples had much lower concentrations than rain, suggesting a difference in washout efficiency. E.

Högström, N. 1973. Residence time of sulfurous air pollutants from a local source during precipitation. Ambio 2: 37-41.

Sulfur emitted from local sources in Uppsala is washed out as sulfate within 1-2 hours or 50-100 km from the sources. These results indicate that local sulfate sources are important (25-50%),

rather than negligible as previously asserted (see Bolin and Grannat 1973). E.

Holtan, H. 1972. Kjemisk-fysiske undersøkelser i IHD's representative område på Filefjell. Unpubl. manuskript. NIVA. 9 p.

The IHD watershed at Filefjell, Norway, is described, and some data for precipitation - and runoff-chemistry are discussed. N.

Holt-Jensen, A. 1973. Acid rains in Scandinavia. Ecologist 3: 378-382.

This is an overview of acid-rain and its impact on soils, forests and fisheries in Scandinavia. E.

Horntvedt, R., and E. Joranger. 1974. Nedbørens fordeling og kjemiske innhold under traer: Juli-november 1973. SNSF-project TN 3/74. 29 p.

The chemistry of precipitation and throughfall was measured at two forested sites, one in an area of southern Norway that receives acid precipitation and one in a relatively unaffected area of northern Norway. N.

Huge, D., and Å. Killingtveit (eds.) 1973. Hydrological data - Norden. Sagelva, Norway. Data 1968-1971. Norweg. Nat. Comm. for the Internat. Hydrol. Decade, Oslo. 67 p.

This report describes the Sagelva site (north coastal region), gives the sampling procedures for precipitation, surface waters and meteorologic data, and lists the raw data for 1968-71. E.

Hultberg, H., and J. Stenson. 1970. Försurningens effekter på fiskefaunaen i två bohuslänska småsjöar. Fauna och Flora. 65: 1-20.

Huitfeldt-Kaas, H. 1922. Om aarsaken til massedød av laks og ørret i Frafjord-elven, Helle-elven og Dirdalselven i Ryfylke høsten 1920. Norges Jæger- & Fiskfor. Tidsskr. 51: 37-44.

The fish-kills (salmon) of autumn 1920 are described, and although the cause was not apparent, the kills were ascribed to the washout of humic substances from the soils following an unusually dry summer. N.

Hutchinson, T. C., and L. M. Whitby. 1974. A study of airborne contamination of vegetation and soils by heavy metals from the Sudbury, Ontario, copper-nickel smelters, p. 175-178. In D. O. Hemphill (ed.) Trace Substances in Environmental Health - VII.

Analysis of Cu and Ni contents of soils and vegetation, and laboratory experiments on toxicity of these metals to plants, indicate that the soils of the Sudbury region contain inhibitory levels of Cu and Ni. E.

Jensen, K. W. 1972. Laks, ørret og pH i Sørlandsvassdrag. Vann 1: 1-6.

Jensen discusses the 100-year record of salmon catches from 79 major rivers in Norway and the documentation of declining salmon catches in rivers of Aust- and Vest-Agder counties. He also presents and discusses fish data from 2083 lakes in Telemark, Aust- and Vest-Agder, and Rogaland. 741 of these are barren, most of them since 1940, and this is highly correlated with pH levels in the lakes. N.

Jensen, K. W., and E. Snekvik. 1972. Low pH levels wipe out salmon and trout populations in southernmost Norway. Ambio 1: 223-225.

The gradual decline in pH of many lakes and rivers in southernmost Norway has resulted in drastic declines of fish populations (salmon in rivers, brown trout in lakes). Documentation comes from salmon-catch records for the last 100 years and extensive reports from fishery authorities in each community. This is essentially an English version of Jensen (1972). E.

Jernelöv, A. B. 1973. Mercury fall-out from the atmosphere. In Proc. Symp. Eur. Fed. Protection Wat., Finland. 8 p.

The geochemical cycle of Hg has been altered by man's activities such that Hg fallout is high and increasing. Most of the Hg from a local source is incorporated into the regional or global atmosphere; only a small fraction is washed out locally. E.

Johnson, N. M., R. C. Reynolds, and G. E. Likens. 1972. Atmospheric sulfur: Its effect on the chemical weathering of New England. Science 177: 514-516.

Data from Hubbard Brook, New Hampshire, indicate that sulfuric acid may control chemical weathering processes in areas that receive large inputs of acidic precipitation. E.

Jonasson, J. R. 1973. Migration of trace metals in snow. Nature 249: 447-448.

Jonsson, B., and R. Sundberg. 1972. Has the acidification by atmospheric pollution caused a growth reduction in Swedish forests? Royal College of Forestry, Dept. of Forest Yield Res., Stockholm. Research Note No. 20. 47 p.

A statistically significant reduction in growth between two groups of forest stands (on soils of lesser and greater buffer capacity) of 3-6 permil was found, but due to the non-experimental nature of the data this growth reduction cannot definitely be ascribed to acid precipitation. E (summary).

Jordan, D. H. M., and R. Lloyd. 1964. The resistance of rainbow trout *(Salmo gairdnerii* Richardson) and roach *(Rutilus rutilus* (L.)) to alkaline solutions. Int. J. Air Wat. Poll. 8: 405-409.

Experiments on the survival of fish in alkaline solutions (pH above 9.5) show that acclimatization to alkaline waters lengthens survival times. E.

Junge, C. E. 1956. Recent investigations in air chemistry. Tellus 8: 127-139.

Aerosol measurements made on the US east coast showed that there are two particle size-classes (0.08-0.8 micron and 0.8 to 8 micron). Nitrate appears not to be of industrial origin but rather due to mixing of continental and marine air masses. E.

Junge, C. E. 1960. Sulfur in the atmosphere. J. Geophys. Res. 65: 227-237.

Estimates of the sulfur budget of the global atmosphere indicate that 30% is of anthropogenic origin (excluding sulfate in sea salt particles). Since the concentration of sulfate in Greenland ice back to 1915 has not increased as much as the increase in anthropogenic emissions, much of the sulfur is removed before air masses reach polar regions. This agrees with estimates of residence times of 5 days for SO_2 and 40 days for total S. E.

Junge, C. E., and P. E. Gustafson. 1957. On the distribution of sea salt over the United States and its removal by precipitation. Tellus 9: 164-173.

Data for chloride concentrations in rainwater collected during

1955-56 at 62 US stations indicate that the drop in concentration along the coast and the constant inland levels are due to large-scale vertical mixing in the troposphere rather than by washout. E.

Junge, C. E., and R. T. Werby. 1958. The concentration of chloride, sodium, potassium, calcium, and sulfate in rainwater over the United States. J. Meterol. 15: 417-425.

One-year's data (1955-56) from a US precipitation network showed that the ocean is the major source of Cl, that the soil supplies Na and K, that Ca is highest in dust storm areas of the southwest, that sulfate originates from sea spray but 30% is anthropogenic, and that the average global sulfate residence time is 40 days. E.

Kamijo, H., T. Watanabe, and K. Mashiko. 1974. The attached algal flora of the Nagase-Gawa, a strong acid water river and its tributaries, Fukushima prefecture. Japanese Journ. Ecology 24: 147-152.

At sampling points where the river water was very acid the standing crops were poor and the flora contained only diatoms and green algae. At less acid points blue-green algae were abundant. J (E summary).

Karlén, A. 1972. Svoveldioxidens inverkan på mark och skog, sjöar, vattendrag och fisk. Svenska Reproduktions AB, Stockholm. 8-44.

Katz, M. 1968. The biological and ecological effects of acid mine drainage with particular emphasis to the Appalachian region streams. Appalachian Regional Commission, Washington, D.C., unpubl. report.

Katz, M., and R. T. Oglesby. 1967. A review of the literature of 1966 on wastewater and water pollution control. Biology. J. Water Poll. Cont. Fed. 39: 1049-1096.

This annual literature review includes some references on the effects of acidity. E.

Katz, M., D. E. Sjolseth, D. R. Andersson, and L. R. Tyler. 1970. A review of the 1969 literature on wastewater and water pollution control. Effects of pollution on fish life. J. Water Poll. Cont. Fed. 42: 983-1001.

This annual literature review includes some references on the effects of acidity. E.

Kettner, H. 1974. Beeinträchtigung oberirdischen Gewässer durch anorganische Stoffe, p. 18-32. In H. E. Vogel (ed.) European Fed. Protection Waters, Zürich, Info. Bull. 21.

Data from central Germany on dry deposition and washout of major and trace elements indicate that the effects on fresh waters in this area are 1) an increase in concentration of anions such as Cl, F, SO_4 and 2) an increase in heavy metal concentrations, particularly in sediments. G(G summary).

Kjos-Hanssen, B. 1970. Fiske og surt vann. Fiskedødeligheten har virkelig skutt fart i 1950/60-årene. Tekn. Ukebl. 117: 38.

The adverse effects of acid precipitation on fish populations have increased dramatically during the 1950's and 60's. N.

Kohonen, T. 1974. The washing out of alkaline earths in the watersheds, p. 315-326. In Nordisk Hydrologisk Konference, Copenhagen.

The washout of Ca, K, and Na during 1962-68 was measured at 34 small gauged-watersheds over all of Finland. Washout is related to watershed geology and land-use. E.

Koide, M., and E. D. Goldberg. 1971a. Atmospheric sulfur and fossil fuel combustion. J. of Geophys. Res. 76: 6589-6595.

Sulfate-chloride ratios in ice samples from Greenland indicate that fossil-fuel combustion introduces more S into the atmosphere than natural processes such as volcanism and decomposition of organic matter. Since the amount of S covaries with Pb, a similar source and atmospheric path for these two elements is likely. E.

Koide, M., and E. D. Goldberg. 1971b. Mercury in a Greenland ice sheet: Evidence of recent input by man. Science 174: 692-694.

The increased Hg content in ice over the last several decades is probably due to the dissemination of Hg into the atmosphere by man, thus augmenting the natural Hg supply from degassing of the earth's crust. E.

Kramer, J. R. 1973a. Fate of atmospheric sulphur dioxide and related substances as indicated by chemistry of precipitation. Department of Geology, McMaster University, Hamilton, Ont. Unpubl. report. 143 p. + appendix 44 p.

A 3-year study of precipitation chemistry at 35 stations in

Ontario indicates that high concentrations of some components are due to local anomalies and/or regional sources. The fates of various components are discussed with special reference to lake water-chemistry and biology. E.

Kramer, J. R. 1973b. Atmospheric composition and precipitation of the Sudbury region. Alternatives (Trent Univ., Peterborough, Ontario) 2 (No. 3): 19-25.

A comparison of air quality at Sudbury and New York City shows that "unhealthy" levels of SO_2 are often reached at both localities. Precipitation near Sudbury contains large amounts of sulfate, acid, and heavy metals that have serious effects on the plants, soils and lakes of the region. E.

Kramer, J. R., and W. R. Snyder. 1974. Precipitation scavenging of sulfur oxides using stable sulfur isotopes. Proc. 1974 U.S. Atomic Energy Commission Conference (in press).

The mass balance for sulfur emitted from the Sudbury, Ontario, smelter was calculated using stable sulfur isotopes, and while 76% of the omitted H_2SO_4 is deposited within 100 km of the stack, most of the emitted S is exported from the region. E.

Krishna, D. 1953. Effect of changing pH on developing trout eggs and larvae. Nature 171: 434.

Both eggs and larvae die at pH levels below about 5 and above 9. E.

Laamanen, A. 1972. Areal evaluation of sulfates in dustfall, rainfall, acidity and needle injuries. Work-Environm. Health 9: 26-39.

Acidity and sulfate concentrations in dustfall in urban Finland have resulted in damage to coniferous tree needles. This pollution is increasing in severity but is related to local sources.E.

Låg, J. 1963. Tilføring av plantenæringsstoffer med nedbøren i Norge. Forsk. Fors. Landbr. 14: 553-563.

Låg discusses precipitation chemistry from the period 1870-1951 (5 Norwegian articles) and then the Norwegian data from 1954-60 from the IMI network. N (E summary).

Låg, J. 1968. Relationships between the chemical composition of the

precipitation and the contents of exchangeable ions in the humus layer of natural soils. Acta Agr. Scand. 18: 148-153.

The main results from an analysis of 981 humus samples collected in central Norway are discussed, and it is concluded that an ion exchange occurs between precipitation (often polluted) and raw humus. E.

Låg, J., and E. Steinnes. 1974. Soil selenium in relation to precipitation. Ambio 3: 237-238.

Data from 3000 soil humus samples indicate that the principal source for selenium is precipitation, probably of marine origin, whereas arsenic originates elsewhere. E.

Laney, R. L. 1965. A comparison of the chemical composition of rainwater and ground water in western North Carolina. U.S. Geol. Surv. Prof. Paper 525-C: 187-189.

Analysis of 33 rainwater samples collected during 1962-63 at 8 sites and 321 groundwater samples showed that there is a rapid change in chemistry as the rainwater infiltrates from a calcium sulfate-bicarbonate rainwater to a mixed-cation bicarbonate groundwater. E.

Larson, T. E., and I. Hettick. 1956. Mineral composition of rainwater. Tellus 8: 191-201.

Analysis of 62 rain samples collected 1953-54 near Chicago showed that the sea salt component is negligible and that both N and S are supplied by combustion of fossil fuels. E.

Larson, T. V., R. J. Charlson, E. J. Knudson, G. D. Christian, and H. Harrison. 1975. The influence of a sulfur dioxide point source on the rain chemistry of a single storm in the Puget Sound Region. Water Air Soil Poll. (in press).

Rainwater samples collected during a single storm indicate that a copper smelter influences rain chemistry out to 40 km by increasing the acidity and sulfur content of rain. E.

Le Barre, N. 1973. Lead contamination of snow. Water Res. 7: 1215-1218.

Ledbetter, J. O. 1972. Variation of pollutant concentration with

sampling time. Environmental Letters 3: 159-169.

Temporal fluctuations in air pollutants must be considered when planning sampling schedules, or the resulting errors may be considerably larger than errors in the sampling and analytical methods. E.

Leivestad, H., and I. Pl Muniz. 1974. Fiskedøk ved lav pH. SNSF-project. TN 4/74. 17 p.

Preliminary results using a new technique to measure Na, Cl, pH and HCO_3 in fish blood indicate that the blood of acid-stressed fish has abnormal levels of these components. N.

Likens, G. E. 1972. The chemistry of precipitation in the central Finger Lakes region. Cornell University Water Resources and Marine Science Center, Ithaca, NY, Tech. Rept. 50. 47 p.

Precipitation chemistry data at 5 stations in upstate NY 1970-71 show that the atmosphere is an important source of nutrients for ecosystems and that precipitation is often highly polluted with acid compounds of sulfur and nitrogen that originate from combustion of fossil fuels in the industrial areas of the north-central US.

Likens, G. E., and F. H. Bormann. 1974. Acid rain: A serious regional environmental problem. Science 184: 1176-1179.

Rain with an average annual acidity of pH 4 falls on most of the northeastern US. The acidity has increased during the past 30 years due to different fuel uses and emissions. Little is known about the ecological and economic effects of this acid rain. E.

Likens, G. E., F. H. Bormann, and N. M. Johnson. 1972. Acid rain. Environment 14: 33-40.

This is an introduction to the acid-rain phenomenon in North America, and especially the potential impacts on whole ecosystems, both terrestrial and aquatic. E.

Lillehammer, A. 1974. Norwegian stoneflies. II. Distribution and relationship to the environment. Norsk ent. Tidsskr. 21: 195-250.

This report discusses the stonefly distributions in terms of dispersion and various environmental factors. No chemistry data

are included. E.

Little, P., and M. H. Martin. 1974. Biological monitoring of heavy metal pollution, Environ. Pollut. 6: 1-19.

Using *Sphagnum* moss suspended in nylon nets the deposition of heavy metals from the atmosphere can be measured. This technique was used to measure the Zn, Pb and Cd deposition around a smelter in southern England. E.

Lloyd, R., and D. H. M. Jordan. 1964. Some factors affecting the resistance of rainbow trout (*Salmo gairdnerii* Richardson) to acid water. Int. J. Air Wat. Poll. 8: 393-403.

The resistance to short term exposure to acid waters was unaffected by the acclimatization pH but was increased with increased water hardness. The acid appears to affect the maintenance of buffer capacity in blood, and death was apparently due to acidaemia. Extrapolation of the results suggests that exposure to pH 5.0 waters for 3 months is harmful. E.

Lunde, G., and J. Gether. 1974. Analyse av organiske mikroforurensninger i nedbør. SNSF-project. IR 4/74. 86 p.

A gas chromatograph-mass spectrometer technique for the separation and identification of trace amounts of organic pollutants in precipitation is presented. Measurements of 5 samples showed differences in concentrations and composition of organic micropollutants present in polluted and unpolluted precipitation in Norway. N.

Malmer, N. 1974. Förslag till forskningsprogram över "Försurningens effekter" för budgetåren 1974/75 - 1977/78. Avd. för Ekologisk Botanik, Lunds Universitetet, Sweden. Unpubl. report. 10 p.

This research proposal describes Malmer's plans for acid-precipitation research, 1974-1978. He proposes to undertake broad studies on freshwater, forest and land ecosystems. S.

Matveev, A. A. 1970. Chemical hydrology of regions of East Antarctica. J. Geophys. Res. 75: 3686-3696.

The chemistry of precipitation, snow, and ice is strongly dominated by marine constituents with admixture of some continental material, especially sulfur. E.

McKim, J. M., G. M. Cristens, J. H. Tucker, and M. T. Lewis. 1973. Effects of pollution on freshwater fish. J. Water Poll. Cont. Fed. 45: 1370-1407.

This literature review discusses the effects of all types of pollution on freshwater fish, including heavy metals, pesticides, O_2-depletion, salinity, organic chemicals, radioactive isotopes, and pH. E.

Mellquist, P. 1972. Statistisk analyse av pH-data fra Sira-Kvina-vassdragene. Norges vassdrags - og elektrisitetsvesen VN Rapport 1-72. 10 p.

Extensive statistical treatment of pH, hardness and specific conductance data for 1965-70 from several water sources in southernmost Norway failed to show significant differences between regulated and unregulated water bodies. N.

Michelski, M. F. P., and J. Adamski. 1974. Restoration of acidified lakes Middle and Lohi in the Sudbury area, p. 163-175. In Ontario Industrial Wastes Conferences 1974.

Addition of $CaCO_3$ and $Ca(OH)_2$ to two acid lakes resulted in elevation of pH, decrease in concentration of heavy metals, and a decrease in chlorophyll a concentrations. The latter is probably a short-term effect due to flocculation and precipitation. E.

Miljøverndepartementet. 1974. Internasjonale tiltak for bekjempelse av sur nedbør. Miljøverndepartementet informerer i sept.

This report describes various international efforts to document the SO_2 emissions and transport (OECD project), and to negotiate reductions in SO_2 emissions. N.

Miller, J. M., and R. G. de Pene. 1972. Contribution of scavenged sulfur dioxide to the sulfate content of rain water. J. Geophys. Res. 77: 5905-5915.

Experiments show that SO_4 is readily formed in rain drops in the presence of SO_2 (polluted atmosphere). Furthermore, the sulfate content of rainwater reflects particle washout rather than gaseous washout. In the presence of NH_3 and SO_2 particles of cloud-nucleus size are produced. E.

Mrose, H. 1966. Measurements of pH, and chemical analyses of rain-, snow-, and fog-water, Tellus 18: 266-270.

Analysis of 200 precipitation samples collected 1957-64 at Dresden, East Germany, showed that the acidity (pH 4.5) did not change significantly over this period, while precipitation in West Germany and elsewhere in western Europe is increasing in acidity. This difference is perhaps due to changes in fuel use. Some data on the radioactivity of fog and rain are presented. E.

Muller, E. F., and J. R. Kramer. 1974. Precipitation scavenging in Central and Northern Ontario. Ministry of Environment, Ontario, Canada. Unpubl. report. 11 p.

The deposition of SO_4, Fe, Ni and Cu in Ontario is related to the distance from the Sudbury smelter and was altered after installation of the 381-meter stack. E.

Nordø, J. 1973. Meso-scale and large-scale transport of air pollutants. In Proc. 3rd Int. Clean Air Congress, Düsseldorf. B 105-107.

For several "episodes" the trajectories and concentrations of pollutants in air masses are measured and found to fit a theoretical model of mixing and transport in the atmosphere. E.

Nordö, J. 1974. Quantitive estimates of long range transport of sulphur pollutants in Europe. Annalen der Meteorologie (N.F.), Nr. 9: 71-77.

Using the continuity equation the long-range transport of sulfur can be estimated knowing the emission and wind field. Application of several models shows that calculated deposition rates are within a factor of two of the measured rates. E.

Nordö, J., and K. Hjortnæs. 1967. Statistical studies of precipitation on local, national and continental scales. *Geophysica Norvegica* 26 (12): 1-46.

A statistical analysis of Norwegian precipitation data indicates that orographic release of precipitation is dominent at time scales ranging from 12 hours to 1 month. E.

Novakov, T., S. G. Chang, and A. B. Harker. 1974. Sulfates as pollution particulates: Catalytic formation on carbon (soot) particles. Science 186: 259-261.

Laboratory experiments show that SO_2 is readily oxidized to SO_4 in the presence of soot, and that this mechanism is consistent with field observations. E.

Odén, S. 1968. Nederbördens och luftens försurning - Dess orsaker, förlopp och verkan i olika miljöer. Statens Naturvetenskapliga Forskningsråd, Stockholm, Ekologikommitten, Bull. No. 1. 86 p.

Odéns thorough summary of the acid-rain problem includes a discussion of the European precipitation-chemistry data (1954-1965), the survey of Scandinavian rivers and lakes, and the observed and anticipated effects on aquatic and terrestrial ecosystems. S (E summary).

Odén, S. 1969. Regionale aspekter på miljöstörningar. Vann 3: 93-111.

This is another overview of the increasing acidity, SO_4, and NO_3 contents of precipitation in Scandinavia and the effects on soils, forests, and freshwaters. S.

Odén, S. 1971a. Nederbördens försurning - ett generellt hot mot ekosystemen. In Forurensning og biologisk miljøvern. 63-98.

This overview of acid precipitation and its effects on terrestrial and aquatic ecosystems in Scandinavia is similar to Oden (1968). S.

Odén, S. 1971b. The general eutrophication of the environment. 1. Phosphorous. Dept. of Soil Science, Agricultural College, Uppsala, Sweden. Unpubl. report. 16 p.

Phosphorus concentrations in precipitation and in bog profiles indicate that the atmospheric deposition of P has dramatically increased due to man's activities with the subsequent enrichment of P-poor bog, lake and forest ecosystems. E.

Odén, S. 1972. The extent and effects of atmospheric pollution on soils. FAO Soils Bull. 16: 179-194.

The chemical climate of Europe is changing rapidly (acidity, S, N, chlorinated hydrocarbons), and the effects on soils, forests, and fresh-waters in Scandinavia are large and potentially dramatic. E.

Odén, S. 1973. Markförsurning på grund av kvävelgödsling och atmosfäriskt nedfall av ammonium. Agricultural College, Dept. Soil Science, Uppsala, Sweden. Unpubl. report. 10 p.

The application of N-fertilizers (esp. NH_4) results in soil acidification, especially if nitrification proceeds. In addition the sizeable deposition of atmospheric NH_4^+ further acidifies the soil, and the result is a major CaO-deficit. S.

Odén, S., T. Ahl. 1970. Forsurningen av skandinaviske vatten. Ymer, Årsbok: 103-122.

Over 10 years of chemistry data from lakes and rivers in Scandinavia show a long-term decrease in pH in waters over large areas of southern Norway and Sweden. S (E summary).

Odén, S., and T. Ahl. 1974. The longterm changes in the pH of lakes and rivers in Sweden. Unpubl. report. 13 p.

Monthly data from 15 rivers in Sweden show that the pH is declining by about 0.25 units/year over the period 1965-69. These trends, if they continue, indicate that the pH will reach biologically critical levels in 30-50 years. This paper refers to section 5.2 of Sweden's case study for the UN Conf. on Human Environment (see Bolin et al. 1971). E.

Odén, S., and R. Andersson. 1974. The long-term changes in the chemistry of soils in Scandinavia due to acid precipitation. Unpubl. manuscript.

This paper refers to section 5.6 of Bolin et al. (1971), Sweden's case study. E.

Odén, S. and J. Bergholm. 1971. The chemistry of snow. 1. Ionic separation during melting. Dept. of Soil Science, Agricultural College, Uppsala, Sweden. Unpubl. manuscript.

The first meltwater from snow is considerably enriched in all major ions relative to the bulk snow. E.

OECD Environment Directorate. 1973. Survey on regional sulphur dioxide emission. Air management sector group, Org. for Economic Cooperation and Development, Paris. 79 p.

This restricted document lists SO_2 emissions by country and type of industry. E.

Økland, J. 1969a. Om forsuring av vassdrag og betydningen av surhetsgraden (pH) for fiskens næringsdyr i ferskvann. Fauna 22: 140-147.

Acidification of lake waters in Norway results in adverse affects to fish-food organisms such as *Gammarus lacustris* at pH levels above those found directly harmful to fish. Since lakes in large areas of southern Norway are characterized by very low buffer

capacities large areas already may be adversely affected by acid precipitation. N (E summary).

Økland, J. 1969b. Distribution and ecology of the freshwater snails *(Gastropoda)* of Norway. Malacologia 9: 143-151.

This is a preliminary report on the distribution, ecology, and morphology of snails in Norway from 1350 sites. These data are discussed in terms of immigration patterns and modern environmental factors such as pH and total hardness. E.

Økland, K. A. 1969a. On the distribution and ecology of *Gammarus lacustris* G. O. Sars in Norway with notes on its morphology and biology. Norweg. J. Zool. 17. English version of Økland (1970) E.

Økland, K. A. 1969b. List of localities with *Gammarus lacustris* G. O. Sars in Norway with references and notes. Supplement to Contribution No. 89, Zoolog. Mus. Univ. of Oslo. 36 p.

This is the raw data for Økland 1969a and Økland 1970. Only the sites where *Gammarus* was found are listed, and no chemical data are included. E.

Økland, K. A. 1970. Undersøkelser over marfloen *Gammarus lacustris* - ørretens viktigste næringsdyr. Fauna 23: 1-11.

The distribution of *Gammarus lacustris* from 542 localities in Norway is presented. No finds are reported from waters with pH less than 5.9. N (E summary).

Økland, K. A. 1971. On the ecology of *Sphaeriidre* in a high mountain area in south Norway. Norweg. J. Zool. 19.

Overrein, L. N. 1972a. Sulfur pollution patterns observed: leaching of calcium in forest soil determined. Ambio 1: 145-147.

The deposition pattern of pollutants (H^+, Ca, Mg, Fe, Mn, K, Na, SO_4) originating from a major local source in southern Norway is reported, and the effect of H^+ on soil chemistry (esp. washout of Ca) is discussed. E.

Overrein, L. N. 1972b. Forsuring av jordbunnen. Fysiske, kjemiske og biokjemiske forhold. Vann 1: 1-5.

This is a general discussion similar to Overrein (1972a) N.

Overrein, L. N. 1974a. Luftforurensning - Virkning på skog- og fjellnaturen. Proc. Nordisk Hydrologisk Konference, Copenhagen: 479-487.

An overview of the SNSF-project and its goals is presented. N.

Overrein, L. N. 1974b. Årsberetning 1973. SNSF-project. 31 p.

The 1973 annual report of the SNSF-project describes current research on the effects of acid precipitation on forest and aquatic ecosystems. During 1973 over 30 scientists were engaged in the project with a budget of 3.6 million Norwegian kroner. N.

Ottar, B. 1972. Säure Niederschläge in Skandinavien. Umschau 72: 290-291.

The acidity of precipitation in Scandinavia is increasing and causing reduction of fish populations and, possibly, forest growth. The acid rain is due to the transport of industrial pollutants from central Europe and Great Britain. G.

Ottar, B. 1973. The long range transport of air pollutants. In Proc. 3rd Int. Clean Air Congress, Düsseldorf. B 102-104.

The establishment of the OECD project "Longe range transport of air pollutants" is described including some preliminary results from the sulfur-emission survey and deposition measurements. E.

Ottar, B., and A. Semb. 1973. The OECD-Project, Cooperative technical programme to measure the long range transport of air pollutants. Norwegian Inst. for Air Research, Kjeller. 78 p.

This restricted report describes the establishment of the OECD project, some preliminary air-mass trajectory calculations, the application of such calculations to several "episodes" and the compilation of the SO_2-emission grid for Europe. E.

Ottar, B., and A. Semb. 1974. Transport av luftforurensninger over landegrensene. Vann 2: 77-82.

The Organization for Economic Cooperation and Development (OECD) project "LDTAP" (Long Distance Transport of Air Pollutants) was established in 1972 and involves daily measurements of air and

precipitation-chemistry at stations throughout NW Europe. This network provides base data for calculating the dispersal and transport of air pollutants. N.

Packer, R. K., and W. A. Dunson. 1970. Effects of low environmental pH on blood pH and sodium balance of brook trout. J. Exp. Zool. 174: 65-72.

Trout from acid streams in Pennsylvania (acid mine drainage) show drop in blood pH and increase in Na efflux at pH 3.5. The former appears to explain the inability of trout to live in waters with pH less than 5. E.

Packer, R. K., and W. A. Dunson. 1972. Anoxia and sodium loss associated with the death of brook trout at low pH. Comp. Biochem. Physio. 41A: 17-26.

The lethal effect of HCl, H_2SO_4, and mine acid (pH 2.0-3.25) appears to be due to inhibition of O_2 uptake and to a large increase in Na loss. The mechanism of the lethal effect may be Na loss, especially at pH 3.25 and above. E.

Peirson, D. H., P. A. Cawse, and R. S. Cambray. 1974. Chemical uniformity of airborne particulate materials, and a maritime effect. Nature 251: 675-679.

The concentrations of 30 elements in airborne dust, rainwater, and dry deposition were measured at 12 stations in or near the British Isles during 1972-73. By comparing the elemental concentrations to Sc, the elements can be grouped according to maritime, soil-derived, or anthropogenic sources. The surface of the North Sea is enriched relative to bulk seawater. E.

Persson, G. 1969. The acidity and the concentration of sulphate in precipitation over Europe. Statens Naturvårdsverk, Stockholm. 4p.

Using data from the European precipitation-chemistry network the long-term trends of acidity and sulfate are calculated. While there have been overall increases in Scandinavia and central Europe, no such trend is seen in the data for the British Isles. E.

Ravera, O. 1973. Lead pollution in air and water. In Proc. Symp. Eur. Fed. Protection Wat., Finland. 13 p.

Man's activities have introduced enormous amounts of Pb into the environment, and Pb enrichment is evident in glaciers, seawater,

and terrestrial and aquatic ecosystems. The levels may reach toxicity thresholds and long-term effects may be forthcoming. E.

Rohde, G. 1974. Hazardous heavy metals: Cadmium, mercury, lead and arsenic. WHO Intern. Ref. Cent. for Wastes Disposal, Dübendorf, Switzerland, News No. 6: 1-6.

Toxic heavy-metals present the greatest hazard to man when they are present in the air, for absorbtion is much higher in the respiratory system than in the alimentary tract. The soil-plant system also acts to reduce the danger of heavy-metal pollution through food. E.

Rohde, H. 1970. On the residence time of antropogenic sulfur in atmosphere. Tellus 22: 137-139.

Using data on the S concentration in snow collected near Uppsala, Sweden, the minimum residence time for anthropogenic sulfur is estimated to be 3-5 hours. E.

Rohde, H. 1972. A study of the sulphur budget for the atmosphere over Northern Europe. Tellus 24: 128-138.

q Using OECD data for SO_2 emissions in Europe and the precipitation chemistry data from the European network, the sulfur budget is calculated for northern Europe. This calculation shows that sulfur dispersion has a continental character and that the turnover time for anthropogenic sulfur is 2-4 days. E.

Rohde, H., and J. Grandell. 1972. On the removal time of aerosol particles from the atmosphere by precipitation scavenging. Tellus 24: 442-454.

An estimated turnover time for atmospheric aerosols of 35-80 hours in winter and 100-300 hours in summer was calculated using data from a Swedish precipitation station. Only 10% of particles are thus deposited within 100 km of the source, and because precipitation scavenging of SO_2 is even less efficient, the local dqposition of gaseous S would be less. E.

Rossby, C. G., and H. Egnér. 1955. On the chemical climate and its variation with the atmospheric circulation pattern. Tellus 7: 118-133.

Isopleth maps for Na, Cl, S, and pH based on data from the European precipitation chemistry network show that the deposition of these

elements depends on the origin and history of air masses over northern Europe. Deposition patterns for S and H^+ are related to combustion of fossil fuels. E.

Rühling, Å., and G. Tyler. 1971. Regional differences in the deposition of heavy metals over Scandinavia. J. Applied Ecology 8: 497-507.

The concentrations of several heavy-metals in mosses are much higher in southern than in northern Scandinavia. The only plausible explanation is that these metals are deposited in greater amounts in southern Scandinavia due to the proximity of large industrial areas. E.

Ruehling, A., and G. Tyler. 1973. Heavy metal deposition in Scandinavia. Water, air, and soil pollution 2: 445-455.

By analyzing the concentration of Pb, Cl, Hg, Cr, Ni, Cu, Zn and Fe in mosses, maps showing the relative deposition rates of these elements in Scandinavia were prepared. Southern Norway and Sweden show the highest concentrations, especially of Pb and Cd. E.

Särkkä, M. 1972. The washing out of nutrients in the watersheds. Aqua Fennica 1972: 88-103.

Data from 34 small gauged-watersheds collected during 1962-68 show that the loss of nutrients from Finland is small relative to other more fertile areas of the world, is dependent on fluctuations in runoff, and is related to land-use (esp. N washout). E.

Schjoldager, J. 1973a. Svovelforurensninger i luft og nedbør ved norske bakgrunnsstasjoner. Døgnmålinger nov. 1971-juni 1972. NILU TN 52/73. 79 p.

As part of the OECD project, daily measurements of air and precipitation were made at 23 stations in Norway. Results from the first half of 1972 show that the greatest deposition of sulfur occurs on the southwestern coast and that most of this sulfur is deposited during a few episodes, which are clearly related to meteorologic parameters. N.

Schjoldager, J. 1973b. Svovelforurensninger i luft og nedbør ved norske bakgrunnsstasjoner. Døgnmålinger 2. halvår 1972. NILU TN 65/73. 60 p.

Same as Schjoldager 1973a but for the first half of 1972.

Schlesinger, W. H., W. A. Reiners, and D. S. Knopman. 1974. Heavy metal concentrations and deposition in bulk precipitation in montane ecosystems of New Hampshire, USA. Environ. Pollut. 6: 39-47.

Measurements of Pb, Hg, and Cd during 4 months of 1971 showed that Pb deposition is high, probably because of major upwind industrial areas. These measurements underestimate the total deposition because cloud water condensation and aerosol impaction are not accounted for. E.

Schroeder, H. A. 1971. Metals in the air. Environment 13: 18-32.

The concentrations of 25 trace metals were measured in the US atmosphere. Eight of these are toxic, and four represent known hazards to man (Ni, Cd, Pb, Hg). High levels of these in the atmosphere can be reduced by readily-available abatement measures. E.

Seleyneva, E. S. 1972. Estimation of the background contamination of the atmosphere from the chemical composition of precipitation. Tellus 24: 122-127.

Precipitation chemistry measured during the 1960's at over 40 stations throughout the USSR show clearly that precipitation is a mixture of marine and terrestrial components. The sulfur content over continental areas is 30-40% natural background and the remaining 60-70% a mixture of local sources, both natural and anthropogenic. In polluted areas there is twice as much excess sulfate as background sulfate. Globally about 10% of the sulfur in precipitation is anthropogenic. E.

Shaw, R. W., and D. M. Whelpdale. 1973. Sulfate deposition by precipitation into Lake Ontario. Water, Air and Soil Pollution 2: 125-128.

Individual snow storms may deposit many times more sulfate than the average daily deposition, and the atmospheric contribution of sulfate to Lake Ontario is as important as industrial effluents. E.

Shukla, S. S., and H. V. Leland. 1973. Heavy metals: A review of lead. J. Water Poll. Cont. Fed. 45: 1319-1331.

This literature review covers all aspects of Pb pollution with references from all continents. E.

Sivertsen, A., and E. Snekvik. 1973. Avsyring av Sandvatn og

Lauvtjønna ved kalking, og ny forsurning med tiden (1967-1973). Direktoratet for jakt, vilt of ferskvannsfisk. Unpubl. report. 61 p.

The pH in 2 small, acid lakes in southern Norway was raised by adding lime, but due to continued inputs of acid from precipitation and runoff, the pH gradually declined once again. N.

Sivertsen, A., and E. Snekvik. 1975. Kjemiske forhold ved vannet i elver i Rogaland, Agderfylkene og Telemark m.m. i 1974. Samlerapport nr. 7 over "Sørlandselver" og referanseelver i andre landsdeler. Direktoratet for vilt og ferskvannsfisk, Norway. Unpubl. report. 54 p.

This is the raw data for pH, hardness and specific conductance in monthly or weekly samples of rivers in southernmost Norway and reference rivers in northern Norway. N.

Skogvold, O. F. 1974. Vi får enorme mengder svovelsyre luftveien fra utlandet. Tekn. Ukebl. 121 (17): 21-24.

The SO_2 emissions in Europe are presented and compared with Norwegian sources. N.

Small, S. H. 1960. Wet and dry deposition of fallout materials at Kjeller. Tellus 12: 308-314.

Measurement of radioactive fallout near Oslo during 1956-59 shows that wet and dry deposition and surface-air activity are all interrelated. E.

Snekvik, E. 1969a. Rapport nr. 2: Forsøk med klekking av yngel ved forskjellig pH og overføringsforsøk av rogn til vann med høyere pH og av yngel til vann med lavere pH. Direktoratet for jakt, vilt og ferskvannsfisk. Unpubl. report. 27 p.

Various fish-hatching experiments showed that the critical pH-level for salmon eggs is about 5.0, but that the success is also dependent on total hardness. N. (See Bua and Shekvik 1972).

Snekvik, E. 1969b. Klekkeforsøk 1968/69. Direktoratet for jakt, vilt og ferskvannsfisk. Unpubl. report. 6 p.

Fish-hatching experiments indicate that success is strongly pH-dependent and that various species exhibit varying tolerance to low-pH water. N.

Snekvik, E. 1969c. Forsurning av elver og vann - Innvirkning på ørret- og laksefisket. Vann No. 3: 113-119.

Snekvik describes the increasing acidity of rivers and lakes in southernmost Norway and traces the history of the effects on fish. N.

Snekvik, E. 1969d. Rapport over fiskedød. Direktoratet for vilt og ferskvannsfisk, Norway. Unpubl. report. 9 p.

The fish kills observed in Rogaland and Sørlandet are probably due to high acidity. N.

Snekvik, E. 1970. Rapport fra Telemark. Direktoratet for vilt og ferskvannsfisk. Unpubl. report. 4 p.

Thirty years of pH and fish data from 12 acid lakes in southern Norway are presented. N.

Snekvik, E. 1972. Forsurning av vassdrag i våre sydligste landsdeler. Vann 1: 1-9.

Snekvik discusses 50 years of records concerning pH from lakes and rivers in southernmost Norway. N.

Snekvik, E. 1974a. Audna som fremtidig lakselv - botemidler mot forsurningen. Direktoratet for vilt og ferskvannsfiske, Norway. Unpubl. report. 7 p.

The acidity in Audna river might be counteracted by the use of limestone or even seawater. N.

Snekvik, E. 1974b. Om surt vann og ferskvannsfisk. Klipp fra fiskeriinspektørens årsmeldinger i årene 1915-1961. Direktoratet for jakt, vilt og ferskvannsfisk. Unpubl. report. 22 p.

Snekvik, E. 1974c. Sure innsjøer og fiskebestand. Rapport nr. 2. Rogaland-Agder-Telemark. Direktoratet for Vilt og Ferskvannsfisk, Norway. 50 p.

The raw data on the fish status in 2800 lakes in 67 communities of Rogaland-Agder-Telemark are given. Over 1000 now have no fish, and these lakes generally also have pH less than 5. (See Jensen (1972) for N summary and Jensen and Snekvik (1972) for E summary). N.

Snekvik, E. 1975. Generelt om avsyring av sure vassdrag. Direktoratet for jakt, vilt of ferskvannsfisk. Unpubl. report. 7 p.

To neutralize the deposition of acid in southernmost Norway at least 200,000 tons of calcium carbonate per year would be required. N.

Snekvik, E., A. R. Selmer-Olsen, A. Njøs, and R. Bærug. 1973. Undersøkelser av nedbør fra ulike steder i Norge i årene 1965-71. Melding fra Norges Landbrukshøgskole 52 (13): 1-19.

Chemistry of irregularly collected samples of precipitation is reported, and the data subjected to various regression analyses. Conclusions are that pH is decreasing and that Zn, pH and SO_4 are good pollution indicators. E (N summary).

Snekvik, E., and A. Sivertsen. 1975. Diagrammer fra pH og total hårdhet. Elveserie fra det sydligste Norge med referanseelver i andre landsdeler, for perioden 1926 til og med 1974. Direktoratet for vilt og ferskvannsfisk. Unpubl. report. 41 p.

Data for pH and total hardness from monthly samples of 29 rivers in southernmost Norway and 4 reference streams in northern Norway are plotted. Some early data from 1926-45 are also given. N.

Sorokin, C. 1962. Carbon dioxide and bicarbonate in cell division. Archiv für Mikrobiol. 44: 219-227.

Experiments with the green alga, *Chlorella*, show that cell division proceeds best at pH 6.5-7.5, probably because of the inhibitory effect of dissolved, undissociated CO_2. E.

Stokes, P. M., T. C. Hutchinson, and K. Krauter. 1973. Heavy metal tolerance in algae isolated from polluted lakes near the Sudbury, Ontario, smelters. Wat. Poll. Research in Canada 8: 177-202.

The phytoplankton flora is impoverished in species and numbers in acidic lakes that have high concentrations of Cu and Ni. Experiments show that species isolated from these lakes are able to survive and grow at levels of Cu, Ni and Ag above those toxic to laboratory strains. Thus a metal-tolerance mechanism rather than exclusion seems to govern the algal populations in these polluted lakes. E.

Strøm, K. Münster. 1926. The influence of altered H-ion concentrations

on *Stentor, Diaptomus* and *Daphnia*. Nyt. Magazin for Naturvidenskapene 64: 109-115.

Experiments conducted over pH 6.6-8.0 showed that *Stentor* was only slightly affected by pH variations while *Diaptomus gracilis* and *Daphnia pulex* preferred slightly acid and slightly alkaline waters, respectively. E.

Strømsøe, S. 1971. Air Pollution from fuel combustion in stationary sources. NILU TN 11/71. 32 p.

This report itemizes the emissions of NO_2, SO_2 and particulates from fossil-fuel consumption in Norway and attempts to estimate future trends. E.

Stumm, W. 1973. Zivilisatorische Aktivität, Luftverunreinigung und Gewässerbelastung. In Proc. Symp. Eur. Fed. Protection Wat., Finland. 7 p.

Due to man's activities a great many elements, in particular heavy metals, are enriched in rain relative to seawater and/or the crust. As a result of man's use of energy and materials, degradation of natural systems is unavoidable. G.

Sunde, S. E. 1926. Surt vand dræper laks- og ørretyngel. Norges Jeger- og Fiskeforb. Tidsskrift No. 2: 1-4.

This early report describes fish kills, apparently due to acid water, at hatcheries in southern Norway and the attempts to raise the pH by adding lime. N.

Sutcliffe, D. W., and T. R. Carrick. 1973a. Studies on mountain streams in the English Lake District. 1. pH, calcium and the distribution of invertebrates in the River Duddon. Freshwat. Biol. 3: 437-462.

There are three types of pH regimes in the River Duddon and its tributaries; pH constant and above 5.7, pH constant and below 5.7, and pH fluctuating seasonally about 5.7. The latter regime is characteristic of tributaries in the headwaters. The benthic fauna is closely related to pH, and pH-bicarbonate limits the distribution of benthic invertebrates, generally herbivores. The limiting effects on insects may operate through the food supply. E.

Sutcliffe, D. W., and T. R. Carrick. 1973b. Studies on mountain streams in the English Lake District. II. Aspects of water

chemistry in the River Duddon. Freshwat. Biol. 3: 543-560.

Budgets for Na, K and Ca are calculated for a watershed. Na and K concentrations in stream water are independent of discharge but show a cycle of high concentrations in winter and low concentrations in summer. Some of the tributaries in the watershed are acid (pH 4.5). E.

Sutcliffe, D. W., and T. R. Carrick. 1973c. Studies on mountain streams in the English Lake District. III. Aspects of water chemistry in Brownrigg Well, Whelpside Ghyll. Freshwat. Biol. 3: 561-568.

Although the pH in Brownrigg Well is above 5.7, the concentrations of Na, K, and perhaps Ca are near the lower limit for *Gammarus pulex*. The distribution of most other insect taxa is governed by pH, and these insects probably were more widely distributed prior to the acidification of streams by acid precipitation. E.

Swynnerton, G. H., and E. B. Worthington. 1939. Brown-trout growth in the Lake District. A study of the conditions in "acid" lakes and tarns. Salmon and Trout Mag. 97: 337-354.

The growth rate of trout taken from lakes and ponds of the English Lake District was determined by measuring the annual increments on fish scales. The growth rate is affected by food supply and population pressure, as well as by chemical factors such as pH and alkalinity. E.

Tamm, C. O. 1972. Measuring disturbances of nutrient circulation in ecosystems. IBP i Norden (No. 9): 189-201.

Using tree-ring widths, local and regional changes in growth can be investigated and related to nutritional disturbances such as forest fertilization and soil acidification. E.

Tamm, C. O., and A. Aronsson. 1972. Plant growth as affected by sulphur compounds in polluted atmosphere. A literature survey. Research Note 12. Royal College of Forestry. Dept. Forest Ecology and Forest Soils, Stockholm. 53 p.

This literature review discusses the effects of SO_2 on lichens, forests, and agricultural crops, including the mechanisms of injury, symptoms and physiological pathways. E.

Tamm, C. O., Å. Nilsson, and G. Wiklander. 1974. The optimum nutrition

experiment Lisselbo. A brief description of an experiment in a young stand of Scots pine (*Pinus silvestris L*), Royal College of Forestry, Dept. of Forest Ecol. and Soils, Stockholm. Research Note No. 18. 23 p.

Among several forest fertilization experiments several stands were subjected to changes in soil acidity. None of the treatments has produced a significant change in growth rate after 2-3 years. E.

Thornton, K., and J. Wilhelm. 1974. The effects of pH, phenol, and sodium chloride on survival and caloric, lipid and nitrogen content of a laboratory population of *Chironomus attenuatus* (Walk). Hydrobiologia 45: 261-280.

pH had a significant effect on the survival of *C. attenuatus*. E.

Torgersen, H. 1934. Forsøk med opparbeidelse av sure fisketomme vann. Stangfiskeren. Oslo Sportsfiskeres Årbok: 38-46.

This is a description of an early attempt to combat acid-waters by adding lime. N.

Ulbrich-Eberius, C. J. 1973. Die pH-Abhängigkeit der Aufnahme von $H_2PO_4^-$, SO_4^{2-}, Na und K^+ und ihre gegenseitige Beeinflussung bei *Ankistrodesmus braunii*. Planta 109: 161-176.

Phosphate uptake is maximum between pH 5.5-6.5, and is enhanced by Na (in the light) and Ca (in the dark).

Velds, C. A. 1974. Relation between emissions resulting from burning fossil fuels and pollution of surface and groundwater, p. 69-71. In H. E. Vogel (ed.) European Fed. Protection Waters, Zürich, Info. Bull. 21.

Based on the SO_2 emissions in the Netherlands the theoretical pH of precipitation is calculated assuming that all the SO_2 is deposited within the country. This calculated pH of 3.5 is much less than the measured pH values (lowest average for a station 4.7), thus implying that most of the SO_2 is exported. E (F summary).

Ward, R. C. 1971. Small Watershed Experiments. An appraisal of concepts and research developments. University of Hull. Occasional Papers in Geography No. 18. 254 p.

Small watersheds have been used all over the world as research tools for over 100 years. Ward summarizes the goals, techniques

and results of such studies in this survey of over 300 articles on this subject. E.

Watanabe, T., H. Kamijo, I. Morishita, T. Shinya, and K. Mashiko. 1973. Studies on the eutrophication of Lake Osoresan-ko, a remarkable inorganic acidotrophic lake in Japan. Ann. Rep. Noto Marine Lab. 13: 35-51.

This lake is acid (pH 3.0-3.2) because of the inflow of sulfuric acid from hot springs. Although the number of species of organisms in the lake is low, biotic productivity is high. The phytoplankton composition has altered since the 1930's, with a bloom of *Aphanotheca* observed in 1972-73. The bottom is covered with an aquatic moss, *Leptodictum* sp. to depths of 9 meters. Large numbers of the fish, *Tribolodon hakonesis* live in the lake, clearly able to tolerate waters as acid as pH 3.0, perhaps because of an unusual type of chloride cell in its gills. J (E summary).

Weiss, H. V., M. Koide, and E. D. Goldberg. 1971. Selenium and sulfur in a Greenland ice sheet: Relation to fossil fuel combustion. Science 172: 261-263.

Comparison of Se and S concentrations in an ice profile from Greenland indicate that while sulfur is translocated great distances after fossil-fuel combustion, selenium is mobilized to a much lesser extent, perhaps due to different chemical and physical properties of the tetravalent oxides. E.

White, E. J., and F. Turner. 1970. A method of estimating income of nutrients in a catch of airborne particles by a woodland canopy. Appl. Ecol. 7: 441-461.

By comparing throughfall water with rainwater, and using air-flow impactors to catch particulate matter, the amounts of plant nutrients (Na, K, Ca, Mg, P and N) that are deposited from the atmosphere by dry-fallout and impaction were estimated. E.

Whitehead, H. C., and J. H. Feth. 1964. Chemical composition of rain, dry fallout and bulk precipitation at Menlo Park, California, 1957-1959. J. Geophys. Res. 69: 3319-3333.

Samples collected during 1962-63 in California showed that dry fallout is mainly derived from local sources, rainwater is mainly of marine origin, and bulk precipitation is a mixture fo these two. E.

Whittaker, R. H., F. H. Bormann, G. E. Likens, and T. G. Siccama. 1974. The Hubbard Brook ecosystem study: Forest biomass and production. Ecol. Monogr. 44: 233-254.

A decrease in forest productivity may be due to increasing air pollution and acidic precipitation. E.

Wright, R. F., and C. Lysholm. 1975. Regional survey of lakes in southern Norway, fall 1974. Preliminary analysis of water-chemistry data. SNSF-project. IR 6/75. 24 p.

A systematic survey of 155 lakes showed that acidic precipitation has affected lakes in large areas of southernmost Norway. Because the bedrock and soils in these areas have very low calcium and magnesium contents, the lakes are poorly buffered and are particularly vulnerable to inputs of acidic precipitation. E (N summary).

CLASSIFICATION BY GEOGRAPHIC AREA

WORLD:

Berntine and Goldberg 1971
Bischof 1973
Chester and Stoner 1973a, 1973b
Eriksson 1952a, 1952b, 1959, 1960
Gorham 1961
Jernelöv 1973
Junge 1960
Ravera 1973
Stumm 1973
Ward 1971

EUROPE:

Ångström and Högberg 1952a
Block and Dams 1975
Bolin and Persson 1974
Borneff 1974
Brosset 1973a, 1973b
DeBary and Junge 1963
Descroix 1974
Egner 1955-60
EIFAC 1969
Eriksson 1954
Granat 1972
Kettner 1974
Mrose 1966
Nordø 1973, 1974
OECD 1973
Ottar 1973
Ottar and Semb 1973, 1974
Persson 1969
Rohde 1972
Rossby and Egner 1955
Seleyneva 1972
Velds 1974

SCANDINAVIA:

Barrett and Brodin 1955
Dahl and Skre 1971
Eriksson 1955, 1969
Goffeng 1973
Granat 1974
Holt-Jensen 1973
Oden 1968, 1969, 1971, 1972
Oden and Ahl 1970
Oden and Andersson 1974
Ottar 1972
Rühling and Tyler 1971, 1973

NORWAY:

Andersen 1966
Anon 1974a
Bjor et al. 1974
Braarud and Aalen 1939
Brække 1974a, 1974b, 1975
Brandt 1971
Bua and Snekvik 1972
Dahl, E. 1972
Dahl, E. et al. 1967
Dahl, K. 1920, 1922, 1923, 1926
Dale et al. 1974
Dannevig, A. 1959
Dannevig, G. 1966, 1968, 1970
Dannevig, G. et al. 1971
Dovland 1975
Dovland et al. 1974
Dovland and Semb 1975
Dugstad 1972
Dybdahl 1973
Elgmork et al. 1973
Fleetwood 1969
Førland 1973
Førland and Gjessing 1975
Førland et al. 1975
Fredriksen 1973
Furmyr 1973a, 1973b
Gjems 1970
Gjessing, E. 1974
Gjessing and Gjessing 1975
Grande 1966
Grøterud 1972a, 1972b, 1972c, 1973
Gunnerød 1973
Hagen and Norby 1967
Hagen and Langeland 1973
Haugboth 1973
Henriksen 1972a, 1972b
Henriksen et al. 1974

NORWAY (cont.)

Henriksen and Johannessen 1975
Holtan 1972
Horntvedt and Joranger 1974
Huge and Killingtveit 1973
Huitfeld-Kaas 1922
Jensen 1972
Jensen and Snekvik 1972
Kjos-Hanssen 1970
Låg 1963, 1968
Låg and Steinnes 1974
Leivestad and Muniz 1974
Lillehammer 1974
Lunde and Gether 1974
Mellquist 1972
Miljøverndepartementet 1974
Nordø and Hjortnaes 1967
Økland, J. 1969a, 1969b
Økland, K. 1969a, 1969b, 1970, 1971
Overrein 1972a, 1972b, 1974a, 1974b
Schjoldager 1973a, 1973b
Sivertsen and Snekvik 1975
Skogvold 1974
Small 1960
Snekvik 1969a, 1969b, 1969c, 1969d, 1970, 1972, 1974a, 1974b, 1974c
Snekvik et al. 1973
Snekvik and Sivertsen 1975
Strømsøe 1971
Sunde 1926
Torgersen 1934
Wright and Lysholm 1975

SWEDEN:

Ahl and Oden 1972
Almer 1972a, 1972b
Almer et al. 1974
Andersson, Gun and Grennfelt 1974
Andersson, Gunnar 1971
Andersson, Gunnar, et al. 1971
Ångström and Högberg 1952b
Anon 1972, 1974b
Berzins 1966
Bolin and Granat 1973
Bolin et al. 1971
Börjeson and Aldberg 1974
Brosset 1975
Brosset and Åkerström 1972
Brosset et al. 1974
Dickson 1971
Emanuelsson et al. 1954
Grahn and Hultberg 1974
Grahn et al. 1974
Hanson 1974
Högström
Hultberg and Stenson 1970
Jonsson and Sundberg 1972
Karlen 1972
Malmer 1974
Oden 1971, 1973
Oden and Ahl 1974
Rohde 1970
Rohde and Grandell 1972
Tamm et al. 1974

FINLAND:

Haapala 1972, 1974
Kohonen 1974
Laamanen 1972
Särkkä 1972

BRITISH ISLES:

Allen et al. 1968
Aston et al. 1973
Brownscombe 1972
Cambray et al. 1975
Cawse 1974
Cawse and Peirson 1972
Gilbert 1970
Gore 1968
Gorham 1955, 1958
Griffiths 1973a, 1973b
Hallsworth and Adams 1973
Little and Martin 1974
Peirson et al. 1974
Sutcliffe and Carrick 1973a, 1973b, 1973c
Swynnerton and Worthington 1973
White and Turner 1970

NORTH AMERICA:

Chapin and Uttormark 1973
Likens et al. 1972

CANADA:

Beamish 1974
Beamish and Harvey 1972
Beamish et al. 1975
Conroy et al. 1974
Conroy and Maki 1974
Herman and Gorham 1957
Hutchinson and Whitby 1974
Kramer 1973a, 1973b
Kramer and Snyder 1974
Michelski and Adamski 1974
Muller and Kramer 1974
Shaw and Whelpdale 1973
Stokes et al. 1973

UNITED STATES:

Bormann 1974
Cogbill and Likens 1975
Delany et al. 1973
Dunson and Martin 1973
Gambell 1962
Gambell and Fisher 1964
Junge 1956
Junge and Gustafson 1957
Junge and Werby 1958
Katz 1968
Laney 1965
Larson, T.E., and Hettick 1956
Larson, T.V. et al. 1975
Likens 1972
Likens and Bormann 1974
Packer and Dunson 1970, 1972
Schlesinger et al. 1974
Schroeder 1971
Whitehead and Feth 1964

ANTARCTIC/ARCTIC:

Gjessing and Gjessing 1973
Jonasson 1973
Koide and Goldberg 1971a, 1971b
LeBarre 1973
Mateev 1970
Weiss et al. 1971

MISCELLANEOUS AND THEORETICAL:

Askne 1973
Askne and Brosset 1972
Beamish 1972
Bell 1971
Bell and Nebeker 1969
Biesinger and Christensen 1972
Bornefeld and Simonis 1974
Brosset 1973c, 1974
Carter 1964
Cook 1971
Costa 1966, 1967
Davis and Ozburn 1969
Dondoroff and Katz 1950
Hales and Sutter 1973
Harrison 1958
Jordan and Lloyd 1964
Kamijo et al. 1974
Katz et al. 1970
Katz and Oglesby 1967
Krishna 1953
Ledbetter 1972
Lloyd and Jordan 1964
McKim et al. 1973
Miller and dePene 1972
Novakov et al. 1974
Oden and Bergholm 1971
Rohde 1974
Shukla and Leland 1973
Sorokin 1962
Strøm 1926
Tamm 1972
Tamm and Aronsson 1972
Thornton and Wilhelm 1974
Ulbrich-Eberius 1973
Watanabe et al. 1973

ACID PRECIPITATION AND FOREST SOILS

Chairman, Garth K. Voigt

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ACID PRECIPITATION AND FOREST SOILS

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Many soil processes and properties may be affected by a change in chemical climate such as that caused by acidification of precipitation. The effect of additions of acid precipitation depends at first on the extent to which this acid is really absorbed by the soil and on the changes in substances with actual or potential acidity leaving the soil. There is for instance the possibility that added sulphur dioxide or sulphuric acid may leave the soil either as sulphate ions or as gaseous hydrogen sulphide. In the latter case there is no net acidification. Acidity due to uptake of nitrogen oxides or ammonia later transformed into nitrate results in a net acidification only if the nitrogen ultimately leaves the soils as nitrate. Leaching of ammonium ions or organic nitrogen does not acidify the soil, nor does loss of gaseous ammonia, nitrous oxide (N_2O), or gaseous nitrogen. It must be admitted that our present possibilities are rather small to make up a complete and correct nutrient balance for a site where both leaching and gaseous inputs and outputs are considered.

Once we have established the net uptake of acidifying substances, the impact on the soil depends very much on the soil properties, particularly the total amount of exchangeable cations in the soil and the proportion of those cations which are other than hydrogen ions. A soil with a high proportion of calcium, magnesium, potassium or other basic cations among its exchangeable ions (a high base saturation) is affected differently from a soil with mainly hydrogen ions among the exchangeable cations. The degree of base saturation is well correlated with the acidity of the soil, meaning that on the average a soil with a low base saturation is acid and a soil with a high base saturation neutral to alkaline. An input of more hydrogen ions to an already acid soil means a relatively small change. In a soil with a higher base saturation the input of the same amount of hydrogen ions may seem large in comparison with the soil's own concentration of hydrogen ions, but such soils usually have high buffer capacities and often also large cation exchange capacities. Therefore the hydrogen ions are rapidly absorbed to the colloids in exchange for calcium, magnesium or other basic cations and the changes in the soil solution remain small. However, some slightly acid soils may have a low exchange capacity and a low buffer capacity. Such soils may well be sensitive to atmospheric input of acids (Malmer, 1974; Wiklander, 1974).

At commonly occurring pH-values soil colloids are usually negatively charged and surrounded by cations including hydrogen ions. Different colloids may well have different affinities for various types of ions. The affinity for hydrogen ions may be measured as the strength of the substance in question as an acid but there may also be specific bindings of certain ions in the soil for instance as chelates. The affinity of the soil colloids for different ions is pH dependent and has thus to be taken into account in a discussion of changes in soil acidity. The titration curve for various types of soil colloids, organic as well as inorganic (clay), may be rather different (Wiklander, 1974).

We also have to take into consideration that soils are differentiated vertically in horizons. This differentiation is closely connected with the movement of water in the soil profile and of substances dissolved in that water. In acid soils for instance, organic acids are produced in the humus layer and leached down to a certain depth in the soil where they may be partly destroyed by microbiological processes. Also clay particles may move vertically. Very often minerals weather more intensively in the upper more acid horizons than further down and some of the weathering products may be moved downward and either lost from the profile or precipitated in lower horizons. Strong mineral acids are not destroyed on their way down through the profile and may thereby affect both the rate of weathering and the translocation of the weathering products.

A characteristic trait for forest ecosystems as compared with agriculture ecosystems is the relatively close nutrient circulation during most of the rotation period in a managed forest. In the regeneration phase (either caused by clear felling or by natural events such as forest fire), this nutrient cycling is much less closed and leaching losses may occur. This may mean that some of the effect of changes in chemical climate may accumulate for a long period of time and then become evident in connection with a regeneration phase in the forest. In the case of acidification due to nitrogen compounds, it is quite clear that such effects do occur. In many forest ecosystems nitrogen accumulated during the life of a stand is oxidized to nitrate to a considerable extent after clear-felling. In undisturbed boreal forests there is normally very little nitrate formed and deciduous hardwood forests often have an incomplete nitrification (Ellenberg, 1971).

We also have to consider the effect of other human manipulations on soil acidity. Forest fertilization has such effects, particularly if urea or ammonium ions are supplied and then transformed to nitrate in the soil. Draining operations may also effect soil acidity, both by changing the water movement in the soil profile from very superficial and mainly horizontal in an undrained soil to vertical in a well drained soil.

The various characteristics of soils discussed so far may all be of importance for an evaluation of the effect of acid rain on the soil.

Most of the effects have not yet been quantified but there is no serious obstacle against measurement of these processes. However, we also have to consider another class of soil properties, namely the heterogenity of the soil. Soils are very seldom uniform. Very often soil aggregates occur with different physical and chemical properties on the surface of the aggregate compared with conditions inside the aggregate. The scale of variation may range from fractions of millimeters up to at least decimeters. Also other types of heterogenities may occur, for instance root channels and rock/soil interphases, which may range from centimeters to meters in extension and spacing.

Water percolation through a soil profile may be rather irregular (Tamm & Troedsson, 1957). If all or part of the percolating water follows certain channels in the soil (for instance old root channels), the chemical equilibration between the percolating water and soil particles may be very incomplete. Therefore it is possible and even likely that water percolating through the soil does not always reflect average soil properties. Instead it may be affected considerably more by its origin and thereby by the rain acidity than would be expected from the soil chemical properties as measured on standard soil samples. The rapid percolation of acid rain through certain pathways in the soil, as for example in shallow soils in Norway and Sweden, may also help to explain why lakes and streams may be acidified rapidly, although the soils around them possess a considerable buffering capacity, when studied in the laboratory.

In addition we have to consider that many soil processes, particularly those that affect plant growth do occur on the surface of soil particles or the surface of living organisms. These surface processes, especially in the top horizon of the soil, may be affected by acid rain long before we can measure changes in average properties in the soil. We know that several of these processes are very sensitive to pH, for instance nitrogen fixation and nitrogen mineralization. Also purely chemical processes such as adsorption and/or desorption of heavy metals are strongly dependent on pH conditions.

The effects of acid precipitation on surface processes--both biological and chemical--in the soil may be at least as important for site productivity as changes in "bulk properties" of the soil. We shall have to look more carefully for possible effects on processes restricted to soil particle surfaces than has been done so far, if we are to evaluate correctly the impacts of acid precipitation.

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POTENTIAL EFFECTS OF ACID PRECIPITATION ON SOILS IN THE HUMID TEMPERATE ZONE

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INTRODUCTION

Acid precipitation is not a new phenomenon. As long as water has fallen on the surface of the earth it has probably contained varying amounts of oxides of carbons, nitrogen and sulfur that increase hydrogen ion activity. This was certainly true when volcanism prevailed. With the appearance of life spasmodic geologic expulsions of elements into the atmosphere were supplemented by more rhythmic biochemical cycles of organic matter production and decomposition. Since the Industrial Revolution consumption of fossil fuel has increased additions of atmospheric contaminants. In the first two and one-half centuries of industrialization combustion of coal caused large discharges of sulfur. In the latter half of the present century oxides of nitrogen have increased sharply because of the advent of the gasoline engine. According to Robinson and Robbins (1968) 73×10^6 tons of sulfur were emitted in the mid-1960's. They estimated that 70 percent of this came from combustion of coal and 16 percent from combustion of petroleum products. Other estimates of man's contamination of the environment based on pollution of river waters with sulfate range from 3.7×10^6 tons (Bertine and Goldberg 1961) to 33×10^6 tons (Berner 1971). Kellogg et al. (1972) consider that 50×10^6 tons of sulfur per year are contributed to the atmosphere by man. Annual discharges of NO and NO_2 into the atmosphere from man's activities are estimated to be about 50×10^6 tons. This is compared with estimated natural emissions of 500×10^6 tons NO_2, 5900×10^6 tons NH_3 and 1000×10^6 tons N_2O (Robinson and Robbins, 1968).

In the past few decades increasing evidence has linked atmospheric pollutants to undesirable plant responses but the influence of these pollutants on soil processes and characteristics has received little attention. The purpose of this paper is to examine potential effects of acid precipitation on soil and to relate these effects to acidification resulting from natural pedogenic processes or from

modification of these processes by agricultural practices. In this discussion we will emphasize the effects of sulfur and nitrogen on soils occurring in humid temperate zone forested regions.

SOIL FORMATION

From its inception soil formation is an acidifying process. The parent material may vary greatly in composition and state of subdivision but it is generally composed of silicate minerals containing different amounts of aluminum, iron, calcium, magnesium, potassium, sodium, manganese, and other elements. It may be igneous, metamorphic or sedimentary. It may have formed where it is exposed or it may have been transported varying distances by geologic agencies. Chemical equilibria established during the formation of the parent rocks and minerals from which the soil is ultimately formed have been disturbed and new equilibria are continually being established through the process of weathering.

Chemical weathering involves hydrolysis, hydration, oxidation-reduction reactions, carbonation and solution of the compounds and elements found in the parent material. Particle surfaces on which weathering begins are frequently not acidic. Abrasion pH values of many silicate rocks and minerals are commonly alkaline ranging as high as pH 8 or 9. As the more easily dissolved constituents such as calcium, potassium, magnesium and sodium are removed in solution the soil system becomes more and more dominated by hydrogen and aluminum ions.

The effects of chemical weathering are greatly accelerated as the quantity and variety of organic matter added to the soil increase. Consumer organisms, particularly bacteria and fungi, show corresponding changes in quantity and variety. Metabolic by-products from these organisms include carbon dioxide, organic acids and other compounds that not only increase acidity but also enhance solubility of mineral constituents by chelation. In many cases root systems of higher plants have specific organisms associated with them which promote availability of otherwise insoluble mineral constituents to the higher plant or which promote fixation of atmospheric nitrogen. Thus plant growth and production of more organic matter is enhanced.

With time the biogeologic system approaches the dynamic equilibrium imposed by climate and by the limits of the system itself and a characteristic soil evolves which reflects these combined influences. Nutrient cycling is essential in maintaining the progressive tendencies of vegetative systems and again, because of the dominance of microbial metabolism, the net effect is production of acidifying conditions. A brief discussion of the cycles of nitrogen and sulfur will serve to illustrate this process.

NITROGEN IN SOIL

The cycle of nitrogen in soil as an integral part of the overall cycle of nitrogen in nature has been reviewed by Stevenson (1965) and again by Wollum and Davey (1975). Over 97 percent of the earth's nitrogen is held in primary igneous rocks with substantially smaller amounts occurring in ancient sedimentary rocks. Most of this nitrogen does not circulate biologically, however, and the primary source of nitrogen in the soil is the atmosphere which contains only about two percent of the total nitrogen on earth. In the atmosphere, however, N_2 is the dominant gas, occupying about 80 percent of the gaseous volume. Combined forms of nitrogen including ammonia, nitrate, nitrite and organic nitrogen may also occur. These originate from soil or from oceans, from industrial sources or from fixation of atmospheric nitrogen by lightning, by photochemical oxidation or by the passage of meteorites.

Nitrogen is transferred from the atmosphere to the soil by precipitation, by direct absorption of gaseous forms from the atmosphere and by biological fixation. Amounts added in rainfall vary greatly. Allison (1965) cites data showing additions of 1.7 to 22.3 kg/ha/year of inorganic nitrogen with an average of 8.7 kg. Over 2/3 of this is ammonia nitrogen. Eriksson (1952) gives values for Europe and the United States ranging from 0.74 to 21 kg per hectare per year. Values from the White Mountains in New Hampshire over an eleven year period average 19 kg/ha/year (personal communication from F. H. Bormann). While these amounts are generally insignificant for field crop production they are of considerable importance to natural ecosystems which in many instances tend to accumulate nitrogen. Because of increasing use of fossil fuel it is likely that amounts of nitrogen in precipitation will increase. Addition of nitrogen to the soil by absorption of gaseous nitrogen from the atmosphere has been reported to be of the same order of magnitude as additions in precipitation although there is not universal agreement on this subject (Allison, 1965).

The most efficient means for transferring gaseous nitrogen from the atmosphere to the soil is biological nitrogen fixation. This process may involve blue-green algae, free-living bacteria, bacteria associated with non-leguminous plants. Obviously the amounts of nitrogen added to the soil by these agencies will show much variation. Values given by Allison (1965), Jensen (1965) and Vincent (1965) for all of the nitrogen added may total as much as 100-200 kg/ha/year with most of this being added by leguminous crops. Additions in natural ecosystems are probably considerably less.

However nitrogen is provided it eventually becomes a constituent of plant protein or other nitrogen containing compounds in the plant. In natural forest ecosystems plant or animal tissues containing combined nitrogen are deposited on the forest floor where decomposition

begins. Details of this process vary with the type of tissue and the types of organisms involved but the broad outlines of decomposition in all cases are generally similar. Complex nitrogen-containing molecules are hydrolyzed to smaller and smaller polypeptides and peptides, to constituent amino acids and eventually to ammonia. Under favorable conditions variable amounts of ammonia are transformed to nitrate. This conversion which can be carried out by heterotrophic organisms as well as specific autotrophs is an acidifying process with two hydrogen ions being released for each nitrate ion produced according to the following highly simplified reaction:

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + H_2O + 2H^+$$

Nitrogen can be absorbed by microbes or by higher plants either as ammonium or nitrate and recycled through another generation of plant tissues or nitrate may be reduced releasing nitrogen in gaseous form or it may be leached from the system. In managed agricultural soils the reactions are essentially the same except the amounts of nitrogen involved are much larger due to additions of nitrogenous fertilizers. Thus the potential for acidification is high and must be counter-balanced by periodic application of ground limestone.

SULFUR IN SOIL

The ultimate source of sulfur in soil is the rock material from which the soil is derived. The lithosphere contains about 0.06 percent sulfur (Jordan and Ensminger 1958). Unweathered igneous rocks may contain from 0.05 to 0.3 percent sulfur with basic igneous rocks generally containing more sulfur than acid igneous rocks (Whitehead, 1964). Sulfur in unweathered igneous rocks occurs primarily as sulfides of iron, copper, nickel and other metals. These same combinations may occur in somewhat higher concentrations in sedimentary rocks with values ranging from 0.03 percent sulfur in sandstones to 0.26 percent in shales. Limestones contain an average of about 0.11 percent sulfur (Rankama and Sahama, 1950).

In well-drained soils in the humid temperate zone sulfides released by rock weathering are oxidized by chemical and microbial reactions to sulfate which is either absorbed by plants or removed by leaching. The mechanisms of oxidation of sulfides are extremely complex and have not been fully resolved. The overall reaction stoichiometry for oxidation of pyrite can be represented by the following:

$$FeS_2 + \frac{15}{4} O_2 + \frac{7}{2} H_2O \longrightarrow Fe(OH)_3 + 2H_2SO_4$$

where four moles of hydrogen ions are produced, two from the oxidation of ferrous iron and two from the oxidation of sulfide (Stumm and Morgan, 1970). Presumably other metal sulfides are oxidized in a similar fashion. The rate of sulfur oxidation is of interest from the point of view of soil reaction, nutrient balance and soil formation. Wiklander (1958) indicated that when a silty subsoil high in iron sulfide was exposed to air for 120 days the pH value dropped from 6.3 to 2.9. Much of the sulfur in soil surface horizons is present in organic forms with only small amounts of sulfate. This relationship varies with soil type. Evans and Rost (1945) showed that organic sulfur constituted more than 70 percent of the total sulfur in the A horizon of chernozem and black prairie soils in western and southwestern Minnesota. The A horizons of podzol soils of northern Minnesota, however, contained less than 50 percent organic sulfur. These samples were of the mineral soil and did not include the humus layers in the podzol soils.

In subsoil horizons, however, appreciable amounts of sulfate may accumulate and constitute a major portion of the total sulfur (Neller, 1959). This is especially true in acid soils where sulfate adsorption by soils and clays reaches a maximum in the pH range from 2 to 4 (Williams and Steinbergs, 1962). Adsorption occurs on surfaces of mineral colloids particularly hydrated aluminum or iron hydroxide or on clay minerals particularly kaolinite. Several mechanisms of adsorption have been suggested (Schell and Jordan, 1959) including adsorption at exchange sites and occlusion between lattice sheets.

In addition to weathering sulfur is added to the soil by rainfall (Jordan et al. 1959, and other papers in this Symposium), by direct adsorption of SO_2 from the atmosphere by plants and by soil (Alway, Marsh and Methley, 1937; Fried, 1948; Ensminger, 1958 and Whitehead, 1964) or as a component of a fertilizer or soil amendment for agricultural or horticultural purposes. Crop responses to sulfur additions have been reported in Africa, Asia, Australia, Brazil, Canada, France, Japan, New Zealand, Norway, Spain, Sweden and West Germany (Freney, Barrow and Spencer, 1962; Nelson, 1965).

In the United States considerable attention has been given to sulfur in relation to crop needs (Hart and Peterson, 1911; Shedd, 1914; Ames and Boltz, 1916; Stewart, 1920; Greaves and Gardner, 1929; Alway, 1940; Kelley and Midgley, 1950). According to Nelson (1965) 40 percent of the sulfur consumed in the United States finds its way into the manufacture of fertilizers and consumption for this purpose was, at that time, increasing at an annual rate of five percent. Whitehead (1964) indicated that where the atmosphere supplies more than about 10 kg of sulfur per hectare per year, sulfur deficiency is unlikely to occur. Tisdale and Rucker (1964) ascribe increasing occurrence of sulfur deficiency to an absolute decrease in the amount of sulfur being added to the atmosphere as the result of the shift from coal to natural gas and petroleum fuels that contain less sulfur

than coal, to increasing use of high analysis fertilizers that do not contain sulfur as a by-product, to the production of higher yielding crop varieties that place greater demands on the sulfur supplying ability of the soil and to losses of sulfur through leaching. While these observations might apply to situations where highly specialized agronomic crops are being grown, it seems highly unlikely that sulfur deficiency will occur where forest vegetation is growing on unmanaged soil.

The relatively small amounts of sulfate usually found in the upper horizon suggests that this form of sulfur is quickly leached. Lysimeter studies (McKell and Williams, 1960) have corroborated this and estimates on a global basis indicate that the rivers of the world carry considerable amounts of sulfate to the ocean each year. Eriksson (1963) estimated that for the period around 1960 the total annual amount of sulfate carried to the sea was 240×10^6 tons which included 45×10^6 tons from rock weathering, 30×10^6 tons applied to the soil as fertilizer and 165×10^6 tons from precipitation or dry deposition. Berner's (1971) calculations for flux of sulfate to the oceans via the world's rivers showed a total of 368×10^6 tons which included 268×10^6 tons coming from natural sources and 100×10^6 tons coming from pollution from various sources. Berner considered his estimate of the quantity contributed by pollution to be conservative.

Plants take up most of their sulfur from soil as sulfate. Simple organic sulfur compounds may also be utilized but the intense microbial activity in the immediate vicinity of plant roots suggests that this is not a significant source. In unmanaged soils then, sulfur available for plant growth will come either from the atmosphere or from conversion of organic sulfur compounds to sulfate by microbial decomposition. From this point on sulfur mineralization and immobilization bears a close resemblance to mineralization and immobilization of nitrogen (Walker 1957; Barrow 1960). According to Walker the amount of sulfate formed from organic matter is affected by total sulfur in the organic matter and by the carbon/sulfur ratio, and pH in much the same way as the formation of mineral nitrogen is influenced by corresponding factors. Whitehead (1964) found the ratio of nitrogen to sulfur in soils to vary from about 6:1 to 9:1 and Williams, Williams and Scott (1960) observed a close relationship between the contents of soil sulfur and soil nitrogen in Scottish soils with correlation coefficients as high as 0.984.

Transformations of sulfur in soil are primarily microbial and while there are organisms specifically associated with oxidation of elemental sulfur and simple sulfur compounds it is likely that many different types of heterotrophic bacteria and fungi are involved in the sulfur cycle.

Microbial transformations of sulfur have been described in detail by Alexander (1961) and Freney (1967). Sulfate absorbed by growing plants is transformed into a large number of organic compounds in various parts of the plant. Numbers and characteristics of these compounds vary with the plant species. In the forest these tissues are eventually deposited on the forest floor and here further transformations associated with decomposition take place. Decomposition end products vary depending upon climate, microclimate, soil type, the nature of the material being decomposed and the nature of the decomposing organisms. The simple inorganic sulfur compounds resulting from decomposition are then reassimilated into the tissues of microbes or higher plants or are leached from the soil profile or lost in gaseous form to the atmosphere. Many details of the decomposition process are not known but generally speaking under anaerobic conditions mercaptans and hydrogen sulfide will accumulate while in the presence of atmospheric oxygen sulfate is commonly the end-product (Stevenson, 1964).

As in the case of weathering reactions that release sulfur from parent rocks many reactions associated with organic matter decomposition are potentially acidifying although oxidation to sulfuric acid or intermediate acids may be buffered to a far greater extent by the organic system than is the case in rock weathering. In poorly drained anaerobic situations sulfide may accumulate and when such soils are allowed to oxidize pronounced increases in acidity may occur. Hill and Shearin (1970) observed decreases of as much as three pH units when soils from tidal marshes of Connecticut and Rhode Island were dried for 18 days. Initial pH values in these soils ranged from about 5 to 7. In marsh soils that had been exposed for clay mining pH values ranged from 3.6 at the surface to 2.2 at a depth of about four meters.

THE NATURE OF SOIL ACIDITY

In addition to soil acidity generated by microbiological energy transfers the contribution of inorganic components must be considered. The role of hydrogen and aluminum in soil acidity has perhaps been studied more intensively than any other single soil property, yet many questions remain unanswered. Jenny (1961), in reflecting on the "soil acidity merry-go-round", noted that during a half century of work many investigators had gone full circle from early theories that acid soils were Al-saturated, through the period when soils were considered to be H-saturated polybasic acids, and back to the present notion that the properties of acid soils are largely determined by aluminum. Given this history of differing interpretations of what in essence were identical experimental findings, it is clear that experts on the nature of soil acidity expound their ideas at their own risk.

We will not attempt a comprehensive review of soil acidity here since a recent monograph edited by Pearson and Adams (1967) presents an excellent summary of current views. The chemistry of soils receiving external sources of strong acids from rainfall or from the oxidation of reduced nitrogen compounds should resemble in many respects the chemistry of acid sulphate soils which were the subject of a recent international symposium (Dost, 1973). The chemistry of aluminum in these soils was reviewed by Frink (1973) and provides the basis for much of the following discussion.

Acidity of soils in the pH range of present concern is believed to be controlled by the hydrolysis of aluminum according to the first-stage hydrolysis reaction:

$$Al^{+3} + H_2O = AlOH^{+2} + H^{+}$$

where water of hydration of aluminum ions has been omitted for convenience. The thermodynamic equilibrium constant for this reaction has the familiar form:

$$K = \frac{(AlOH^{+2})\ (H^{+})}{(Al^{+3})}$$

where parentheses indicate ion activities. If these ion activities are expressed as negative logarithms, and the equation rearranged, we have:

$$pH = pK - pAlOH + pAl.$$

Since the pK for this reaction is approximately 5.0, soils containing aluminum ions would be expected to be well buffered at pH = 5.0, i.e. when pAlOH = pAl.

This buffering is indeed observed in soils, although the pH of maximum buffering capacity has been shown to decrease with increasing concentration of aluminum (Frink and Sawhney, 1967). The source of aluminum in acid soils is the soil itself. A fully H-saturated soil clay may have a pH as low as 2.5 but it rapidly increases to about pH 3.5 as aluminum and other ions are released by decomposition of the clay. Thus, this decomposition serves to set some lower limit on soil pH unless large amounts of free acidity are produced more rapidly than can be neutralized by the clay as is the case in some acid sulphate soils (Dost, 1973). Forested soils in Connecticut (Lunt, 1948) rarely have pH values as low as 3.5. Hence it appears unlikely that modest amounts of acidity in rainfall, when compared with the potential acidity from nitrification of litter, will lower the pH of unmanaged soils below pH 3.5.

Organic acids from decomposing organic matter also provide an important source of acidity in forest soils, but less is known of their reaction. Most organic acids are weakly dissociated and would not be expected to contribute to soil acidity at low pH values. Organic acids are known to form complexes with aluminum, however, which makes interpretation of their role more difficult.

The relative importance of these various sources of acidity, i.e. organic acids, aluminum hydrolysis and hydrogen ions from strong acids has also been examined by titration curves of soils and soil clays. As Jenny (1961) pointed out, however, interpretation of data has lagged far behind their collection. Titration curves of acid soils show a number of buffer ranges which still defy complete analysis. In general, when base is added to an acid soil, free acid, if present, is neutralized first, followed by the neutralization of aluminum with a pronounced buffer range. A third and final neutralization range is observed which may include neutralization of clay lattice hydroxyl groups and both free and complexed organic ligands.

When acid is added to a neutral soil, this process is presumably reversed, but very few detailed studies are available. Agronomic practices have been developed more or less empirically for predicting the amount of aluminum or elemental S required to lower soil pH for crops requiring an acid environment. Titration curves of neutral soils with acid, however, show a pronounced hysterisis which has not been examined in any detail. It is likely that much of the discrepancy between the shapes of titration curves of acid soils with a base and the reverse, or back-titration curves, reflects lack of equilibrium rather than irreversible changes in the soil.

The foregoing discussion has largely neglected cation and anion exchange properties of soils since these properties complicate interpretations of soil acidity considerably. One complication is the changes in cation exchange capacity brought about by changes in soil acidity; the second is measurement of soil acidity itself.

Considering the first problem, cation exchange capacity (CEC) of acid soils is generally observed to increase substantially with increasing soil pH. The nature of this pH dependent charge is uncertain but is thought to be associated with the third, or final, buffer range observed in titration curves. The magnitude can be quite large: a soil with pH 4.2 was found to have a neutral-salt CEC of 1.4 meq/100g and an additional pH dependent CEC of 5.7 meq/100g determined at pH 8.2 (Sawhney, Frink and Hill, 1970). Acidifying a neutral soil will likely decrease its CEC, but again some hysterisis is observed. In a recent study of acid soils Gebhardt (1973) found little change in pH-dependent CEC in the range pH 3.5-4.0. Hence, the CEC of acid forest soils is not likely to be altered by acid rainfall.

So far we have assumed that soil acidity is easily measured and therefore is well defined. This assumption is particularly important if we are to examine trends with time. Thus, how valid is it?. First, we have the usual problem of analytical methods changing with time. Prior to about 1930, soil pH was measured with indicator dyes, interference from colored or turbid soil extracts, and the ability of the eye to compare colors. Experience suggests that measurements with dyes generally indicate a higher pH than that measured with the glass electrode and that relative errors of 0.5 pH units would not be unlikely. Electrometric methods were developed and the first measurements in the 1930's were made with the quinhydrone electrode since it could be used with a simple potentiometer. The quinhydrone electrode was a vast improvement over dyes, but is sensitive to the presence of oxidizing or reducing agents as well as to the hydrogen ion. Use of the glass electrode began with the development of the vacuum tube potentiometer and continued to the highly sophisticated digital instruments common in today's soils laboratories.

What is measured when we blithely insert the glass and calomel electrodes in a soil suspension and report the pH, sometimes to three significant figures? A simple experiment of placing both electrodes first in the clear liquid and then in the soil paste reveals differences of as much as 0.5 pH units with the paste usually appearing more acid. This so-called "suspension effect" has plagued soil scientists since its discovery and the issue is not yet resolved. Other factors affecting the measured pH are the soil water ratio and the salt content of the suspension.

The suspension effect arises because there is no known method for measuring individual ion activities; i.e. one cannot measure the potential of a single reversible electrode but must use a pair. The glass electrode is commonly used to measure the hydrogen ion activity (pH) by comparing its potential with that of a nonspecific calomel electrode making electrical contact with the solution via a salt bridge. However, at the liquid junction between the salt bridge and the solution, a diffusion potential arises which is a function of the mobilities of the cations and anions in the bridge and the activities of ions on either side of the junction. The use of saturated KCl in the calomel electrode and salt bridge is thought to minimize the junction potential, since the mobilities of K and Cl are nearly equal. This assumption is reasonably satisfactory for dilute aqueous solutions and enables one to measure the activity of hydrogen ions in such systems with some confidence.

In a sol or suspension of charged particles, however, the junction potential may be large, apparently due to a reduced mobility of the counter ions near charged surfaces. Other explanations have been suggested but regardless of the cause, the effect is real and can result in substantial differences in apparent pH depending on where the electrodes are placed. Other factors such as the effect of the

soil water ratio are also attributed to the suspension effect: as the suspension concentration increases the suspension effect also increases and the measured pH decreases.

Increasing the salt concentration has several effects: first, it alters the junction potential, although the direction and magnitude of the change is different with different salts. Second, increasing the salt concentration decreases the potential difference between the clay surface and the equilibrium bulk solution and decreases the measured pH. This is often attributed to displacement of H and Al ions from exchange sites but may be equally well described by changes in electrical potential across the double layer. However, salt also has some specific effects which are better described in terms of exchange reactions. At low salt concentrations where diffusion between clay platelets is restricted, or in the presence of ions causing lattice closure, the hydrolysis of adsorbed aluminum is enhanced. This increase in hydrolysis, which is presumed due to the specific sorption of some hydrolyzed species of aluminum, results in a lower pH of the clay suspension that would be predicted from simple electrostatic considerations.

Various investigators have proposed ways of minimizing these errors in measurement of soil pH. The most common method is the addition of a 1 N salt solution (frequently KCl) to swamp effects produced by varying salt concentrations among different soil samples. This has at least one drawback: the ionic strength is so high that calculations of ion activity coefficients are impossible and hence thermodynamic constants based on pH measurements in 1 N salt solutions are unsatisfactory. An alternative is the measurement of pH in 0.01 N $CaCl_2$, a concentration considered near that of natural soil solutions, yet with an acceptably low ionic strength. No method is considered completely acceptable and hence Van Olphen (1963) cautions against direct comparisons of the pH of soil suspensions with those of true solutions.

LYSIMETER STUDIES IN CONNECTICUT

In the same way that man has altered the composition of the atmosphere by industrial activities the composition and nature of soils have been altered wherever man has practiced agriculture. This experience provides guidelines for evaluating potential soil changes caused by atmospheric contaminants.

Agriculturists have known for at least two centuries that rainfall contains plant nutrients such as nitrogen and other dissolved constituents. The earliest chemical analyses were apparently reported by Marggraf (in Miller, 1905) who found "nitric acid, chlorine and

lime in rain-water collected during the winter of 1749-1750".

Analyses continued until the major constituents in rainfall were identified. Thus rain contains the anions nitrate, sulfate, chloride and their accompanying cations ammonium, calcium, magnesium, potassium, sodium and hydrogen.

Since the amount of nitrogen in rainfall represents a significant portion of the total nitrogen budget for many crops, several long term studies of the composition of rainfall are available. Measurements of ammonia and nitrate nitrogen were begun at Rothamsted Experimental Station in the 1850's and these early results were summarized by Miller (1905). Chlorine and sulfuric acid were also determined during some of this 50 year period. Not all analyses were conducted at any one time, but analyses during 1881-1887 for sulfate and chloride and during 1888-1894 for ammonia and nitrate are shown in Table 1.

Table 1. Chemical composition of rain-water at Rothamsted, England 1881-1894 (Miller, 1905).

Constituent	Rainfall, cm	kg/ha
N_2O_5	72	1.1
NH_3	72	3.1
SO_3	76	19.5
Cl	76	16.4

Several items need be considered in the interpretation of such data. First, agriculturists generally report analyses of this sort in lbs/acre or kg/ha, since these are units of importance in agriculture. Where records of rainfall are available, it is possible to calculate the apparent concentration in the rain in ueq/liter, a unit common in studies of precipitation. However, since the samples were generally composited and stored for some time before analysis, the apparent distribution of nitrogen between nitrate and ammonia forms should be viewed with caution. Other changes in chemical composition may also occur during storage, but are probably less serious.

More troublesome are the changes in analytical methods that have occurred over the years. Few generalizations as to the effects of such changes are possible, since comparative studies of analytical methods are not very rewarding and few are available. However, it is likely that both the precision and the accuracy of early methods were low. Moreover, rain-water is quite dilute and even present day methods may lack the necessary sensitivity; hence an error of a factor

of 2 would not be unlikely in the analyses shown in Table 1.

A more subtle problem but potentially the largest source of error in interpretation of early data is the chemical form reported by the analyst. For example, the study at Rothamsted speaks of nitrate, nitric nitrogen and nitric acid in the text but the tabular data identifies this form of nitrogen as N_2O_5. This is understandable, since chemical terminology had not reached its present level of standardization. However, the most serious problem is knowing whether the 1.1 kg/ha is reported as N_2O_5 or as N. The history of analytical chemistry suggests that analyses during this era are likely to be reported as the oxide. However, the NH_3 and N_2O_5 are subsequently added together and called "nitrogen." If this be the case, the N_2O_5 should have been reported as N. Thus, we are left with a considerable uncertainty in any attempt to determine changes with time.

Taking the data at face value, however, rainfall at Rothamsted during 1881-1894 apparently contained 4.2 kg/ha of ammonia and nitrate nitrogen. Miller (1905) notes that about 1.5 kg/ha of organic nitrogen was also found, for a total of about 5.7 kg/ha. The amounts of sulfur are also difficult to interpret, since they are reported as SO_3, but in any event are somewhat lower than in rainfall in Connecticut. In this connection Miller (1905) notes: "Compared with London rain the amount of sulphuric acid found at Rothamsted is small." Unfortunately, the data for London are not given. The amount of chloride in the rain appears similar to amounts found today in areas of similar proximity to the ocean.

Data from lysimeter studies in Connecticut from 1929-1948 provide valuable information on inputs of various cations and anions in rainfall and amounts of these constituents removed by crops and by leaching. Chemical composition of precipitation during that period is shown in Table 2. and is taken from Windsor Lysimeter Series A (Morgan,

Table 2. Chemical composition of precipitation at Windsor, Connecticut, 1929-1948, in kg/ha.

	1929-34	1935-39	1939-44	1944-48
$N(NO_3 + NH_4)$	5.0	3.1	6.6	7.4
SO_4-S	19.0	30.9	34.4	22.8
Cl	12.2	21.5	36.3	24.0
K	6.2	11.2	8.5	4.2
Ca	13.7	27.8	13.1	17.3
Mg	3.0	6.5	8.1	4.1
Na	11.9	12.1	5.3	7.1
Rainfall, cm.	91	118	98	102
Lysimeter series	A	D	E	H

1936), D (Morgan, Jacobson and Street, 1942), E (Jacobson, Swanson and Smith, 1948) and H (unpublished).

Unfortunately the separate analyses of nitrate and ammonia were combined as N in the published reports. Unpublished data for NO_3 in rain for 1937-1948 show a mean input of 3.8 kg/ha during that period with no apparent trends with time. The mean for the data shown as N in Table 2. is 5.5 kg/ha; hence we assume that 5.5-3.8 or 1.7 kg/ha must have been ammonia.

Thus, the rain is assumed to have had the following average composition for the period 1929-1948 with 102 cm of precipitation.

Mean 1929-48

	kg/ha	μeq/liter
Anions		
NO_3-N	3.8	27
SO_4-S	26.8	164
Cl	23.5	65
		256
Cations		
NH_4-N	1.7	12
K	7.5	19
Ca	18.0	88
Mg	5.4	43
Na	7.3	31
		193

Assuming that the excess of anions over cations is balanced by hydrogen ions, the calculated acidity is 63 ueq/liter of H or pH - 4.2. Given the uncertainty of analyses of samples composited and stored for various periods of time, it appears that the rainfall during that period was perhaps nearly as acid as that presently being reported for the Northeastern United States (Cogbill and Likens, 1975). However, it is not our present purpose to examine trends with time but rather to examine the effects of this rain on soil.

First, what are some possible effects? The acidity in rainfall at pH 4.2 corresponds to 63 ueq/liter of hydrogen ions. Under 114 cm of rainfall, the yearly average in Connecticut, this would require the equivalent in neutralizing power of about 36 kg/ha of $CaCO_3$. Since agronomic practice frequently dictates the application of several thousand kg/ha of limestone, the acidity in rainfall does not seem a direct threat to agricultural soils. Changes in unmanaged soils might be expected and we will examine experimental data for both managed and unmanaged soils shortly.

One might also expect that the alkalinity of lake waters might be affected. The State Board of Fisheries and Game (1942), surveyed 47 Connecticut lakes during 1937-1939 and found that the alkalinity of the softest lakes was about 150 ueq/liter HCO_3^-. Recently, Norvell and Frink (unpublished data) have reexamined 23 of these lakes to determine if changes in fertility and productivity had occurred. An extensive sampling study during 1973-1974 revealed that although many other changes had occurred, the softest lakes still contained about 150 ueq/liter of HCO_3^-. Acid rain at pH 3.8 would contain 150 ueq/liter of hydrogen ions capable of neutralizing this bicarbonate alkalinity but apparently this has not occurred during the 35 years between these two lake surveys in Connecticut. Beeton (1965) found that concentrations of sulfate and chloride have nearly doubled in Lake Erie and Lake Ontario in the last 50 years and Winkler (1970) attributes much of this to the polluted atmospheres around the lake. Unfortunately, the State Board of Fisheries and Game report (1942) did not include SO_4 or Cl so we do not know if similar changes occurred in Connecticut lakes.

Returning to the effects of rain on soil, numerous lysimeter experiments were conducted in Connecticut during the period when rainfall analyses are also available (Table 2.). Looking first at managed soils, considerable information is available on the effect of various cropping practices and fertilizer formulations on the composition of water draining through the soil. Drainage in lysimeters only occurs by saturated flow (owing to the lack of capillary suction below as in a normal soil) and hence the results are not identical with those expected in undisturbed soils. However, they should be adequate for our present purpose.

Table 3 shows the amounts of various constituents removed by leaching when tobacco is grown with conventional fertilization techniques. The amounts added to the crop include contributions from both fertilizer and rainfall. Amounts removed by the crop are shown, as well as the net change in the soil during the 9-year period.

Table 3. Effects of rainfall on Merrimac sandy loam planted with tobacco, 1931-1940 (Morgan, Jacobson and Le Compte, 1942).

Constituent	Added kg/ha	Removed		Net change kg/ha
		Crop kg/ha	Leaching kg/ha	
N	228	94	50	+84
SO_4	69	9	59	+ 1
Cl	31	9	17	+ 5
K	197	110	65	+22
Ca	31	49	60	-78
Mg	40	21	17	+ 2
Na	85	6	67	+11

The fertilizer used supplied about 80% of the nitrogen in organic forms (cottonseed meal and castor pomace) with 20% as inorganic sodium nitrate. However, organic meals readily nitrify during the growing season and of 50 kg/ha of nitrogen in the leachate, 49.7 kg/ha was NO_3 with the remaining 0.3 kg/ha as NH_4.

Since the contributions of rainfall to the nitrogen budget of a heavily fertilized crop such as tobacco are almost negligible, little can be said of the fate of the approximately 5.5 kg/ha of N contributed by rain. As with other sources of nitrogen, however, once past the root zone of crops NO_3 continues to move downward unless it is lost by dentrification. Small amounts of SO_4 and Cl were removed by the crop and the remainder was leached as might be expected since anions are generally not retained in large quantities by soils.

The fate of the cations is more complex. Sodium is not tightly held and leaches almost completely through these sandy soils. Magnesium, in this case, was about evenly distributed in the crop and leachate and no significant net change was observed. The most pronounced changes are evident in the budget for K and Ca. Potassium is readily fixed by clay minerals (for a recent review of these fixation reactions see Sawhney, 1972) and accumulated at the annual rate of 22 kg/ha. Thus, one would expect that most of the 7.5 kg/ha of K in rain would be fixed in soils of the northeast whether they are cropped or not. Calcium, on the other hand, was significantly depleted in the soil by leaching during the nine-year period.

The pH of the soil decreased from 5.5 at the start of the experiment to pH 5.0 at its conclusion. The effect of the acidity of the rain, however, is small in comparison with the acidity of the various soil amendments. For example, about 270 kg/ha of $CaCO_3$ would be required to neutralize the acidity generated by the nitrification of

the 180 kg/ha of meals used in this experiment (De Roo, 1958). Hence, acid rain seems of little importance in tobacco culture.

The leaching of various fertilizer cations and anions was also examined in uncropped soil at Windsor (Jacobson, Swanson and Smith, 1948). Although the amounts added are far greater than those in rainfall, the results illustrate the effects of the additions of large amounts of basic and acidic constituents to soils. In one portion of the study, urea was added to Merrimac sandy loam in 20 cm-deep lysimeter tanks at the rate of 224 kg/ha of N annually for 5 years. The cations Ca, Mg, K or Na were added annually in amounts calculated to be chemically equivalent to the amount of nitrate produced by complete nitrification of urea. (For example, this would require 320 kg/ha of Ca.) The various cations were added as the salts of sulfate, chloride or carbonate and the leachate analyzed for the 5 year period 1939-1944. Table 4 indicates the effects of these treatments on leaching and soil acidity. Not shown are the nitrogen losses, but these can be summarized by saying that all the added nitrogen was leached completely from the soil as NO_3, the average annual loss being 253 kg/ha or about 30 kg/ha more than was added.

Table 4. Effects of various cations and anions on leaching losses in uncropped Merrimac sandy loam (Jacobson, Swanson and Smith, 1948).

Salt Added	pH	Cation Budget		
		Added kg/ha	Leached kg/ha	Difference kg/ha
As Carbonate				
Ca	5.0	320	380	- 60
Mg	5.3	195	142	+ 53
K	5.0	626	320	+306
Na	5.1	368	301	+ 67
As Chloride				
Ca	4.5	320	576	-256
Mg	4.4	195	207	- 12
K	4.6	626	379	+247
Na	4.6	368	328	+ 40
As Sulphate				
Ca	4.2	320	554	-234
Mg	4.2	195	213	- 18
K	4.5	626	366	+260
Na	4.3	368	335	+ 33

Since the acidity of the added urea corresponds to about 400 kg/ha of $CaCO_3$, we might expect some substantial decreases in soil pH from its original value of pH 5.6. Table 4 shows that indeed soil pH decreased in all treatments. The decline was least where carbonates were added, with the mean for all four cation treatments being pH 5.1. In this series of treatments, the calculated basicity from the added carbonates always exceeded the calculated acidity expected from the nitrification of urea; hence the reason for this decline in soil pH is not clear. The most likely explanation is that soils are slow in equilibrating with any added base or acid and that the observed pH is a function of the rates of the various reactions rather than a true equilibrium value. In the absence of any added base, urea alone lowered the pH of the soil to 4.3, so the carbonates obviously prevented some of this increase in acidity.

Differences in soil pH in the other cation/anion combinations are evident, but probably are not significant within the anion groups. The mean pH for the chloride group was 4.5 and for the sulfate group 4.3. It is likely that the pH of the sulfate group is significantly lower than the chloride group but the data are not adequate for statistical analysis. Moreover, it is noteworthy that this leaching did not lower the pH below that of the control treated with urea alone.

Leaching losses of cations follow the pattern observed earlier in soils cropped to tobacco (Table 3). Sodium is not readily retained and is leached almost completely. Magnesium also appears to leach readily, with a slight release from soil minerals possible. Calcium, however, was leached in amounts much greater than those added, and soil minerals were obviously decomposed. From 40 to 50% of the added potassium was fixed in these soils and was not lost by leaching.

In summary, these data suggest that changes in soil or nutrient status due to the small amounts of cations and anions in rainfall will be modest in most agricultural soils. In unmanaged soils, however, we might expect more substantial changes and we next examine some data from studies of forest soils in Connecticut.

Lunt (1948) summarized the results of both pan and tank lysimeter studies under red pine and hardwood stands during the period 1934 to 1936 and 1938 to 1940. The rainfall analyses in Table 1. while not at the same site, are considered representative for Connecticut during that period. The pan lysimeters which were undisturbed and contained active tree roots show an interesting comparison with data from the tank lysimeters containing disturbed soil and no roots (Table 5).

The data reveal that in the absence of roots, large amounts of nitrogen and other elements are lost by leaching from forest soils. In the presence of roots, however, the amounts lost are very low, and are indeed less than the amounts added in rain (Table 2). Hence,

Table 5. Leaching losses of several elements from the surface horizon of forested soils (Lunt, 1948).

Element	Lysimeter Type*	Annual loss, kg/ha	
		Red Pine	Mixed Hardwoods
N	Tank	48.9	93.2
	Pan	1.2	1.6
S	Tank	37.0	42.2
	Pan	2.2	6.2
K	Tank	26.4	49.3
	Pan	1.1	4.1
Ca	Tank	53.9	27.7
	Pan	3.4	2.5
Mg	Tank	-	7.9
	Pan	-	1.6

*Installed 10 cm below the ground line. Tanks are disturbed soil with no roots, pans are undisturbed with roots present.

plant nutrients in rain are apparently taken up at least in part by vegetation and are an important part of the nutrient budget of forest stands.

Lunt (1951) also examined the changes in pH and nutrient status under red pine during the period 1929-1944. He compared the pH of the control plot with the pH of a plot receiving about 4500 kg/ha of limestone in 1929 and 2250 kg/ha in 1930. The pH value in the control plot declined to 3.8 in the litter layer from an initial pH of about 4.3-4.4, but changes in the 0-2.5 cm layer of mineral soil were not significant. Limestone of course initially increased the pH of the litter layer to over 7 but this value gradually declined to the level of the control plot.

During the 15-year period for which records of soil acidity are available, about 3980 kg/ha of litter was returned annually to the forest floor. The litter raked from other plots contained about 0.5% N; thus we estimate that about 20 kg/ha of N were added annually to these limed and unlimed plots. Nitrification of this protein N and the general course of litter decomposition undoubtedly contributes to the acidity.

SUMMARY AND CONCLUSIONS

Acid precipitation is not a new phenomenon. Nitrate, sulfate and chloride along with substantial quantities of hydrogen ions were found in rain by analysis during the late 18th and early 19th centuries. Recently, man's activities have increased emissions of oxides of nitrogen and sulfur and the acidity of rain has increased accordingly.

We have examined some possible effects of this acid precipitation on soils in the humid temperate zone of the northeastern United States. Additions of acid in rainfall to agricultural soils are insignificant in comparison with acidity produced by agricultural soil amendments. Moreover, this acidity is readily neutralized by additions of limestone in the normal course of agricultural practice.

In unmanaged soils, acid rainfall might be expected to have more pronounced effects. However, acidity produced by biological cycling of nitrogen and sulfur compounds in forested stands exceeds that found in rainfall at present. Moreover, the pronounced buffering exerted by soil minerals and organic matter tends to minimize changes in soil pH when acids are added.

If acidity in precipitation should increase substantially or if the buffering capacity of the soil ecosystem is seriously reduced, we would expect detrimental changes in soil productivity. At present, however, acid precipitation does not appear to pose a serious threat to soils in the Northeast.

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CHANGES IN CHEMICAL PROCESSES IN SOILS CAUSED BY ACID PRECIPITATION

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INTRODUCTION

The acidification of precipitation is an accomplished fact. The only question that remains is wheter the present trend of acidification is to continue into the future, and if so, to what degree. A related question is, are the consequences of acid precipitation reversible and to what extent, or over what time period? Research conducted over the last twenty years has been addressed to the problem of monitoring the composition of rainfall (and precipitation in general) (e.g. Cogbill and Likens, 1974). Except for the rather obvious and blatant examples of the effects of acid precipitation such as the dissolving of much of the inscription on Cleopatra's needle in Central Park, New York City (cited in many introductory geology texts) and the etching of surfaces in metropolitan areas, the more subtle and long term effects of acidified precipitation have been more elusive. Only recently have workers begun to appreciate the longer term effects that are occurring. Some of these effects may in fact be irreversible within the time span of modern "civilized" man.

Foliage damaged by isolated acid precipitation events may recover or be replaced within the same growing season. Lake ecosystems which have become nearly abiotic because of lowered pH may recover naturally in the space of a few years with the cessation of acid precipitation or their recovery may be accelerated with proper chemical treatment. However, certain processes, although capable of being arrested upon cessation of the acid precipitation, are essentially irreversible over a time scale of tens and even hundreds of years. For example, certain types of soils are readily leached of trace nutrients which reduces the productivity of those soils. The re-establishment of proper levels of nutrients within the appropriate levels of the soils may take either artificial fertilization or hundreds of years of chemical weathering and plant activity.

The most recent trend in research related to acid precipitation is oriented toward the predictive area, i.e., what projections can we make about the effects of prolonged acid precipitation on various components of the ecosystem.

This paper examines the changes in the nature of precipitation brought about by acid precipitation and the anticipated changes in mineral stability and element mobility in the rock-water chemical system.

This effort has been supported by the Complete Tree Institute, University of Maine at Orono, Maine, U. S. A., Professor Harold E. Young, Director.

CHANGES IN PRECIPITATION CHEMISTRY

If the pH of water were controlled soleby by the CO_2 - H_2O system, the following equilibria prevail:

$$CO_{2\,g} = CO_{2\,aq} \qquad K_{CO_2} = 10^{-1.43} \qquad (1)$$

$$CO_{2\,aq} + H_2O_\ell = H_2CO_{3\,aq} \qquad K_0 = 10^{0} \qquad (2)$$

$$H_2CO_{3\,aq} = HCO_{3\,aq}^{-} + H^{+}_{aq} \qquad K_1 = 10^{-6.4} \qquad (3)$$

$$HCO_{3\,aq}^{-} = CO_{3\,aq}^{=} + H^{+}_{aq} \qquad K_2 = 10^{-10.3} \qquad (4)$$

$$H_2O_\ell = H^{+}_{aq} + OH^{-}_{aq} \qquad K_W = 10^{-14} \qquad (5)$$

Under normal atmospheric pressure for CO_2 ($10^{-3.5}$ atm.) and at 25°C, the result of these relationships is a pH of 5.6 and the following concentrations of the carbon-bearing species:

$$H_2CO_{3\,aq} \simeq 10^{-5}\ m/\ell = 620\ ppb.$$

$$HCO_{3\,aq} \simeq 10^{-5.6}\ m/\ell = 153\ ppb.$$

$$CO_{3\,aq} \simeq 10^{-10.45}\ m/\ell = 0\ ppb.$$

$$CO_{2\,aq} \simeq 10^{-4.9}\ m/\ell = 553\ ppb.$$

However, it is probably a reasonable assumption that there are other naturally occurring acids present in precipitation. Hydrogen sulfide is generated in large amounts in many near surface environments and released to the atmosphere where it is subject to oxidation and conversion to sulfuric acid. Additionally, volcanic emanations contain appreciable quantities of sulfuric and hydrochloric acid. Lastly, gaseous and aerosol organic acids may constitute a significant fraction of the total acidity of precipitation. Although most of these organic acids are weak, they constitute a buffer mechanism much like the carbonate system. Thus, considering all natural sources of acidity in precipitation, we might reasonably expect the pH of rain to range from 5.7 down to perhaps 5.0 or somewhat lower.

Counteracting natural and unnatural acid loads in precipitation are particles intercepted by falling precipitation or acting as nuclei. Most inorganic particles in the atmosphere would tend to react with the acid and consume the acid. Thus pH's in the range 7 to 8 are not uncommon in areas where there is abundant windblown dust, particularly evaporitic salts, in the precipitation. Consequently the natural pH range for precipitation might range from about 5 to 8.

The best evidence for anthropogenic sources of acid in rain is based on the time studies of the Swedish and Norwegian workers (e.g. Oden, 1968) who have documented the pH of precipitation for several decades. both the temporal and geographic variation of pH and the associated strong acids in the precipitation have been correlated with industrial sources. Similarly in the United States, although less well documented with respect to long term trends, the geographic relationship between pH and culture is well established (Cogbill and Likens, 1974).

The levels of $SO_4^=$ and NO_3^- in rainwater suggest that the bulk of the excess acidity may be attributed to these two acids. For example, if we take representative values of $SO_4^=$ = 4.5 ppm and NO_3^- = 3.0 ppm (Cogbill and Likens, 1974), the H^+ contribution from these two acids is $10^{-4.03}$ and $10^{-4.32}$ m/ℓ respectively. This would lead to a pH of 3.86. In this situation the acid contribution of the CO_2-H_2O system is negligible. Under these conditions where the pH is established by the strong acids, the carbonate equilibria are shifted such that HCO_3^- goes from the original value of $10^{-5.6}$ to $10^{-7.4}$ m/ℓ. These relationships are shown graphically on Figure 1. Thus we have a drastic reduction in available HCO_3^- in water as a result of the shift in the pH. However, examination of Figure 2 shows that the other acid radicals are essentially not shifted in their abundance.

All other things being equal, there should be a tendency for rainfall to have a higher amount of dissolved solids with greater acidity. Although the largest part of dissolved material in precipitation is commonly composed of cyclical salts that are dominated by NaCl, the dissolved load in rainfall varies drastically. The sources of this variation is probably manifold, but one strong possibility is that in

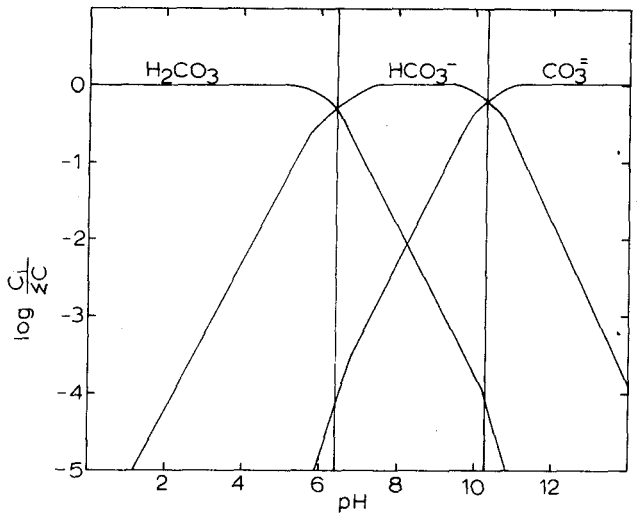

Figure 1. Concentration of carbon-bearing species in the system CO_2-H_2O as a function of pH. Calculated for 25°C. Thermodynamic data from Garrels and Christ (1965).

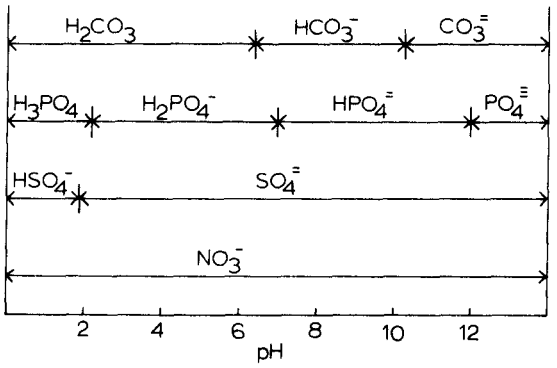

Figure 2. pH range for dominant species of various weak and strong acids. Calculated for 25° C. Thermodynamic data from Garrels and Christ (1965).

strongly acid rain, there is considerable incongruent and congruent solution of particulate material, particularly silicate minerals of various compositions. This would be an extremely difficult thing to document but undoubtedly it has and will continue to occur.

An interesting consequence of the increased load of $SO_4^=$ in precipitation is the increased capability of solutions to oxidize other material. Consider a solution saturated with respect to atmospheric oxygen pressure (0.20 atm) and containing about 12 ppm dissolved O_2. This is equivalent to 0.75×10^{-3} m/ℓ of oxygen atoms which correspond to 1.5×10^{-3} m/ℓ of electrons if all the oxygen is reduced to the -2

valance by redox equilibria. For rain (and ultimately groundwater) containing 5 ppm $SO_4^{=}$, the equivalent oxidation capacity is 0.4×10^{-3} m/ℓ electrons, or 25% of that of the dissolved oxygen. Stagnant groundwater or groundwater removed from contact with the atmosphere commonly has H_2S. The reduction from $SO_4^{=}$ to H_2S permits many redox equilibria to occur.

THE EXTENT OF CHEMICAL WEATHERING

Except in situations where rainwater and/or groundwater is in contact with extremely soluble material, or is in contact with less reactive material for very long periods of time, equilibrium is generally not reached, only approached. This is suggested on several grounds. The equilibrium pH for most silicate-water reactions is generally in excess of 7 and groundwaters in temperate humid climates generally do not have pH's in excess of 7. Consider, for example, the following congruent equilibrium:

$$\underset{\substack{xl \\ olivine}}{Mg_2SiO_4} + 4H^+_{aq} = 2Mg^{++}_{aq} + \underset{aq}{H_4SiO_4} \qquad (6)$$

$$K = 10^{20.33}$$

For rainwater with an initial pH of 5.0 and no initial Mg^{++} or H_4SiO_4, the final equilibrium pH (ignoring carbonate equilibria for simplicity) would be on the order of 8.7, $Mg^{++} = 10^{-4.7}$ m/ℓ, and $H_4SiO_4 = 10^{-5}$ m/ℓ. These collective values are seldom realized, commonly for kinetic reasons or because of competing reactions.

Alternatively, consider an incongruent reaction such as:

$$\underset{xl}{3KAlSi_3O_8} + 2H^+_{aq} + 12H_2O_\ell = \underset{xl}{KAl_3Si_3O_{10}(OH)_2} + 2K^+_{aq} + \underset{aq}{6H_4SiO_4} \qquad (7)$$

$$K = 10^{-8.47}$$

Under a regime of pH values from 5.0 to 8.0, Al is considered geochemically inert. Taking the initial pH of the rainwater to be 5.0 and K^+ and H_4SiO_4 to be = 0, if equilibrium prevails, the final values will be

$$pH_f \simeq 13$$

$$K^+ \simeq 10^{-5} \text{ m/}\ell$$

$$H_4SiO_4 = 3 \times 10^{-5} \text{ m/}\ell$$

Again, these values are not realized in nature for various reasons.

Considering reactions (6) and (7) under more acidic conditions, because the K's are not changed by a change in the initial pH, one can predict that (a) the reactions will proceed from left to right to a greater extent and (b) the final pH will not be as high in either case and (c) the reactions should be more rapid.

For equation (6) with $pH_0 = 4$

$$pH_f \simeq 8.04$$

$$Mg^{++} \simeq 10^{-4} \text{ m/}\ell$$

$$H_4SiO_4 = 3 \times 10^{-4} \text{ m/}\ell$$

and for equation (7) with $pH_0 = 4$

$$pH_f \simeq 10.3$$

$$K^+ \simeq 10^{-4} \text{ m/}\ell$$

$$H_4SiO_4 = 10^{-4} \text{ m/}\ell$$

Furthermore, the assumption that equation (7) is the proper reaction is no longer completely valid, as will be discussed in a subsequent section.

The extent to which mineral-water equilibria in the natural environment are affected by the acidification of precipitation can be precisely evaluated. Similarly the absolute amount of material which <u>might</u> be removed from soil can be evaluated. For example, when considering nutrient capital for the purposes of constructing nutrient budgets or cycles, the soil capital is commonly identified as the upper 30 cm of inorganic soil or the rooting zone.

Consider a rooting zone, 30 cm deep, consisting of material of granitic composition, with a bulk density of 1.5. We may ask the question, how long would it take for <u>all</u> the K, Na, and Ca to be leached from the soil? If we assume that solution is congruent and that these three elements are removed primarily by acid attack by downward percolating precipitation (100 cm per year, net), the following argument prevails:

(1) There are 45g of inorganic material/cm^2 in the rooting zone

(2) Of this 45g, approximately 12g are K, Na, or Ca oxides and the approximate weighted atomic weight of these is 35. Therefore we have about 6g of elemental K, Na, and Ca (= 0.18 moles) or ≃ .24 equivalents.

(3) If precipitation with pH 4.0 is allowed to displace these metals by acid attack, then each liter of precipitation will remove approximately 10^{-4} m of ΣK + Na + Ca. (This assumes that the pH goes from 4.0 to 6.0, or 99% of the acid is consumed).

(4) Each liter/cm^2 corresponds to 10 years. 2.25×10^3 liters will remove all the K, Na, and Ca from the rooting zone in 2.25×10^4 years (22,500 years). A reduction in the initial pH to 3.0 yields a "time until impoverishment" of 2,250 years, still a long time.

This rather simplistic argument does demonstrate that for certain rock types, initially high in certain nutrients, impoverishment by acid rain is unlikely. However, many rock types are not so invulnerable. In the above model, I have ignored the solution of Mg (a similar argument would ensue). Similarly the solution of Al and Fe was ignored but will be treated below.

pH INSENSITIVE REACTIONS

A number of reactions which are insensitive to pH values over a wide range occur in soils. Three types of reactions are common:

(1) No release of cations or anions during congruent solution: This type of reaction is illustrated by:

$$SiO_{2_{xl_{Qtz.}}} + 2H_2O_\ell = H_4SiO_{4_{aq}} \qquad K \simeq 10^{-4} \qquad (8)$$

Only above a pH of 9 (Figure 3) does the solubility of quartz exceed 10^{-4} m/ℓ. It should be pointed out that, for kinetic reasons, the amount of H_4SiO_4 in soil solutions or aqueous ecosystems is not determined by the solubility of quartz. The upper limit is established by the solubility of amorphous silica. The lower limit is established by siliceous organisms.

(2) Σ Cation charges released = Σ anion charges released: - with no H^+ or OH^- involved in the stoichiometry: An example of this type of reaction is the solubility of a salt:

$$NaCl_{xl} = Na^+_{aq} + Cl^-_{aq} \qquad K = 10^{1.58} \qquad (9)$$

However acid rain does have an effect on some equilibria of this type

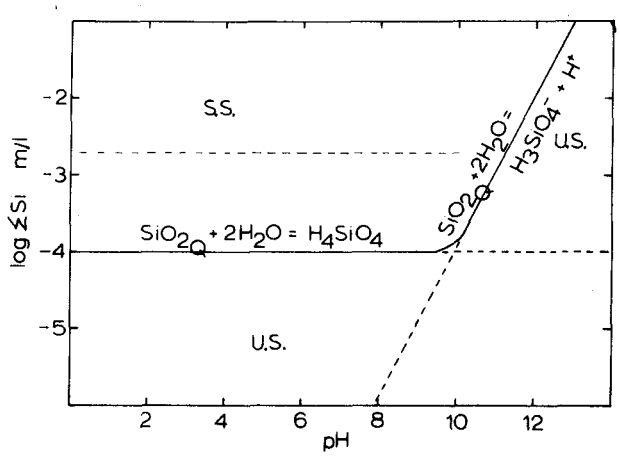

Figure 3. Solubility of quartz as a function of pH. Upper dashed line is the solubility of amorphous silica. S.S. = supersaturation. U.S. = undersaturation. Calculated for 25°C. Thermodynamic data from Garrels and Christ (1965).

because of the "common ion effect" ($SO_4^=$ and NO_3^-). For example:

$$PbSO_{4_{xl}} = Pb^{++}_{aq} + SO^{=}_{4_{aq}} \qquad K = 10^{-7.87} \qquad (10)$$

With $SO_4^=$ levels approaching 10^{-4} m/ℓ in most aqueous ecosystems, we are reducing the mobility of Pb to about 10^{-4}.

(3) No release of cations or anions during incongruent solution. An example of this type of reaction is the conversion of kaolinite to gibbsite:

$$Al_2Si_2O_5(OH)_{4_{xl}} + 5H_2O_\ell = 2Al(OH)_{3_{xl_{Gibb.}}} + 2H_4SiO_{4_{aq}} \qquad (11)$$

$$K = 10^{-4.67} = H_4SiO_{4_{aq}}$$

Again, one should note that there is a tacit assumption of no Al mobility.

pH SENSITIVE REACTIONS

Because of the dissociation equation for water (5), any reaction written so as to consume H^+, can also be written so as to release OH^-, and vice versa. Thus the solubility of gibbsite at low pH may be written (Figure 4):

$$Al(OH)_{3_{xl_{Gibb.}}} = Al^{+++}_{aq} + 3OH^-_{aq} \qquad K = 10^{-36.2} \qquad (12)$$

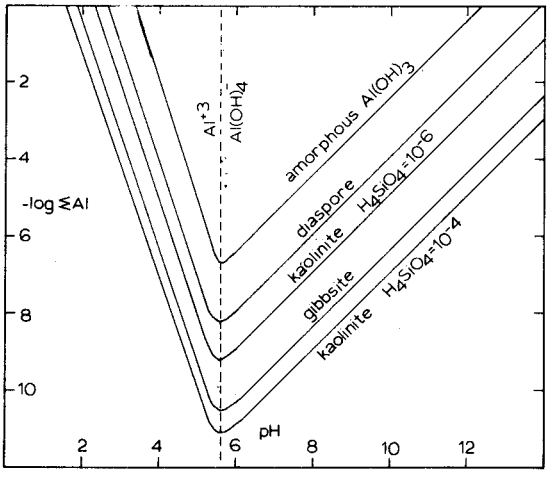

Figure 4. Solubility surfaces of gibbsite, $Al(OH)_3$; amorphous $Al(OH)_3$; diaspore, (AlOOH); and kaolinite, $Al_2Si_2O_5(OH)_4$ for two $H_4SiO_{4_{aq}}$ concentrations as a function of pH. Calculated for 25°C. Thermodynamic data from Garrels and Christ (1965).

or the equivalent

$$Al(OH)_{3_{xl_{Gibb.}}} + 3H^+_{aq} = Al^{+++}_{aq} + 3H_2O_\ell \qquad K = 10^{-5.68}$$

Similarly, aluminum silicate minerals may react either incongruently (equation 7) or congruently with acidified rain (equation 7 would be more typical of reactions with rain having $pH_0 \geq 5.0$), for example (see Figure 4):

$$Al_2Si_2O_5(OH)_{4_{xl}} + 6H^+_{aq} = 2Al^{+++}_{aq} + 2H_4SiO_{4_{aq}} + H_2O_\ell \qquad (13)$$

$$K = 10^{+2.05}$$

The congruent solubility of Al-bearing phases is a function of $(H^+_{aq})^3$. Thus changes in pH sharply change the mobility of this element and Al-phases.

Eh SENSITIVE REACTIONS

Most oxidation-reduction equations in natural aqueous systems involve hydrogen ions (although not all!; see Figure 5). The one I wish to consider is the solubility of the mineral hematite (Fe_2O_3), the stability of which is nearly coincident with that of goethite (FeOOH), a common soil mineral. The solubility of hematite may be represented (written as an oxidation):

$$2Fe^{++}_{aq} + 3H_2O_\ell = Fe_2O_{3_{xl_{hem.}}} + 6H^+_{aq} + 2e^- \qquad (14)$$

Inorganic Eh - pH Solubility Relationships (for metals)					
Oxidation State of Metals in Solid	Oxidation State of Metals in Solute	Charge on Solute	Example	ΔSol. with inc. in Eh	ΔSol. with inc. in pH
Red.	Red.	0	$As_2O_{3_{xl}} \rightarrow H_3AsO^{\circ}_{3_{aq}}$	0	0
Red.	Red.	+	$Fe^{++}\text{-Sil.}_{xl} \rightarrow Fe^{++}_{aq}$	0	Dec.
Red.	Red.	-	$As_2O_{3_{xl}} \rightarrow H_2AsO^{-}_{3_{aq}}$	0	Inc.
Red.	Ox.	0	$As_2O_{3_{xl}} \rightarrow H_3AsO^{\circ}_{4_{aq}}$	Inc.	Inc.
Red.	Ox.	+	$Fe^{++}\text{-Sil.}_{xl} \rightarrow Fe^{+++}_{aq}$	Inc.	Dec.
Red.	Ox.	-	$As_2O_{3_{xl}} \rightarrow H_2AsO^{-}_{4_{aq}}$	Inc.	Inc.
Ox.	Red.	0	$FeS^{-1}_{2_{xl}} \rightarrow Fe^{++}_{aq} + 2H_2S^{-2}_{aq}$	Dec.	Dec.
Ox.	Red.	+	$Fe_2O_{3_{xl}} \rightarrow Fe^{++}_{aq}$	Dec.	Dec.
Ox.	Red.	-	$Fe_2O_{3_{xl}} \rightarrow FeO(OH)^{-}_{aq}$	Dec.	0
Ox.	Ox.	0	$As_2O_{5_{xl}} \rightarrow H_3AsO^{\circ}_{4_{aq}}$	0	0
Ox.	Ox.	+	$Fe_2O_{3_{xl}} \rightarrow Fe^{+++}_{aq}$	0	Dec.
Ox.	Ox.	-	$As_2O_{5_{xl}} \rightarrow H_2AsO^{-}_{4_{aq}}$	0	Inc.

Figure 5. Changes in solubility of phases as a function of pH and Eh.

or

$$Eh = 0.72 - 0.059\log [(Fe^{++})] - 0.177\ pH$$

This equation applies over almost all of Eh-pH space of interest on Figure 6.

As was the case for Al, the solubility of Fe-phases is dependent upon the $(H^+)^3$ value. An independent (of Eh) change in pH sharply changes the mobility of Fe and the stability of Fe-phases.

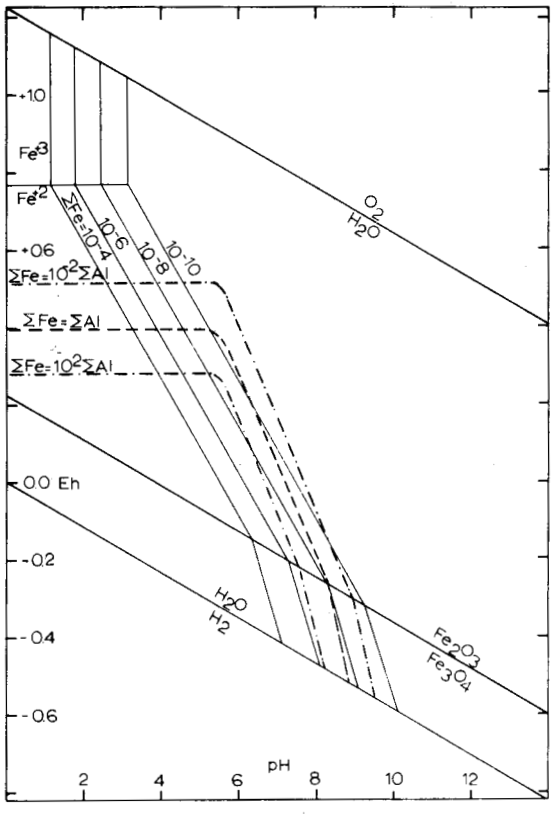

Figure 6. Solubility of hematite (Fe_2O_3) and magnetite (Fe_3O_4) as a function of pH and Eh. Calculated for 25°C. Thermodynamic data from Garrels and Christ (1965).

An independent (of pH) change in Eh will also change the mobility of Fe. As was pointed out earlier, the high $SO_4^{=}$ values in precipitation result in an Eh buffering capacity which is of the same order of magnitude as the oxygen dissolved in the precipitation.

RELATIVE MOBILITY OF ELEMENTS

One might consider the mobility of elements in a particular environment to be relatively constant over time. However, the change in mobility elicited by a change in the pH of rainwater will be related to the stoichiometry of the incongruent (or congruent where appropriate) solution of the phases that contain the elements in question. Consider for example the solubilities of quartz (SiO_2), orthoclase (a feldspar) ($KAlSi_3O_8$), olivine (Mg_2SiO_4), and gibbsite [$Al(OH)_3$]. The respective solution equations are

$$SiO_{2_{xl_{Qtz.}}} + 2H_2O_{\ell} = H_4SiO_{4_{aq}} \qquad (8)$$

$$3KAlSi_3O_{8_{xl}} + 2H^+_{aq} + 12H_2O_\ell = KAl_3Si_3O_{10}(OH)_{2_{xl}} + 2K^+ + 6H_4SiO_4 \quad (7)$$

$$Mg_2SiO_{4_{xl}} + 4H^+_{aq} = Mg^{++}_{aq} + H_4SiO_{4_{aq}} \quad (6)$$

$$Al(OH)_{3_{xl}} + 3H^+_{aq} = Al^{+++}_{aq} + 3H_2O_\ell \quad (12)$$

It is clear that the potential effect of a decrease in pH from, e.g. 4 to 3 is to change the mobility by a factor of 10^0, 10^1, 10^2, and 10^3, respectively.

It is clearly possible to reverse relative mobility of certain elements. Consider Figure 7 on which are plotted solubility contours

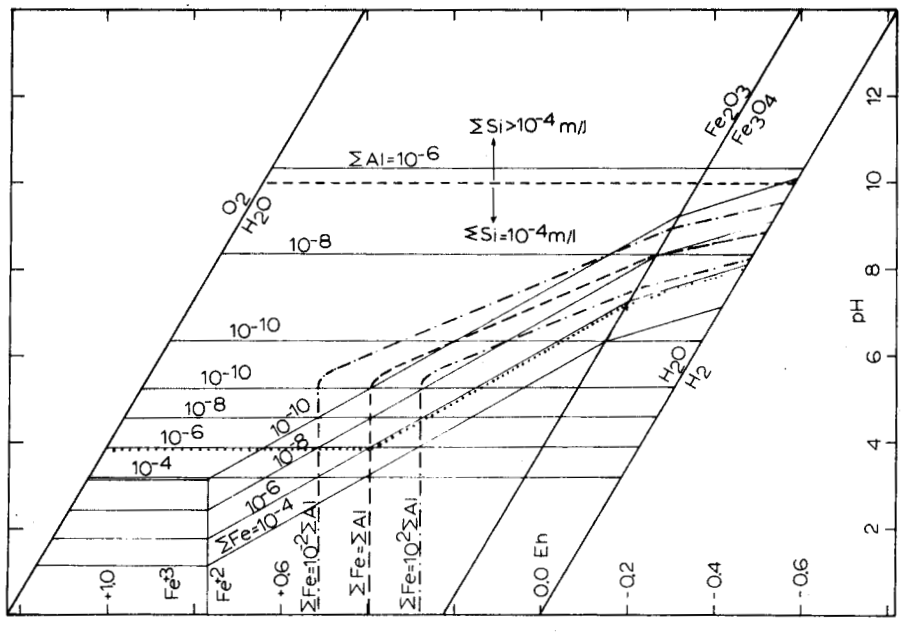

Figure 7. Solubility of quartz, SiO_2; gibbsite, $Al(OH)_3$; and hematite, Fe_2O_3, as a function of Eh and pH. All contours are in m/ℓ. Calculated for 25°C. Thermodynamic data from Garrels and Christ (1965).

for the phases hematite (Fe_2O_3), gibbsite [$Al(OH)_3$]- the most insoluble Al-bearing phase and thus the most stable Al-phase, and quartz (SiO_2). Slight variations in solution characteristics (Eh and pH) can result in

$$Al_{aq} > Fe_{aq} > Si_{aq}$$

$$Al_{aq} > Si_{aq} > Fe_{aq}$$

.
.
.

etc.

As pointed out previously, in nutrient-rich or non-essential element-rich substrate the absolute losses due to acid precipitation may be negligible over the short term. However, increases in the levels of dissolved elements may have significant impact in aqueous ecosystems. This would be true of essential elements in minerals (e.g. Fe^{++} from FeOOH) as well as the trace elements coprecipitated with or adsorbed on soil minerals (e.g. Mn^{++} adsorbed on or coprecipitated with FeOOH). Furthermore, because of the obvious increase in mobility of Al and consequent destruction of clay minerals, the cation exchange capacity of the soil may be altered over a long period of time.

CONCLUSIONS

The acidification of precipitation, primarily rain, causes several significant changes in the characteristics of rainfall. They are:

1. Decreased pH.
2. Increased H^+ buffering.
3. Increased Eh buffering (caused by $SO_4^=$).
4. Increased dissolved solids.

The possible results of this precipitation falling on soil are:

1. Increased mobility of most elements. The change in mobility is essentially: monovalent divalent trivalent cations.

2. Increased loss of existing clay minerals. However, this may under certain circumstances be compensated for by the production of clay minerals which do not have essential (stoichiometric) alkalies or alkali earths.

3. A change in cation exchange capacity - in some situations an increase, in others a decrease.

4. A general proportionate increase in the rate of removal of all cations from the soil. In initially impoverished or unbuffered soils the removal may be significant on the time scale of 10 to 100 years.

5. An increased flux of nutrients through ecosystems contiguous with the soil and through aquatic ecosystems "below" the soil zone.

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ACID PRECIPITATION EFFECTS ON SOIL pH AND BASE SATURATION OF EXCHANGE SITES[1]

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ABSTRACT

The typical values and probable ranges of acid-precipitation are evaluated in terms of their theoretical effects on pH and cation exchange equilibrium of soils characteristic of the humid temperature region. The extent of probable change in soil pH and the time required to cause such a change are calculated for a range of common soils. Hydrogen ion input by acid precipitation is compared to cation inputs from nutrient cycling and other sources. For example it can be calculated that 100 years of acid precipitation (10,000 cm at pH 4.0) could be expected to shift the percentage base saturation in the top 20 cm of a typical midwestern forest soil (cation exchange capacity of 20 meq/100 g) downward 20%, thus lowering the pH of the A1 horizon by approximately 0.6 units, if there are no countering inputs of basic materials.

INTRODUCTION

As our understanding of air pollutants expands it becomes increasingly evident that the forms and effects of these substances as they pass through terrestrial systems may be of equal or greater importance than their final sink. To date most research has been directed toward the effects of air pollutants on plant growth and development (Tamm and Aronsson 1972) while the effects of air pollutants on the soil has received little attention (Bohn 1972). Acid precipitation, a by-product of air pollution, is a phenomenon receiving increased attention in the literature. We believe that the influence of acid precipitation on soil pH and cation exchange equilibria may prove to be the most significant effect of all. It is likely to be quite permanent and have far reaching

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[1]This work supported by NSF (RANN) Grant GI-35106.

influences both on the vegetation growing upon it and the waters draining from it. This paper will use extant data to determine the theoretical effects of acid precipitation on pH and cation exchange equilibria of soils. The magnitude of H^+ ion input by acid precipitation will be compared to cation inputs from nutrient cycling and other sources, and the probable change in soil pH and the time required to cause such a change will be calculated.

DISCUSSION

Likens and Bormann (1974) have noted that water in the atmosphere is generally in equilibrium with prevailing CO_2 pressures and will produce a pH of about 5.7; while Nihlgard (1970) reports a slightly lower value (5.2) for incident precipitation in southern Sweden. Soviet scientists have recorded values ranging from 5.1 to 6.1 (Mina 1965). However, pH values as low as 2.1 have been observed in north central New Hampshire (Likens et al. 1972). Fisher et al. (1968) reports that weekly samples of precipitation collected over a two year period at the Hubbard Brook Experimental Forest were frequently less than 4.0. Mean annual values of 3.9, 3.9, and 4.0 have been reported for three locations in up state New York (Likens 1974). According to data presented by Fisher et al. (1968), Likens et al. (1972) and Likens (1974), H^+ accounts for 44 to 69 percent of the cations in precipitation, while the anions are $SO_4^=$, 59 to 62 percent; NO_3^-, 21 to 23 percent; and Cl^-, 14 to 20 percent.

Acid precipitation entering the soil has three possible fates: (1) it may be neutralized by free bases such as $CaCO_3$ or $NaCO_3$, (2) the acid water may pass through into the ground water or drainage water in soils that are already quite acid and/or have low cation exchange capacity, e.g., sands with low organic matter contents, and the most common situation, (3) acidic ions enter into exchange reactions with cations already present on the soil cation exchange complex.

The ability of soils to store cations and to resist rapid changes in pH is due to their negatively charged particles which behave like cation exchangers (Fig. 1). It is the interaction of H^+ from acid precipitation with this cation exchange capacity (C.E.C.) that determines the effect of the added acidity on soil properties. Cation exchange capacity in soils is almost exclusively a property of decayed organic matter and silicate clays (Table 1) and is usually quantified in milliequivalents per 100 g of soil (meq/100 g).

The composition of the cations attracted to the humus and clay particles determines the soil pH and availability of many plant nutrients. A high C.E.C. results in a high nutrient storage capacity and a resistance to pH shifts. If most of the cations are basic in nature such as Ca^{++}, Mg^{++}, K^+ and Na^+, we say the soil has a high "percent base

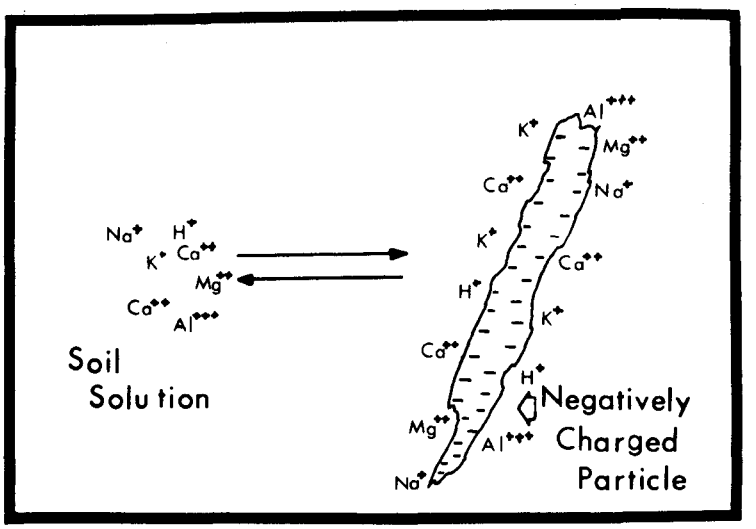

Figure 1. Equilibrium between cations in solution and those absorbed on soil colloids.

Table 1. Cation Exchange Capacities of Soil Components

	C.E.C. meq/100 g
Organic Matter (Humus)	200*
Silicate Clays	
vermiculite	150
montmorillonite	100
kaolinite	10
illite	30
Hydrous Oxide Clays	4
Silts and Sands	negligible

*Variation is commonly 40% of these mean values.

saturation". Since the large ratio of exchangeable ions to those in the surrounding solutions is on the order of 1000:1, the compostion of the soil solution, including pH, is controlled by the degree of base saturation on the exchange sites. The relationship shown in Figure 2

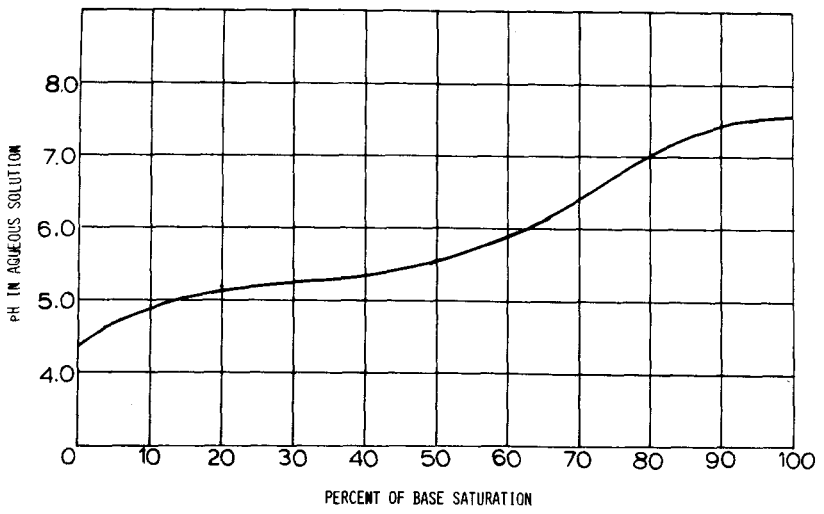

Figure 2. Typical relationship of soil pH to the percent base saturation of the soil cation exchange sites (Lathwell and Peech 1964).

was developed by Lathwell and Peech (1964) for some soils in the northeastern United States. Similar relationships are available in most regions. In general as base saturation goes down so does pH, but not in a linear fashion.

Utilizing existing information about the soil one should be able to determine the magnitude of pH shift that is likely over a given number of years of acid precipitation at a known pH. The following is an example of how one might proceed utilizing a simple set of assumptions. We chose a 1000 square cm area for convenience in unit size and the fact that 1 cm of precipitation then equals 1 liter.

$$1 \text{ cm of precipitation} = 1 \text{ L}/1000 \text{ cm}^2$$

If we examine 20 cm of soil depth we could expect 26,000 g in the reference area if the soil bulk density is 1.3 g/cc, a common value for surface soils.

$$1000 \text{ cm}^2 \times 20 \text{ cm} \times 1.3 \text{ g/cm}^3 = 26{,}000 \text{ g soil}$$

With a C.E.C. of 20 meq/100 g (common in Alfisols and Mollisols, high in Spodozol regions) there would be 5.2 equivalents (eq) of exchange capacity under 1000 square cm to a depth of 20 cm.

$$26{,}000 \text{ g soil} \times 20 \text{ meq}/100 \text{ g soil} = 5.2 \text{ eq}$$

Consider the acid input and its affect on this soil system. On our reference area, 100 cm of pH 4.0 rain (one year's precipitation) would

provide .01 eq H^+ to react with the exchange sites (5.2 eq) under the 1000 cm^2 reference area 20 cm deep.

$$100 \text{ cm precipitation} = 100 \text{ L } H_2O/1000 \text{ cm}^2$$

$$\text{pH } 4.0 = .0001 \text{ eq } H^+/L$$

$$.0001 \text{ eq } H^+/L \times 100 \text{ L} = .01 \text{ eq } H^+$$

That is assuming that pH is a fair measure of total acidity which is true only if it is a strong acid, completely dissociated. With a precipitation PH of 4.0 we could get 1 eq. H^+/1000 eq cm in 100 years; at pH 3.7, 50 years would be required; and at pH 3.0, 10 years would be required. Under these conditions, how long would it take to get a measurable pH shift and how great would it be? If all the H^+ input (1 equivalent in this example) exchanges for basic cations in the top 20 cm of soil we can calculate the shift in percent base saturation. In this example total exchange capacity equals 5.2 eq., one equivalent of acid exchanging with one equivalent of base would produce a 19% base saturation decrease. Using Figure 2 we see that such a shift would result in a pH drop to 5.2 if the initial pH were 6.0. Results differ somewhat depending on the starting pH. If the soil is lower in C.E.C., the shift in base saturation would be proportionately greater and the pH shift somewhat greater depending on the initial pH and percent base saturation.

With fairly well buffered soils, those with a moderate amount of clay or humus, the movement of pH is going to be slow in terms of experimental time, but fast geologically, This indicates that in many experiments measuring changes in soil pH due to acid precipitation is not a reasonable research goal. Further, in the preceeding example certain simplifying assumptions were made: (1) cation input is H^+ only, (2) exchange of H^+ for basic cations is complete, and (3) there are no counteracting forces. These assumptions might lead to the conclusion that complete removal of basic cations to a depth of 20 cm is likely in 520 years if the precipitation has a pH of 4.0, since this would result in an input of 5.2 equivalents of H^+ per 1000 cm^2. This is not likely, however, since the above assumptions do not hold.

There are many countering forces that will reduce the final affect of acid precipitation. Four such countering forces are neutralization by basic substances in the polluting medium itself, nutrient recycling, mineral soil decomposition and exchangeable cations present on negatively charged soil particles. Cation input of H^+ only is not the case as was assumed in the example calculation. Many acidic anthropogenic substances are neutralized by basic substances of similar origin. As shown in Table 2, there is a significant input of the cations Na^+, K^+, Ca^{++}, and Mg^{++} in precipitation. The precipitation input at Indianapolis given by Carroll (1962) has a concentration of .26 ppm Na, .12 ppm K, .69 ppm Ca, and .27 ppm NH_4. Converted to equivalents there are a total of .06 meq of basic cations per liter compared to .1 meq

Table 2. Basic Cations in Precipitation From Several Locales in the United States

	Inputs kg/ha/yr			
	Ca	Mg	Na	K
Indianapolis, IN (Carroll 1962)	6.9	-	2.6	1.2
Walker Br, TN (Henderson et al. 1975)	14.2	2.2	4.0	3.4
Coweeta, NC (Henderson et al. 1975)	5.0	1.1	4.4	2.3
Hubbard Br, NH (Fisher et al. 1968)	2.7	0.6	1.6	0.7
H. J. Andrews, OR (Henderson et al. 1975)	5.0	1.0	1.8	0.2

H^+/liter in pH 4.0 rain. Therefore we could not expect the exchange of H^+ for other cations on the exchange sites to proceed as rapidly or completely as it would if H^+ were the only cation, since other ions will also be competing for exchange sites and thus decrease the effectiveness of the added H^+. The basic cations in precipitation are directly offsetting and have the same effect as the agricultural practice of liming to restore base saturation to a high level.

Likewise, basic substances leached from living plant tissue react with acidic substances to neutralize their acidity. For example, Tamm (1951) and Madgwick and Ovington (1959) report ten-fold increases in calcium content of precipitation collected beneath the forest canopy while Voigt (1960) reports a five-fold increase. Likens et al. (1967) reports average inputs of calcium magnesium, potassium and sodium to the soil of 3.0, 0.7, 2.5, and 1.0 kg/ha respectively. These examples serve to illustrate that significant quantities of basic materials are available to react with acidic materials prior to entering the soil.

A second source of neutralizing substances is the annual litter fall. Gosz et al. (1972) estimated annual litter fall at Hubbard Brook to be 5700 kg/ha. Calcium, potassium, manganese, magnesium, and sodium inputs from the same study were 40.7, 18.3, 10.3, 5.9, and 0.10 kg/ha respectively. In a similar study on a pine forest annual litter fall was 1657 kg/ha with 10.6 kg/ha of calcium, 8.2 kg/ha of potassium, 6.1 kg/ha of magnesium, 1.9 kg/ha of manganese, and 0.5 kg/ha of sodium, (Scott 1955).

Total weight of litter on the forest floor in the northeast as determined by Scott (1955) ranges from 6000 to 133,000 kg/ha with most forests having between 25,000 and 35,000 kg/ha. McFee and Stone (1965) reported a mean forest floor weight of 243,000 kg/ha under undisturbed forests in the Adirondack Mountains of New York containing 101 kg/ha of potassium, and 185 kg/ha of calcium. Obviously, litter fall will be effected by stand age and site quality but the values presented give some indication of the total amount of material deposited as well as the

input of basic elements, which may slow the soil acidification process. Forest vegetation recycles a significant amount of basic cations (Table 3) which act as countering forces in the soil acidification process.

Table 3. Basic Cations Returned to the Soil Surface as a Part of the Annual Litter Deposition Under Forests

	kg/ha/yr			
	Ca	Mg	Na	K
Walker Br, TN (Henderson et al. 1975)	46	8.0	-	19
Coweeta, NC (Henderson et al. 1975)	44	-	-	18
Hubbard Br, NH (Gosz et al. 1972)	40	5.9	-	-
H. J. Andrews, OR (Henderson et al. 1975)	67	-	-	8

The transport of basic cations from deep in the soil back to the surface will have a moderating effect depending on the type of vegetation and the acidity of its decay products. The quantity of basic ions in this litter is frequently as much as .02 equivalents per 1000 cm^2 per year which is more than the acid input expected from 100 cm of pH 4.0 precipitation. However, these are not new bases, but rather ones recycled from the soil below. Still the effect would be to slow down cation loss and the rate of acidification.

Another countering force is the release of basic cations by weathering or decay of the soil minerals themselves. This is difficult to measure and will vary tremendously depending on the nature of soil parent material. The values in Table 4 are estimates based on balance

Table 4. Estimates of Cations Released by Soil Weathering

	kg/ha/yr			
	Ca	Mg	Na	K
Walker Br, TN (Henderson et al. 1975)	58.0	47.0	-	-
Coweeta, NC (Henderson et al. 1975)	0.8	1.8	4.3	2.0
Hubbard Br, NH (Bormann and Likens 1970)	8.0	1.8	4.6	0.1

sheet approaches but give us an idea of the magnitude of this countering effect. In old, highly weathered soils developed from rocks low in calcium and magnesium this would not be important whereas in some soils, especially shallow soils over calcareous materials, it would be an effective countering force.

As pointed out by Norton[2], the aluminum in the soil, which is very important in acid reactions, becomes very soluble and the aluminum oxides behave as bases at low pH giving up OH^-. Further the accelerated decay of silicates in the soil may cause an increase in the release of bases or it may lead to the destruction of clays and the loss of some of the exchange capacity.

The exchange or replacement of basic cations by H^+ should be predicted by laws of mass action such as the Donnan equilibrium where the ratio of two monovalent ions in the soil solution should be the same as the ratio of adsorbed ions on the organic matter and clay.

$$\frac{(H^+)_{ad}}{(M^+)_{ad}} = \frac{(H^+)_s}{(M^+)_s}$$

In the case of monovalent-divalent systems the divalent cation is held more tightly and the relationship given by Gapon (1933) approximates the situation.

$$\frac{(H^+)_{ad}}{(M^{++})_{ad}} = \frac{(H^+)_s}{\sqrt{(M^{++})_s}}$$

These relationships do not hold very well when H^+ is one of the ions involved since it is held very tightly on clays and often enters into the clay lattice displacing a structural ion such as aluminum. These relationships along with the mixed input of cations point out that all acid ions do not replace basic ions and therefore the acidification of the soil is slower than our initial estimate.

The quantity of exchangeable basic cations that tend to buffer the soil against acidification is quite large in many soils. Cline and Lathwell (1963) found in the top 70 cm of a clayey soil exchangeable calcium averaged 7.7 meq/100 gm, magnesium 9.0 meq/100 gm, potassium 0.4 meq/100 gm, and sodium 0.2 meq/100 gm. In the same study a silty profile was found to contain 21.7 meq/100 gm calcium, 4.1 meq/100 gm magnesium, 0.3 meq/100 gm potassium, and 0.1 meq/100 gm sodium. Follett and Trierweiler (1973) report the average calcium, potassium, magnesium, and manganese levels for soils used for the production of field crops in Marion County, Ohio to average 5318, 262, 930 and 32 kg/ha respectively. Calcium, potassium, magnesium, and manganese levels at 3057, 250, 520, and 104 kg/ha respectively are generally lower in unglaciated Washington County, Ohio. These two examples illustrate

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[2]See paper this volume.

that a considerable amount of exchangeable basic material does exist in the mineral soil and as such is available to offset incoming acidity.

There are some other limits on the speed and extent of acidification. For example, as the pH of the precipitation approaches the soil pH, the affects are lessened because the equilibrium of solution ions to exchangeable ions is not affected.

SUMMARY

Acidification of soils is a complicated, many faceted process that is important in plant nutrition, but even with its many complications it would be useful in planning research to calculate the theoretical effects using the techniques above to determine the probable changes in soil pH and base saturation. This will be an important aid in research planning by directing our efforts toward finding parameters that will change measurably during the experimental period. When planning research on acid precipitation effects consideration should be given to those parameters which can be quantified in studies of only a few years duration. Our discussion points out the resistance of most soil systems to pH change, the small likelihood of rapid soil degradation due to acid precipitation, and the difficulty of evaluating this and associated changes in the normal experimental time frame.

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ACIDITY OF PRECIPITATION AS INFLUENCED BY THE FILTERING OF ATMOSPHERIC SULPHUR AND NITROGEN COMPOUNDS - ITS ROLE IN THE ELEMENT BALANCE AND EFFECT ON SOIL

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INTRODUCTION

The data presented here are based upon element balance investigations in a beech forest in Central Germany (Ellenberg 1971).

Being located in an altitude of about 500 m above sea level with an annual precipitation of about 1000 mm, and an acid soil with loess as the main constituent, the test site represents a typical environment for many Central European forests.

Situated apart from larger industrial centers or big cities, it may also - for Central European conditions - be considered as a clean air region with a relatively low level of air pollution.

METHODS

The methods used to measure the element stores and the element fluxes in the forest ecosystem were described in earlier papers (Mayer 1971, 1972; Ulrich et al. 1972a, b; Pavlov 1972). They included the use of

(a) faingauges for collection of wet precipitation (wetfall) and dry deposition (dryfall) beneath the tree canopy and on a non-forested area close to the forest test site.

(b) stemflow collectors

(c) funnels to collect the litterfall

(d) funnel lysimeters for collection of the element flux coupled with seepage water below the humus layer

(e) tension lysimeters for collection of the element flux below the root zone

(f) plant and soil chemical analysis to determine the element content of the different parts of the ecosystem.

RESULTS

Some results of the element flux measurements, expressed in kilograms per hectare per year and kiloequivalents per hectare per year, respectively, are given in table 1 and 2. Each flux was sampled continuously over 5 (or 3) years and analyzed monthly. These data were summed up for annual values.

Table 1 : Solling Beech Site - Annual Element Input
(Average Values 1969 - 1974)

a.	Water l/m^2	H	Na	K	Ca	Mg	Fe	Mn	Al	Cl	S	P	N	NO_3-N
		kilograms per hectare per year												
(1) Non-forested area (above canopy)	1080	.90	8.2	3.8	13.9	2.2	.90	.6	1.2	17.9	24.5	.71	23.7	7.1
(2) Beneath canopy	796	1.21	12.5	22.9	26.0	3.7	1.2	3.0	1.5	31.6	44.2	.55	24.7	7.4
b.		kiloequivalents per hectare per year												
(1) Non-forested area (above canopy)		.90	.36	.1o	.69	.18	.02	.02	.13	.50	1.53	.07	1.69	.51
(2) Beneath canopy		1.21	.54	.59	1.30	.30	.05	.11	.17	.89	2.76	.05	1.76	.53

Table 2 : Solling Beech Site - Annual Element Fluxes
(Average Values 1969 -1972)

a.	Water l/m^2	H	Na	K	Ca	Mg	Fe	Mn	Al	Cl	S	P	N
		kilograms per hectare per year											
(1) Litterfall	-	-	.7	16.	16.2	1.6	1.8	5.1	.5	.8	3.2	4.0	49.4
(2) Seepage below root zone (100 cm)	531	.30	10.6	5.9	16.6	3.4	.1	5.6	12.7	33.	27.4	.05	6.
b.		kiloequivalents per hectare per year											
(1) Litterfall	-	-	.03	.41	.81	.12	.06	.19	.06	.02	.20	.39	3.53
(2) Seepage below root zone		.30	.46	.15	.83	.28	0.	.21	1.41	.94	1.71	.005	.43

For most elements the input by precipitation (wetfall plus dryfall) to the soil beneath the tree canopy is considerably larger than that to the canopy surface, as measured with the aid of raingauges on a non-forested area. Two effects may be responsible for this:

(1) Leaching of metabolites originating from the internal turnover of the trees, mainly from the leaf surfaces.

(2) Washing out of substances from leaves, branches and stems. The origin of these substances are airborne particles and atmospheric aerosols intercepted by the trees from the atmosphere.

From an ecological view this latter process is of main importance because it represents the filtering effect of the forest towards atmospheric substances. These substances have to be regarded as an input to the forest ecosystem in addition to the input measured as wetfall plus dryfall above the canopy surface or on non-forested areas.

For a judgement of the effectiveness of the forest in cleaning a polluted atmosphere, and of the impact of the filtered substances on the forest ecosystem itself, the magnitude of both fluxes - leaching and filtering - is required. Since there exists no experimental approach to separate the fluxes an indirect way for their assessment was proposed (Mayer et al. 1974).

This method, applicable only on deciduous forests, is based upon the assumption that during the leafless winter time the internal turnover of the trees does not contribute significantly to the element content of the precipitation within the forest stand. In fact, most investigators describe the leaching process to take place at the leaf surfaces (Yamada et al. 1966, Tukey 1970). The difference between the element input coupled with precipitation to the forest soil and that to the forest canopy must be - during the state of defoliation of the trees - due to the filtering of atmospheric substances by the trees. For the summer months no similar procedure for calculation is available. A reasonable estimate for the filtering is received by using the same ratio between free area input and filtering for the winter as well as for the summer months. This assumption may be justified by the fact, that concentration of elements in the atmosphere affects both of these incoming fluxes in the same way.

On the other hand the estimate is rather on the minimum side for the same filter efficiency is assumed for the foliated as well as for the defoliated state of the trees.

Following this procedure, the filtering and leaching have been calculated on a seasonal base (winter: November - April, summer: May - October).

Average annual values are given in table 3.

Table 3 : Solling Beech Site - Annual Element Input by Filtering from the Atmosphere

	Na	K	Ca	Mg	Fe	Mn	Al	Cl	S	P	N	NO_3-N
(1) $kg.ha^{-1}.year^{-1}$	3.8	7.3	8.6	1.3	.5	1.5	.5	12.5	14.9	.09	4.8	1.4
(2) $keq.ha^{-1}.year^{-1}$	.17	.19	.43	.11	.02	.06	.06	.35	.93	.01	.34	.10

The input/output difference for the forest ecosystem gives the changes in the element stores within the system. The annual changes in the element stores (increments) of the trees have been measured (cf. Mayer 1971), results are given in table 4 (1).

Table 4 : Solling Beech Site - Annual Changes in Element Stores
(positive = gains ; negative = losses)

	H	Na	K	Ca	Mg	Fe	Mn	Al	Cl	S	P	N
a.	kilograms per hectare per year											
(1) In trees (bole)	-	.1	6.6	7.7	1.7	.7	3.4	.1	.1	.5	2.1	13.1
(2) In soil	1.7	-1.3	-1.4	-1.8	-1.6	.9	-6.9	-11.1	-2.9	11.5	-1.35	9.4
b.	kiloequivalents per hectare per year											
(1) In trees (bole)	-	.00	.17	.39	.14	.02	.13	.01	.00	.03	.20	.94
(2) In soil	1.7	-.06	-.03	-.09	-.13	.03	-.26	-1.23	-.08	.72	-.13	.67

It is now possible to calculate the annual changes in element stores within the soil, ΔCS, from

$$\Delta CS = IN_1 + IN_2 - OUT - \Delta CP$$

where IN_1 = input by wetfall plus dryfall (table 1 (1))

IN_2 = input by filtering (table 3)

OUT = output by seepage below root zone (table 2 (2))

ΔCP = changes in element stores in the trees (table 4 (1))

Results of this calculation are given in table 4 (2). Negative figures are standing for element losses, positive values for element gains.

DISCUSSION

To take a closer look on the effects of acidity some relevant figures are drawn from tables 1 - 4 and repeated in table 5, together with the input of hydrogen ions to the mineral soil as measured with the aid

Table 5 : Solling Beech Site - Annual Hydrogen Balance

	kiloequivalents per hectare per year		
(1) Precipitation input to canopy (wetfall plus dryfall)	.90	1.53	.51
(2) Filtering (sum of S plus NO_3- N)	1.03	.93	.10
(3) Precipitation input to soil surface	1.21	2.76	.53
(4) Buffering of H^+-ions within stand = (1) + (2) - (3)	.72		
(5) Input to mineral soil	2.00		
(6) H^+-ion production by litter decomposition = (5) - (3)	.79		
(7) Output with seepage below root zone	.30		
(8) Buffering of H^+-ions within mineral soil = (5) - (7)	.70		

of funnel lysimeters.

Under the conditions prevailing in the test area it may be assumed that most of the sulphate and nitrate found in the precipitation entered the atmosphere not as neutral salts but rather as sulphur dioxide and nitric or nitrous oxides. These oxides were then transformed by oxidation and dissolution to form finally sulphuric and nitric acid. In these processes each equivalent of nitrogen and sulphur requires one equivalent of hydrogen ions.

Comparing the sum of sulphate and nitrate in the incoming precipitation with the amount of hydrogen we realize that more than half of the respective acids are neutralized by bases, that is by other air contaminants like calcium oxide CaO.

In the same way the sulphur and nitrogen filtered from the atmosphere by trees and then washed out by rain contribute to the acidity. again the acidity is neutralized to a great extent by filtered air contaminants or by plant metabolites. The hydrogen ion input into the mineral soil as measured in lysimeters is 2 keq . ha^{-1} .$year^{-1}$, from which 60% = 1.21 keq . ha^{-1} . $year^{-1}$ originate from the precipitation input, 40% from the litter decomposition with mineralization of nitrogen and sulphur compounds.

While in calcareous soils nearly the total amount of hydrogen ions is neutralized, in the acid soil under consideration, where aluminium forms the buffer system for the soil solution, still more than 80% of the acidity is neutralized.

This buffering of the soil solution takes place in the upper 20 to 30 cm of the soil, most accentuated in the uppermost 1 to 2 cm of the mineral soil. Here pH values of as low as 3 are observed.

Comparing the input-output data from the Solling beech forest with those of a spruce forest in the same area, table 6, (Mayer et al. 1974), it can be seen that the hydrogen ion and sulphur fluxes in the spruce forest exceed the ones of the beech forest considerably, so that all effects associated with acidity of precipitation are expected to be more accentuated here.

Table 6 : Comparison Beech/Spruce

	kilograms per hectare per year			
	H		S	
	Beech	Spruce	Beech	Spruce
(1) Precipitation input to canopy (wetfall plus dryfall)	.9	.9	24.5	24.5
(2) Precipitation input to soil	1.21	2.61	44.2	75.4
(3) Output with seepage below root zone	.30	.35	27.4	43.

CONCLUSIONS

The element balance data allow to draw some conclusions regarding the effect of acidity of precipitation on the forest ecosystem:

The buffering of protons - and to a minor extent accumulation of Fe in the mineral soil balanced by the loss of Al, Mn and - to a smaller extent - Na, K, Ca and Mg. This is possible by the weathering of silicates, or - as in the case of K, Ca and Mg - by desorption from the exchangeable fraction.

These processes definitely change the soil chemical conditions in the uppermost 1 to 2 cm of the soil. While tree growth is probably not affected by the acidification of this layer, a disturbance of all plants rooting very close to the soil surface, as e.g. germinating plants, is to be expected.

Ulrich et al. (1968) have shown, in which way this could happen: In a germination experiment with oats they found evidence that the damage of plants grown on soils with pH around 3 or lower was due to an

inundation with Al and Fe, and perhaps Mn. The high concentration of these elements in the soil solution at low pH led to a blocking of the phosphate transport from the seeds to the shoots. This process may be a sound explanation for the difficulties met in recent years in the natural reproduction of beech in Germany. Another effect of the acidity of precipitation is probably the accumulation of sulphur in the soil, which becomes evident from the element balance. The question in what form sulphate is accumulated is still under study. It may be tied up in only slightly soluble minerals of the alunite - jarosite group, known from acid soils (van Breemen, 1972). In this minerals of the type $AlOHSO_4$ each sulphate requires one equivalent Al.

The loss of Al, which is shown in table 4 (2) gives the amount annually set free by the weathering of silicates. It corresponds with 80 kg of clay minerals or plagioclase; or with 130 kg if the aluminum set free by weathering is partly tied up in newly formed sulphates. If we keep in mind that the acidification is effective mainly in the top 1 to 2 cm of the soil, this means an annual loss of about 1% of the total clay and plagioclase of the loess soil. From this reasoning a manmade podzolization of the upper A-horizons seems possible.

Finally the acidification of the soil and the associated loss of Mg may become a problem in the supply of this nutrient element in near future. A great number of recent leaf and needle analysis' point into this direction. The same is true for manganese. By the annual loss of nearly 6 kg/ha the total store in the upper 20 cm of the soil is depleted by 0.3%. As a consequence the Mn-concentration in rivers and in young river sediments reach considerable values.

ABSTRACT

Acidity of throughfall precipitation is increased by the filtering of sulphur and nitrogen from the atmosphere by trees. An element balance for a beech forest is given. As a consequence of acidification the soil chemical conditions are changed in a way, that plants rooting close to the soil surface are affected. Losses of nutrients may pose a problem in forest plant nutrition in the near future in Central European forests on light or medium textured acid soils.

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THE EFFECTS OF ACID RAINFALL AND HEAVY METAL PARTICULATES ON A BOREAL FOREST ECOSYSTEM NEAR THE SUDBURY SMELTING REGION OF CANADA

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ABSTRACT

Sulphur dioxide emissions have occurred on a gigantic scale at Sudbury from nickel-copper smelters. Soil erosion has followed the destruction of large areas of forest. Rainfall has been found highly acidic, frequently less than pH 3.0 in 1971. Metal accumulation in the soils (to distances of 50 km) have occurred for nickel and copper. The combination of heavy metal particulate fall-out and acid rainfall has caused soils to become toxic to seedling survival and establishment. Erosional loss has contaminated lakes and water courses with consequent long distance transport of metal loads. The very low soil pH's are associated with mobility of toxic aluminum compounds in these soils. The effects of high acidity and high sulphur and heavy metals have been to cause fundamental changes in soil organic matter structure. These profound and damaging changes may be only indicative of the extreme local conditions or may be a harbinger of what can be anticipated in other acid rain areas.

INTRODUCTION

The Sudbury area of Ontario contains one of the world's major ore deposits of nickel and copper, as well as sizeable quantities of many other metallic sulphides. Initial discoveries were made in the 1880's and smelting dates back some 80 years. Three smelters have operated, with the largest one being at Copper Cliff, 8 km west of Sudbury, a smaller one, also owned by the International Nickel Company of Canada, at Coniston, 14.4 km east of Sudbury, and a third, owned by Falconbridge

Nickel Company, 16 km north-east of Sudbury at Falconbridge. Because of the massive quantities of ore smelted each year and because of its high sulphur content, the emissions of sulphur dioxide have been on a scale unmatched elsewhere in the world. Production figures have mounted steadily since 1939. In 1972, in excess of 3 million short tons of sulphur dioxide gas was emitted into the atmosphere. This potentially phytotoxic gas has caused extensive damage over a very large area, with widespread destruction of the mixed boreal forest of the region, and damage to forests over an even greater area. Despite the improvements brought about in pollution control, the introduction of sulphur acid and sulphur-producing plants and the construction of increasingly tall smokestacks, damage to vegetation continued to spread at least until the introduction of the world's tallest smokestack of 1250 feet (403 metres) at Copper Cliff in 1972 and the closing down of the Coniston smelter also in 1972.

Dreisinger (1970) reported that in the region during the period 1964-68, the area having at least an atmospheric average SO_2 concentration of 0.005 ppm covered 2,181 square miles (5,600 km^2), while 246 square miles (630 km^2) had average levels of 0.020 ppm or more. In terms of potentially injurious fumigations during the May-September growing season, an area of 2136 square miles (5,470 km^2) was found to be subjected to one or more fumigations and 569 square miles (1400 km^2) were subjected to 10 or more such episodes.

The sulphur dioxide emissions in the area amount to a significant fraction of the total for North America. Estimates range as high as 25% of the smelter total and 10% of the sulphur dioxide total. Damage to the forests has been partially selective in that outside the central core of almost total destruction a range of species susceptibilities have been shown. The coniferous species and especially white pine (*Pinus strobus*) are the most susceptible. White pine is almost absent within 12 miles (19.3 km) of the smelters and growth is poor and damage was frequent for a further 7 miles (11 km) (Linzon 1958). There appeared to be reduced radial and volume increments and increased tree mortality of this tree, in direct proportion to the closeness of the source of sulphur dioxide. Some tree species, such as red maple *(Acer rubrum)* and red oak (*Quercus rubra*) are more resistant, perhaps as a result of their deciduous nature, and survive to within 5 km of the smelters. They are partially defoliated in most years and the crowns die back, with new shoots developing from basal branches. Leblanc and Rao (1966) suggested that the sulphur dioxide fumigations are responsible for the paucity of lichens near Sudbury.

The soils of the area are incipient podzols and range in pH, in non-fumigated areas, from 3.8-5.2. They are shallow and with a low organic content. The area was glaciated within the last 12,000 years and glacial till fills some of the valleys to a depth of 30 feet. The whole region is dotted with innumerable lakes, which previously had a high reputation for sports fishing. Apart from Sudbury itself, with

approximately 90,000 inhabitants, the population of the area is sparse. Soil erosion has taken place over a very large central area, so that much of the higher ground over at least 160 square miles (416 km^2) is devoid of soil and vegetation and consists of blackened rocks.

The lakes of the area have received increasing attention, with the realization that many of them to the south-west of Sudbury have become acidic within the past 15 years, and their fish populations eliminated! (see Beamish [1975] in this volume). This effect has damaged lakes in Killarney Provincial Park as far as 50 miles (80 km) away. The prevailing winter wind directions are to the south-west and snow analyses have indicated highly acidic snows melting, with resultant acidic run-off into lakes in spring time. Gorham and Gordon (1960) found acidic lakes with high sulphate values to the north-west of Falconbridge. Stokes, Hutchinson and Krauter (1973) and Stokes and Hutchinson (this volume) have found lakes with pH values as low as 4.0 within a few kilometres of the smelters, and have described depletion of phytoplankton populations in these lakes. They also showed the heavy metals, nickel and copper, to be present in toxic concentrations in many of these lakes. Isolates of some surviving algal strains (of a small number of species) were found to be much more tolerant of heavy metals, especially the locally contaminating ones, nickel and copper, as well as being more tolerant of low pH than similar non-Sudbury strains.

Both Gorham (1975) and Norton (1975) have already referred to the theoretical possibility of solubilization of aluminum compound, and of manganese components of clay minerals at excessively low soil pH's. Norton stressed the necessity of soil pH's below 3.0 and the presence of free sulphuric acid to achieve this, and concluded that such extremes were unlikely to be achieved by acid rains, in view of the normal buffering capacity of soils (lakes in the Sudbury region are mainly, but not exclusively, poorly buffered and naturally oligotrophic). A similar mobilization of other potentially toxic heavy metals could be anticipated at such low soil pH's, whether these metals were naturally present in the soils or were anthropogenic additions.

The large sulphur dioxide emissions in the Sudbury area and their effects on vegetation and soil chemistry have been studied in some detail (Hutchinson and Whitby, 1974, Whitby and Hutchinson 1974, and Whitby, 1974). They concluded that widespread acid rains were occurring in the Sudbury area, with pH levels down to less than 3.0 in the years 1970 and 1971. Soil pH values and pH values through the soil profile from the surface downward and with distance from the Coniston smelter (the one studied) showed an increase with depth and distance. Heavy metals were a serious and complicating factor. For example, in 1971, 192 tons of nickel, 145 tons of copper, 1130 tons of iron and 4.5 tons of cobalt per 28 days were released as airborne contaminants from two of the three smelters at Sudbury. Soils are toxic to seedling establishment over a wide area. Metals have accumulated in the foliage of naturally-occurring living vegetation. The effects on soil chemistry,

especially on organic composition, have been profound.

The possibility of metal contamination around smelters has been recognized for a long time, e.g. Harkins and Swain (1908). More recently, the long distance dispersal of metal particulates from smelters has also been recognized. Kerin (1971) and Djuric et al. (1973) reported on lead, zinc and manganese contamination in the vicinity of lead, zinc and steel works in Jugoslavia. Lead was found to be very finely dispersed and spread over an even greater area than sulphur dioxide near Mezica, Jugoslavia. Buchauer (1971) reported on zinc and cadmium contamination near the zinc smelter at Palmerton, Pennsylvania, U.S.A., and concluded that metal contamination caused greater vegetational damage than did sulphur dioxide. Acid rain-metal interactions have been rather neglected to date. This paper attempts, for the Sudbury region, to consider the consequences, in an area of normally acidic, incipient podzolic soils, of massive inputs of both potentially toxic metals and acidic rainfall.

It should be noted that much of the damage has been caused as a result of past fumigations and that the new 1972 403 metre stack at Copper Cliff has markedly improved air quality in the town of Sudbury itself.

METHODS

SITES

The main study was carried out along transects from the Coniston smelter, which was chosen because it is situated off the main ore bodies of the Sudbury basin and provides largely uninhabited areas to the east, south and north. The sample sites for both soil, vegetation and rainfall were chosen at the tops of the numerous small hills in the area. Unlike the valley, glacially derived soils, those on the hill tops are less glacially contaminated and are largely derived from the parent bed rocks. The soils originally were grey-wooded podzols. Most soil horizons were severely eroded around Coniston. In all, 25 sites were sampled and profiles taken. Samples were taken at least 100 m from roads to minimize traffic inputs.

VEGETATION AND SOIL ANALYSES

Vegetation samples were collected in 1969-1971, in June and August each year. Species selection was complicated by the lack of many species common to the mixed coniferous forests at sites close to the smelters. This zone of species impoverishment extends 16 to 24 km from the Coniston smelter, due to sulphur dioxide damage. Nine sites were sampled for vegetation, leaves from separate trees or herbs of the

same species were mixed and the composite sample washed with a dilute detergent, rinsed in five changes of distilled water and dried at 60°C. Homogenized samples were used for metal analysis.

Rainfall samples were collected during the summers of 1970 and 1971 in 2-litre polyethylene containers set above the ground. Samples were collected monthly and stored at 4°C prior to analyses. Those for metal analyses were acidified with a small quantity of nitric acid, to prevent deposition of metals on the surface of the container.

Soil reaction and conductivity of the soils was measured on field-wet samples, with addition of enough water to produce a water:soil ratio of 1:1 for pH and 2:1 for conductivity. Soils for metal and sulphate analysis were dried at 105° for 24 hours, sieved through a 0.2 mm mesh and homogenized. Two g samples were placed in Teflon dishes, digested with Analar 40% HF:40% H_2SO_4, and dissolved in 18% HNO_3. A dilution to 50 ml was made and analyzed for 18 metals by atomic absorption spectrophotometry. Duplicates were run of all samples and reagent blanks and background corrections lines used where necessary. Two tenth g plant samples were used, pre-digested for 16 hours in 1:1 73% HNO_3:73% $HClO_4$, heated to 75°C for completion of the digestion and then diluted to 10 ml. Metals were analyzed as above.

RAINFALL

Total volume, pH and conductivity of rainfall were measured shortly after collection. The samples were filtered to remove insoluble components and 5 ml of 73% HNO_3 was added to keep in solution those metals which tend to be precipitated or adsorbed. When precipitation was low, samples were made up to 50 ml and analyzed as for soil samples.

SOIL-WATER EXTRACTS

Soil water extracts were prepared for analysis by using a 1:3 ratio of air dried soil to distilled water and shaking for two hours at room temperature. Samples were then filtered through Whatman #42 paper prior to use as a bioassay medium or for analysis.

WATER SOLUBLE SULPHATE

Soil water extracts were obtained as above but using a ratio of 1:5 dried soil to distilled water. A 1 ml extract was added to 9 ml reagent, consisting of 43 g ammonium acetate in 0.275 N acetic acid. One ml of 6 N.HCl "seed" was added to each solution and stirred for one minute. Five tenths g barium chloride was added and allowed to react for two minutes. The resulting suspension was stirred and absorbance measured in a Beckman spectrophotometer at a wavelength of 420 mμ.

Sample readings were compared with standard sulphate absorption curves and the results expressed as ppm dry soil weight.

BIOASSAYS

The simple techniques used for both field and laboratory bioassay experiments are described in Whitby and Hutchinson (1974).

EXTRACTION AND ANALYSES OF SOIL ORGANIC MATTER AND FULVIC ACID FRACTIONS

A somewhat complicated procedure was followed for the extraction and purification of the modified Sudbury soil organic matter. This was developed with the assistance of Dr. M. Schnitzer and is a modification of his previously described methods. Details will be published elsewhere.

RESULTS AND DISCUSSION

ACIDITY OF RAINFALL AND DRY PRECIPITATION

During the summers of 1970 and 1971 dustfall and rainfall collectors were located at a number of sites at increasing distance from the Coniston smelter. Two transects were used, one to the south, which would also be influenced by Copper Cliff, and one to the east, which is subject to Falconbridge influence as well as Coniston. Data are presented for two contrasting periods, i.e. 1) in 1970, June 23- July 21, when rainfall was heavy and scrubbing of the atmosphere occurred, and 2) July 21- August 4, 1970 when no wet precipitation occurred and the dry fallout was diluted to 50 ml with distilled water for analysis. Data for pH conductivity and sulphate are give in Tables 1 and 2. A comparative wet period is given for 1971, Table 3.

It is clear that both conductivity and sulphate content of rainfall or dry fallout increase with proximity to the smelter sources, and that pH decreases to highly acidic levels. Rainfall is both strongly acidic and of a very high sulphate content in the Sudbury region. More complete analyses are given in Whitby (1974) but the data presented in Tables 1-3 are representative. Sulphate contents are highest when wet precipitation occurs, suggesting effective scrubbing of the sulphur dioxide laden air during rainfall. The much lower dry precipitation values indicate a much wider dispersal of sulphur dioxide during dry periods. The volumes of rainfall affect conductivity quite markedly, influencing both hydrogen ion concentration, dissolved salts and metallic ions. Rainfalls of less than pH 4.0 appeared the normal

Table 1. pH, conductivity and sulphate content of rainfall-dustfall in samples on a transect from the Coniston smelter during period June 23 - July 21, 1970

Distance miles		km	Amt. rainfall collected (ml)	pH	Conductivity μ mhos	Sulphate $mg/m^2/28$ day
1.0	S	1.6	628	2.85	450	2108
1.0	N	1.6	1290	3.67	186	1761
1.1	S	1.7	740	2.96	448	5456
1.2	S	1.9	1350	3.40	190	1536
4.6	S	7.4	1470	3.25	168	1761
8.4	S	13.4	834	3.72	64	329
12.0	E	19.2	580	4.34	45	347

Table 2. pH, conductivity (μmhos) and sulphate content ($mg/m^2/14$ days) in dry precipitation following in transects from the Coniston smelter during the period July 21 - August 4, 1970. No rainfall fell in this period. Volumes were made to 45 ml with deionized water for pH and conductivity. 5 ml of dil. HNO_3 was added for sulphate and metal analyses.

Distance miles		km	pH	Conductivity	Sulphate
0.95	S	1.6	1.60	11,100	94
1.0	S	1.6	2.79	930	62
1.0	N	1.6	2.36	2,725	198
1.1	S	1.7	2.09	3,650	136
1.2	S	1.9	2.74	950	75
4.6	S	7.4	3.80	129	87
8.4	S	13.4	4.64	42	74
12.0	E	19.2	6.16	65	93

within at least 10 miles of Sudbury. Wind direction is of considerable importance with respect to point sources but was not measured in this study. Rather, bulk samples over 28 day periods were used.

HEAVY METALS IN RAINFALL

The airborne dispersal of heavy metal particulates in the Sudbury area was measured as influenced by distance from smelters, by wet or dry precipitation. Data are presented in Tables 406 for equivalent periods to those for pH etc. Nickel, copper, cobalt and iron are smelted in the

Table 3. pH, conductivity (μmhos) and sulphate content ($mg/m^2/28$ days) of dustfall-rainfall collected in the Coniston-Sudbury area in 1971, May 13 - June 10.

Distance from Coniston miles		km	Volume rainfall collected (ml)	pH	Conductivity	Sulphate
0.5	S	0.8	1250	2.93	1850	5456
1.0	N	1.6	1200	2.76	2170	1401
6.5	E	10.4	1080	3.53	320	620
8.4	S	13.4	960	3.70	335	620
35.0	S	56.0	1225	4.25	170	533
65.0	S	104.0	1100	4.10	94	131

Table 4. Metal analyses of rainfall-dustfall collected at various distances from the Coniston smelter during the period June 23 - July 21, 1970. (expressed as $mg/m^2/28$ days).

Distance miles		km	Nickel	Copper	Cobalt	Iron	Zinc	Lead
1.0	S	1.6	271	122	8.5	144	5.7	1.2
1.0	N	1.6	161	58	3.7	103	8.6	2.5
1.1	S	1.7	273	131	8.7	111	6.0	9.4
1.2	S	1.9	95	85	4.2	34	7.4	3.7
4.6	S	7.4	16	22	0.5	47	4.9	4.5
8.4	S	13.4	2	3	0.2	5	2.3	nd
12.0	E	19.2	8	2	0.1	7	5.4	nd

nd = below detection limit

area, while zinc and lead are not, but are present in the ore in trace amounts. It is apparent from the data that the metals nickel, copper and iron are deposited or rescrubbed from the air in large quantities close to the smelter. Zinc and lead did not show such a clear-cut trend. Location of site is an important variable. For example, iron was deposited in large quantities at a site 1.6 km north of Coniston (Table 6) when, presumably, winds from the Falconbridge iron ore recovery plant were involved. Deposition during a dry period (Table 5) was a good deal less at sites close to the smelter than during a wet period (Tables 4 and 6). In dry periods the particulates were much more widely dispersed, presumably over a much greater area. It is apparent that metal inputs into the surrounding ecosystems are considerable and are combined with a highly acidic rainfall and very high sulphate inputs. These conditions could potentially lead to high solubility of the heavy metals in the soils and a) their availability for

Table 5. Metal analyses of dry precipitation-dustfall collected at various distances from the Coniston smelter during the period July 21 - August 4, 1970. Data are given as $mg/m^2/14$ days.

Distance miles		km	Nickel	Copper	Cobalt	Iron	Zinc	Lead
0.95	S	1.6	2.6	2.5	0.2	10	0.7	nd
1.0	S	1.6	4.1	2.8	0.3	10	1.1	nd
1.0	N	1.6	23.3	10.2	0.6	28	1.0	nd
1.1	S	1.7	4.1	5.1	nd	9	0.7	nd
1.2	S	1.9	2.3	3.5	0.1	8	0.6	nd
4.6	S	7.4	1.7	3.9	0.4	7	0.4	nd
8.4	S	13.4	0.4	0.4	nd	0.4	nd	nd
12.0	E	19.2	0.9	0.7	0.1	3.0	0.5	nd

Table 6. Heavy metal concentration of rainfall-dustfall collections along transect from Coniston smelter, collected from May 13 - June 10, 1971. Concentrations are given in $mg/m^2/28$ days.

Distance miles		km	Vol. rain ml.	Nickel	Copper	Cobalt	Iron	Zinc	Lead
0.5	S	0.8	1250	288	205	5.5	53	6.9	8.9
1.0	N	1.6	1200	127	67	2.6	1513	3.6	5.7
6.5	E	10.4	1080	13	5	0.9	75	3.6	1.2
8.4	S	13.4	960	11	15	0.1	129	3.5	5.1
35.0	S	56.0	1225	3	3	0.3	69	2.5	3.5
65.0	S	104.0	1100	1	6	nd	74	5.1	2.9

plant uptake and b) loss through run-off into water bodies.

EFFECTS ON SOIL pH AND HEAVY METAL CONTENT

Examples of the soil pH and its variation with profile depth and with distance from the smelter are given in Table 7. It can be seen that surface soils within approximately 7.4 km from the Coniston smelter now have a pH of less than 3.0. In some cases this very low pH is continued to a depth of 10 cm in the profile. In the data presented, 'normal' soil pH's for the region are only reached at distances in excess of 19 km. These very low pH's appear to be the result of both wet and dry precipitation of sulphur dioxide contaminated air, and indicate the strong likelihood of free sulphuric acid in many surface soils.

Table 7. The pH, conductivity (umhos) and percentage loss on ignition values for soils taken at three depths (0, 5 and 10 cm) along a transect running from the Coniston smelter

Distance from smelter miles	km	Depth (cm)	pH	Conductivity	L.O.I.
0.5	0.8	0	2.19	630	6.5
		5	2.43	220	5.8
		10	2.50	208	5.8
0.95	1.5	0	2.82	552	8.7
		5	2.87	386	9.1
		10	3.02	214	9.9
1.2	1.9	0	2.76	850	10.5
		5	3.04	356	11.5
		10	3.29	167	10.3
2.4	3.8	0	3.66	228	9.7
		5	3.59	216	9.2
		10	3.66	215	9.4
4.6	7.4	0	2.92	234	12.5
		5	2.96	146	26.3
		10	3.09	105	14.3
6.5	10.4	0	3.23	210	12.0
		5	3.35	59	8.4
		10	3.37	45	12.3
8.4	13.5	0	2.95	87	27.3
		5	3.18	39	16.3
		10	3.40	28	12.0
12.0	19.3	0	4.04	67	22.7
		5	3.95	51	10.6
		10	4.19	51	16.3
31.0	49.8	0	3.39	58	6.0
		5	3.27	33	6.4
		10	3.42	25	5.6

Conductivity values are very elevated close to the smelter, compared with those of soils distant from it. Despite the variability, conductivity was generally highest in surface soils, where mobilization of cations and anions and deposition of heavy metals are greatest.

The heavy metal content of the transect soils are given in Table 8. A marked soil-profile effect was shown for nickel, copper and cobalt, with highest concentrations usually occurring in surface soils. These three metals also showed a decline in concentration at soil depths as a function of distance from the smelter. Concentrations of nickel and copper were very high, being in excess of 1000 ppm to a distance of 13.4 km. Nickel was generally at higher concentrations than copper, and is smelted in larger quantities. The pattern of change with distance parallels that for rainfall-dustfall analyses for these metals. Elevated levels of soil nickel and copper compared with expected background levels for uncontaminated igneous rocks, are exceeded at all sites except that at 50 km. This suggests long distance dispersal of airborne particulates, especially as the pattern is that of surface loading.

Table 8. Metal contents of Sudbury area soils collected at 3 depths along transects from the Coniston smelter. Analyses are of total digests, expressed in ppm.

Distance miles	Distance km	Depth cm	Nickel	Copper	Cobalt	Iron	Zinc	Lead	Manganese
0.4	0.6	0	1789	1365	84	22,238	63	40	176
		5	1038	1318	52	25,025	58	28	149
		10	955	1452	53	25,713	62	33	146
0.5	0.8	0	2835	1528	127	43,000	67	68	232
		5	2809	1238	124	49,088	66	64	242
		10	1522	935	82	28,150	57	42	202
0.7	1.0	0	1166	1140	59	19,463	55	45	211
		5	929	1193	50	24,643	57	38	207
		10	662	950	41	26,750	55	38	185
0.95	1.5	0	1847	2007	72	38,350	73	56	207
		5	1611	1864	69	38,080	72	47	204
		10	1163	1740	6	36,460	69	35	204
1.0	1.6	0	2679	1291	122	43,438	75	56	290
		5	1710	1478	88	43,438	78	68	276
		10	1097	1630	67	28,150	92	47	316
1.2	1.9	0	2161	2071	85	18,655	73	58	251
		5	730	1772	34	18,350	53	41	249
		10	649	1578	31	18,600	51	31	251
2.4	3.8	0	831	1140	42	26,750	53	47	161
		5	842	1104	58	26,750	57	42	167
		10	732	1166	43	20,850	55	38	162
4.6	7.4	0	3309	1425	154	76,788	84	52	360
		5	2330	1621	98	68,625	80	78	343
		10	613	944	36	50,463	64	31	354
6.5	10.4	0	356	392	33	28,763	68	28	336
		5	69	21	24	25,725	60	14	317
		10	79	3	24	29,188	63	9	295
8.4	13.5	0	103	1177	6	40,825	78	75	316
		5	409	568	6	38,415	72	35	349
		10	212	191	6	41,395	72	35	353
12.0	19.3	0	652	730	38	22,2 0	62	66	146
		5	553	597	20	18,075	57	75	146
		10	198	285	20	11,125	46	38	134
31.0	49.8	0	83	31	19	8,170	46	17	125
		5	71	27	17	8,185	51	17	122
		10	63	23	19	8,120	50	15	124

Comparisons of the significance values for regression lines of concentration on distance for 18 metals, showed significant decline curves for soil nickel, copper, cobalt, silver, iron, lead, cadmium, manganese and potassium, but no significant distance effect for zinc, aluminum and vanadium, none of which are smelted at Sudbury. A particulary interesting aspect was that where a variety of data transformations were used to compare goodness of fit, a $\log_e$ transformation of concentration gave the best fit for nickel and silver, and a $\log_e$ transformation of distance gave the best fits for copper, iron and lead. Reciprocal and square root transformations also gave significant regression lines. The distance decline curves are typical of fallout

patterns of particles with a logarithmic normal size distribution, and differences between nickel and copper suggest differences in their particulate sizes.

The site at 7.4 km is anomalous in its high values, but is influenced by both Coniston and Falconbridge.

METAL CONTENT OF NATURAL VEGETATION

Fumigations have resulted in a major loss of vegetation in the Sudbury area. However, collections were made in 1970 and 1971 of surviving naturally occurring species of the forests, including those able to survive close to the smelter zones. Washed material was analyzed for its metal content, to determine whether the elevated nickel and copper levels etc. in soil and air were also reflected in the foliage. A total of 14 species were found at sufficient sites to make distance comparisons of metal content feasible. Data for four of these are given in Table 9. The data for aluminum are given because of the possibility of mobilization of aluminum ions at the excessively acidic pH's of some of the soils, and because aluminum is known to be a major controlling toxic metal for plant growth on acidic soils (e.g. Rorison 1960, Clarkson 1968).

The data show a highly significant decrease in nickel, copper and aluminum concentration with distance from the smelter ($p > 0.01$). Cobalt shows a significant but weaker correlation. Zinc shows a trend the other way for *Betula papyrifera*, probably caused by its normal availability through organic complexes in soil humus, much of which is lacking at sites close to the smelter. Aluminum is especially interesting in that it appears that considerable mobility of this element has occurred in soils within 2 km of the smelter, with resultant uptake by plants from soluble aluminum compounds released from clay minerals by the very low pH's of these soils. This will increase soil toxicity markedly and also be a potential problem to water bodies. Bowen (1966) quotes normal metal levels for land plants as follows:- nickel 3 ppm, copper 14 ppm, cobalt 0.5 ppm, and zinc 100 ppm. Aluminum in foliage may occur at levels up to 200 ppm in plants on acidic soils. These levels were regularly exceeded in Sudbury plants for copper, nickel and cobalt, and for aluminum at sites close to the smelter. Zinc, our control metal, did not exceed the norms of Bowen.

It needs to be emphasized that the species tested for metal content are those species capable of surviving in areas of extensive and, previously, repetitive fumigations by sulphur dioxide, and at the same time, capable of tolerating highly acidic and heavy metal polluted soils.

Table 9. Content of Nickel, Copper, Cobalt, Zinc and Aluminum in foliage of four species along a transect from the Coniston smelter, collected in June 1970. Values in ppm on homogenized samples.

Species	Distance miles	km	Nickel	Copper	Cobalt	Zinc	Aluminum
Comptonia peregrina	1.0	1.6	113	57	7	30	250
	1.4	2.2	243	175	12	28	560
	4.6	7.4	-	-	-	-	-
	6.5	10.4	13	11	4	77	55
	8.4	13.5	74	70	5	36	90
	12.0	19.3	59	36	7	50	40
	18.0	28.8	28	29	5	54	90
	31.0	49.8	17	14	4	56	145
Deschampsia flexuosa	1.0		902	726	33	50	2500
	1.4		-	-	-	-	-
	4.6		160	103	12	28	280
	6.5		14	11	6	36	60
	8.4		138	66	8	31	90
	12.0		43	18	6	30	60
	31.0		37	13	6	31	60
Acer rubrum	1.0	N	109	61	7	28	220
	1.0	S	91	38	9	21	125
	1.4		88	42	11	26	220
	4.6		35	17	6	19	40
	6.5		35	26	6	30	35
	8.4		-	-	-	-	-
	12.0		33	28	3	22	80
	18.0		14	16	12	42	40
	31.0		14	20	6	46	20
Betula papyrifera	1.0		148	95	12	98	215
	4.6		111	37	8	90	160
	6.5		101	39	8	100	130
(collected	8.4		72	25	8	150	200
Aug. 1970)	12.0		64	32	8	188	100
	18.0		35	14	7	248	30
	31.0		16	14	5	340	60

pH, SULPHATE AND METAL CONTENT OF SOIL-WATER EXTRACTS

The previous data suggest highly acidic and metal contaminated rainfall and dry fall-out, soil contamination over a very large area and highly elevated levels of nickel and copper in the vegetation growing on these soils. Generally, total metal concentrations of soils are a poor reflection of the availability of these metals in the soil for plant uptake. Many methods of extraction are available, with appropriate claims for their close reflection to true availability for plant uptake. As a simple but probably low estimate of the availability of potentially toxic metals in the Sudbury soils, a simple water extraction technique was used. These extracts were both analyzed and used as a growth medium for seedling growth in laboratory experiments.

Data on analyses are given in Table 10. For all of the soils,

Table 10. Analyses of water extracts of soils collected along a transect from the Coniston smelter. Total analyses of metal and pH values are given in Tables 7 and 8. Metals are given in ppm of extract. A 3:1 water:soil extraction was used for metal analyses.

Distance from Coniston smelter miles	km	Depth cm	pH	Sulphate	Nickel	Copper	Cobalt	Aluminum	Zinc
0.5	0.8	0	3.08	780	127	42	4.6	51	1.0
		5	3.36	100	14	8	0.2	7	0.1
		10	4.48	75	11	6	nd	6	nd
0.95	1.5	0	3.40	325	107	60	3.4	77	0.9
		5	3.59	220	56	20	1.5	52	0.5
		10	3.69	115	19	10	0.4	23	0.1
1.2	1.9	0	3.25	3200	142	60	4.4	99	1.4
		5	3.48	190	36	10	1.0	31	0.3
		10	3.86	430	17	6	0.2	14	0.1
2.4	3.8	0	3.59	80	14	8	0.2	10	0.2
		5	3.57	75	12	6	0.1	10	0.2
		10	3.67	60	14	7	0.1	10	0.2
4.6	7.4	0	3.41	60	9	3	nd	7	0.1
		5	3.54	70	4	2	nd	7	0.1
		10	3.65	60	2	1	nd	4	0.1
6.5	10.4	0	3.86	65	7	1	nd	15	0.4
		5	4.11	50	1	nd	nd	6	nd
		10	4.22	20	1	nd	nd	6	nd
8.4	13.5	0	3.93	20	1	nd	nd	2	nd
		5	4.32	20	nd	nd	nd	nd	nd
		10	4.69	30	nd	nd	nd	nd	nd
12.0	19.3	0	4.39	25	nd	nd	nd	nd	nd
		5	4.46	40	nd	nd	nd	nd	nd
		10	4.70	40	nd	nd	nd	nd	nd
31.0	49.8	0	4.79	30	nd	nd	nd	0.5	nd
		5	4.69	35	nd	nd	nd	0.5	nd
		10	4.44	20	nd	nd	nd	0.5	nd

except that at 50 km the surface soil yielded the extract with the lowest pH and with the highest nickel, copper, cobalt and aluminum concentrations. Nickel occurred in the highest concentrations followed by aluminum and copper. pH increased with depth and distance, as did (generally) sulphate and metal concentrations. Even zinc showed this pattern, suggesting its mobilization at the acidic pH's. Nickel and aluminum were extractable from surface soils at levels greater than 5 ppm out to 10.4 km. Since the extraction technique involves a three-fold dilution of the soil extract, one can well consider the levels available in the soils to be even higher than those reported here. Sulphate levels were excessive within 2 km of the smelters and elevated to 10 km.

PLANT GROWTH ON SOILS AND EXTRACTS

The soil extraction data indicate that potentially toxic heavy

metals are available in the Sudbury soils as a result of their aerial deposition and especially as a result of acidic rainfall. The potential effects on the boreal forest ecosystem of the presence of widespread acidic and metal contaminated soil need to be considered. Seedlings are very rare in the Coniston region. Both nickel and copper are toxic at low concentrations to many aquatic plants, *e.g.* Hutchinson (1973), Stokes, Hutchinson and Krauter (1973). Indeed, copper is both an algicide and a fungicide. Levels as low as 0.1 ppm are inhibitory to many algae. Nickel is somewhat less toxic to algae, but levels of 1 ppm are inhibitory. Aluminum is a further toxic heavy metal, present in quantity in the soil water extracts.

A series of experiments were carried out involving a) studies of germination, growth and metal uptake of naturally- occurring and cultivated plants at field sites along the Coniston transect, b) studies of germination, growth and plant metal uptake into seedlings grown on these soils brought to the laboratory where sulphur dioxide fumigations could be excluded as complicating factors, c) studies of germination, growth and metal uptake of four cultivated plants, radish, tomato, cabbage and lettuce on the water extracts of Sudbury soils, and d) growth of these same four species on single salt, nickel, copper, cobalt, aluminum and sulphate solutions at a range of concentrations and in the presence of a nutrient solution. The concentrations of the metals ranged from 0 to 75 ppm. Details of these experiments are given in Whitby and Hutchinson (1974) and Whitby (1974).

The findings were complementary in that it was found impossible to keep either naturally-occurring or cultivated plants alive for even a few weeks on soils collected within 8 km of the Coniston smelter. Germination did not seem to be affected but symptoms typical of heavy metal damage (Rorison 1960) appeared immediately upon radicle emergence. These included recurvature, growth of roots out of the solution, a blackening of root tips and necrosis of cotyledons. In field experiments, lime additions had a marked effect in improving growth and in decreasing metal uptake (and metal content of water extracts). Oats *(Avena sativa)* survived even at 1.5 km from Coniston and are here used as an example of lime effects. The shoots (tops) of plants grown for eight weeks in the field on unamended soil contained 385 ppm of nickel and roots contained 1381 ppm of Ni. Plants grown on limed soil at the same site contained 43 ppm Ni in the shoot and 424 ppm in the roots. In contrast, at 7.4 km unlimed plants had shoot levels of 88 ppm and 451 ppm Ni in their roots, compared with 19 ppm in shoots and 248 ppm in roots of limed plants. Copper and cobalt levels were also found to be excessive. When grown in the laboratory on these soils, most seedlings died on soils collected from within 7.4 km of Coniston. Lettuce and tomato were especially sensitive and accumulated more than 500 ppm of nickel, copper and aluminum in their tops on the soil from 7.4 km. Liming, which increases pH and reduces heavy metal solubility, had a notable effect in reducing soil toxicity and metal uptake.

The effect of soil water extracts was similar to direct soil

testing in bioassays using tomato and radish. At all sites located closer than 3.8 km from the smelter and irrespective of the depth from which the soil was obtained, there was an almost total inhibition of radicle elongation. Morphological and anatomical symptoms typical of heavy metal toxicity were noted. At distances greater than 3.8 km, the relative inhibition of root elongation compared with the controls, was found to relate to distance from the smelter and to soil depth from which extracts were made. Surface soils were inhibitory to growth (caused 50% reduction in root elongation compared with 50 km controls) to a distance of 10.4 km. This would coincide with water extract levels greater than 5 ppm for both nickel and aluminum in surface soils.

Single salt solutions were used in similar bioassays to test the toxicity of nickel, copper, cobalt, aluminum and sulphate to the test species (Whitby and Hutchinson 1974). Aluminum and nickel were found to be the metals most toxic to tomato, followed by cobalt and copper. Levels of only 2 ppm Ni reduced root elongation by nearly 70% and complete inhibition occurred at 10 ppm. Aluminum reduced growth by approximately 80% at only 2 ppm and by 90% at 4 ppm. Cobalt reduced growth 60% at 2 ppm and caused total inhibition at 15 ppm. (Cobalt was present at 4.4 ppm in soil extracts from 1.9 km, Table 10). Copper reduced root growth by 30% at 2 ppm and almost completely inhibited elongation at 15 ppm.

Variation within treatments was fairly high, often ± 50%, but reflected differing germination times within a species. Sulphate levels of 250 ppm were not found to be inhibitory.

The high toxicity of soil extracts and the proven toxicity of their heavy metal constituents at levels which were often markedly exceeded in many of the soil extracts, leads to the conclusion that the Sudbury soils are probably directly toxic to establishment of seedlings of most species over a very wide area. The seedling establishment experiments in the field and the laboratory, and the improved performance with lime amendments would support this conclusion. One could account for the data by either nickel (a major aerial contaminant) or aluminum alone. Copper and cobalt are also present in sufficient quantities to create serious problems over a more limited area. The aluminum problem is of especial interest in that it seems to be an indirect result of smelter activities. Aluminum toxicity is apparently caused by highly acidic rainfall mobilizing aluminum from clay minerals in the Sudbury soils. This effect was unforeseen and may well be a salutary warning for those concerned with acidic rainfall problems on ecosystems both aquatic and terrestrial, in Scandinavia and in the eastern United States.

The problem is severe enough, without the added complication of synergistic interactions between certain of the polluting metals at Sudbury. The synergistic interactions of nickel and copper have already been described (Hutchinson 1973).

Heavy metal toxicity problems in soils tend to be long term and almost semi-permanent. The ongoing major sulphur dioxide emissions from the new superstack at Copper Cliff have undoubtedly improved local air quality. The new resultant prospect of increasingly widespread acidic rainfall over hundreds of square kilometres, with attendant mobilization of metals such as aluminum in soil, is not one to be taken lightly.

EFFECTS ON SOIL ORGANIC MATTER

The chemical and physical properties of organic matter extracted from soils collected at 1.6, 7.4 and 52 km from Coniston have been studied in detail. The work was done in collaboration with Dr. M. Schnitzer of Agriculture Canada, Soil Research Institute. Attention has focused especially on the properties of fulvic acid extracts obtained from the Sudbury soils. Schnitzer and Khan (1972) point out that the bulk of organic matter in most soils and water consists of humic substances. Important characteristics exhibited by all humic fractions are their resistance to microbial degradation, ability to form stable water-soluble and water-insoluble salts and complexes with metal ions and hydrous oxides, and to interact with clay minerals and organic chemicals which may be toxic pollutants. Humic substances are critical to soil fertility, both physically and chemically. They facilitate the transport and availability of nutrients, especially trace metals, and improve aeration and drainage. Factors which may affect the functioning of humic substances in a deleterious way deserve special attention.

Details of the analyses of the extracted organic matter will be given elsewhere, and a general resume will merely be presented here. The properties of the soils and the water extracts used for organic matter extractions are given in Table 11. The soil from 1.6 km was of particularly low pH, i.e. 2.4.

The normal range of nitrogen values for podsolic soils is 0.10 - 0.20 %, and an approximate sulphur value for podsolic soils is 0.1%. The sulphur content of soil from 52 km was 0.09%, that from 7.4 km 0.34% and that from 1.6 km 0.90%.

The results of percentage loss on ignition, ash and ash reaction with concentrated HCl at room temperature for unpurified organic matter are given in Table 12. Notable findings were the high ash content of the 1.6 km soil, the colour of the ash, its solubility in cold core HCl and the excessively high copper and nickel contents in the ash compared with the 52 km control. The soil from 7.4 km was intermediate but closer to the control in its properties.

The titratable acidity of purified podsolic fulvic acid to pH 7.0 is normally 7.15 meq/g. When titrated with 0.05 N sodium hydroxide in the presence of 0.1 N KCl, unpurified samples from 1.6 km gave 6.5 meq/g

Table 11. Properties of soils and water extracts used for organic matter extractions.

	1.6 km	7.4 km	52 km
Soil pH	2.4	2.8	3.2
% L.O.I.	20.5	15.1	7.6
% Ash	79.5	84.9	92.4
% Carbon	5.30	8.40	2.33
% Nitrogen	0.32	0.81	0.15
% Sulphur	0.92	0.34	0.09
% Organic Matter	10.60	16.80	4.66
Total Nickel (ppm)	1847	1809	83
Total Copper (ppm)	2007	1425	31
Water Extract pH	2.7	3.2	3.5
Water Soluble Nickel (ppm)	321	25	nd
Water Soluble Copper (ppm)	180	9	nd
Water Soluble Sulphate (ppm)	1300	500	60

nd = not detectable

and from 52 km gave 1.4 meq/g. This suggests significant differences in the acidic functional groups - COOH and phenolic-OH.

Purified extracts of organic matter were prepared by treatment with diluted HCl-HF and dissolution by 0.5 N.NaOH. Because of the high ash content 6N HCl was also used on the samples from 1.6 km to separate the organic matter from the ash. The chemical compostion of purified organic matter is given in Table 13, together with the titratable acidity. The carbon content of the 1.6 km soil was very low as was its nitrogen content. In contrast, the sulphur concentration was abnormally high. Titratable acidity also differed markedly between the soils. It remained high for the sample from 1.6 km, indicating a large number of functional groups, but was normal, (for fulvic acid) in the purified extracts of soils from 7.4 and 52 km. This indicates the effect of unlocking the functional groups by removal of metallic ions (ash).

The infra-red spectra of the purified fulvic acid fractions were examined following methylation. Major differences were found between the methylated samples from 1.6 km and that of normal fulvic acid. Methylated samples were also prepared for gas chromatograph. Again, the sample from 1.6 km was atypical for fulvic acid. Not only were many of the components of podsolic fulvic acid absent but there are a large

Table 12. Properties of unpurified organic matter.

Soils	1.6 km	7.4 km	52 km
% Loss on ignition	35.4	50.2	46.3
% Ash	64.6	49.8	53.7
Colour of Ash	grey-green	bright red	brick red
Reaction with cold conc. HCl	soluble	partially soluble	insoluble
Nickel (ppm) in unpurified extract	76,300	1,380	160
Copper (ppm in unpurified extract	15,460	340	170
Nickel (ppm) in ash	118,100	2,770	295
Copper (ppm) in ash	23,930	680	315

Table 13. Chemical composition of purified organic matter.

	1.6 km	7.4 km	52 km
% Ash	32.3	5.6	3.8
% Carbon *	15.9	36.6	43.8
% Nitrogen *	0.2	1.7	1.5
% Hydrogen *	5.8	5.2	5.3
% Oxygen *	47.5	54.8	48.2
% Sulphur *	30.6	1.7	1.3

* corrected for ash content

number of S=O groups (not present in fulvic acid) and many compounds that were detected at low temperatures, some of which probably contain sulphur groups. It seems that sulphur has replaced carbon atoms and it is likely that the control benzene rings are now surrounded by sulphonic groups (SOH_3) rather than carboxylic groups. Peaks for tri, penta and hexa benzene carboxylic methyl esters were missing. The resultant drastically modified organic matter tends to act as a sulphonic ion resin, with very strong metal binding capacity. Exchange properties will be very different from those of fulvic acid and the role as nutrient reservoir and sink for plant growth will have been drastically altered. Further studies are needed into many of these aspects of organic matter changes in the Sudbury soils.

If the long distance dispersal of sulphur dioxide leading to acid rainfalls and acidic soils and of heavy metals was merely a land and air problem, it would be sufficiently serious as regards the destruction of the forest ecosystem and contamination, in view of the vast acreages involved. However, the problem does not stop there. Lakes as far as 80 km from the town have become acidic in recent years. Metals accumulate in the snow and run-off in acidic melts in the spring. Sheet erosion of thousands of acres has already occurred. Sediment loads in the Wanapitei River which drains the eastern end of the area are very high. Nickel concentrations in the river water 80 km away averaged 42 ppb in 1974. Sediment cores taken in the same river have a surface 10 cm with nickel content rations of up to 400 ppm and copper to 150 ppm. Large quantities of nickel and copper are released in solution as fine particulates into Georgian Bay of Lake Huron. This erosion and leaching of metals from the acidic soils is likely to continue for the foreseeable future. The severity of the Sudbury effects, especially as regards a) mobilization of aluminum in the soil, b) the profound changes in organic matter structure found and c) the widespread phytotoxicity of the soils as a result of nickel and copper accumulations may be merely a consequence of the severity of the Sudbury conditions experienced at least up to 1972. The disturbing implication would be if these changes and effects were to be repeated on even wider scales in areas with appropriate soils and levels of precipitation and with sulphur dioxide or nitrogen oxide inputs. Both Scandinavia and Eastern North America are such areas and one hopes that useful lessons for the future may be gleaned from the Sudbury studies.

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EFFECT OF SULPHUR DIOXIDE ON PRECIPITATION AND ON THE SULPHUR CONTENT AND ACIDITY OF SOILS IN ALBERTA, CANADA

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ABSTRACT

Rain and snow in Alberta are seldom acid. The S content of snow is so low that the snow pack gives a deposition of less than 1 kg S/ha, even downwind from large SO_2 emission sources. Rainfall contributes at the most 4 kg S/ha yearly near SO_2 sources, and only about 1 kg S/ha in clean areas. However, rain intercepted by forest trees exposed to SO_2 emission becomes acid (pH 3.5 to 4.5) and has a S content of 3 to 4 times greater than rain. Soils absorb large amounts of S from emissions (up to 50 kg S/ha annually) but much of the S is found in non-sulphate form. Soils are slowly acidified by the SO_2 at a rate estimated at 1 pH unit in 10 to 20 years. Water surfaces will absorb SO_2 emissions at a rate of about 4 to 15 kg S/ha annually. Particulates deposit 3 to 4 times as much S as is deposited by rainfall.

INTRODUCTION

Sulphur gas emission from natural gas processing and oil sand extraction annually contributes about 225,000 tonnes of sulphur (S) to the atmosphere in Alberta. The S content of rain and snow was measured in Central Alberta more than five years ago and showed only 2 to 4 kg S per ha annual deposition (Walker, 1969). Central Alberta contains half of the S gas emissions in the province, and deposition of 2 to 4 kg S per ha yearly indicates a wide dispersion of S gas in Alberta and beyond.

Our work during the last two years has shown that the S content in dry fallout is often greater than ten times the S content in wet fallout,

in non-forested areas. Wet fallout intercepted by a forest canopy was found to contain up to four times the S content of free wet fallout. In both forested and agricultural areas the cumulative S contribution of wet fallout and dry fallout was sufficient to cause soil acidification. The approximate rate of acidification was estimated at 1 pH unit reduction per 10 to 20 years of emission.

METHODS AND MATERIALS

Ninety-three fallout monitoring stations (Figure 1) were installed in Alberta and Western Saskatchewan. Site locations were based on source distributions and prevailing winds.

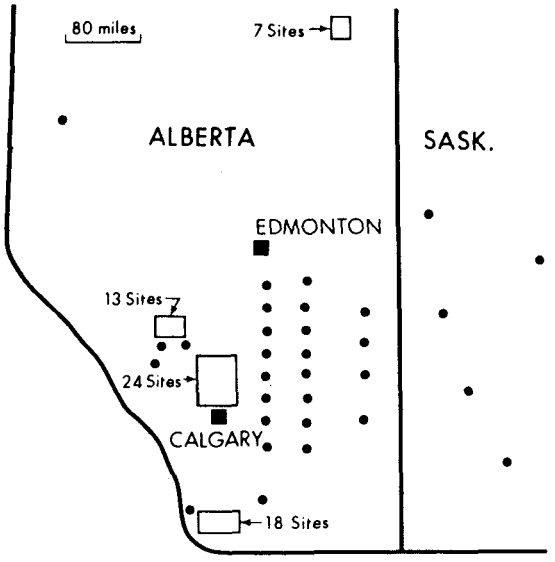

Figure 1. Location of sulphur monitoring stations in Alberta

Rain was collected weekly at each site over a four month period during the summers of 1973 and 1974. Snow was sampled at selected stations during late winter. Two types of intercepted wet fallout (throughfall and stemflow) were measured at eight selected sites in 1973 and at 18 sites in 1974. Wet fallout samples were analyzed to determine pH and SO_4-S.

Particulate fallout was measured at 11 selected stations from July to October, 1974 using a modified Nipher gauge. Particulates were analyzed for SO_4-S content.

In addition at all stations the rate of SO_2 absorption by soils and resultant pH depression were determined. Replicated samples of three soil types common to all stations were used for this study.

One-litre containers of soil were placed under a solid roof (closed canopy) at each station so that they received no wet fallout but were exposed to free air movement (wind) under the roof. All containers were watered, up to field capacity, weekly. As well, at selected stations, similar soil containers were placed in the open, subjected to all fallout. The latter containers were of two types, with plants (barley, alfalfa, bromegrass) and without plants. The vertical pH gradient and SO_4-S gradient over the 12 cm soil depth was determined in each soil container.

At each station, the absorption of SO_2 by a free water surface under a closed canopy (roof) was also measured. In addition, at six stations standard soil containers, using a 5 cm surface layer of live sphagnum peat moss as the upper soil layer, were exposed to wet and dry fallout.

The SO_4-S was determined by a modification of the method of Dean (1966). The SO_4-S in rain and snow was taken as being total S after it was found the S in rain and snow was in SO_4-S form. The total S of soils and plants was determined by digesting in nitric and perchloric acids and the SO_4-S was measured on the digests.

RESULTS AND DISCUSSION

1. pH AND SO_4-S IN WET FALLOUT

The results of SO_4-S and pH determinations in snow at stations surrounding an oil sand extraction plant in a forested area are shown in Table 1. Below the hatched line in the table are results from a site in Northern Saskatchewan located 450 km away from any S emission sources.

The daily gaseous emission of S from the plant shown in Table 1 exceeds 150 tonnes. The total winter accumulation of S in the snow pack five km from the plant was less than 1 kg/ha, only slightly greater than accumulation 450 km distant. Noting that 150 tonnes/day could represent the deposition of 1 g of S per day on a land area of 150,000 ha, it is apparent that the contribution of SO_4-S in snowfall during the winter months is insignificant. Similar results were found in the vicinity of a gas processing plant in a forested area emitting 84 tonnes of gaseous S per day with SO_4-S content of 0.15 to 0.82 kg/ha in the snow pack. Similarly, the pH of snow pack adjacent to S emission sources was nearly the same value as the pH of the snow pack in remote Western Canada sites (approximately pH 5 to 6).

Table 1. The soluble sulphur and pH of snow near an oil sand plant in the Spring of 1974

Distance and Direction from Plant	Date	S in Snow (kg SO_4-S per ha)	pH of Snow
3 km N.W.	February 22	0.18	4.7
3 km N.W. (on river)	February 22	0.60	5.2
5 km South	February 22	0.15	5.2
10 km South	February 22	0.48	4.8
55 km S.W.	February 22	0.33	5.2
2.5 km S.E.	April 10	0.20	5.0
4 km S.E.	April 10	0.21	5.4
24 km S.W.	April 10	0.25	5.2
Northern Sask.	February 8	0.10	5.0

Table 2 gives results of pH and SO_4-S determinations in rain

Table 2. Characteristics of rain during a 3-month period in the summer of 1973 in Alberta

Location	Number of Stations	Average pH	Average SO_4-S Content (ppm)	S Brought Down by Rain (kg/ha/3 months)
Remote Station	4	6.3	0.7	0.5
Exposed Station Southern Plant	4	6.3	2.7	1.5
Calgary-Olds Area	24	6.7	1.6	1.5
West Central Forest	6	5.5	1.5	1.9
Northern Forest	2	6.2	1.4	1.5

collected in the vicinity of four S emission areas and in remote stations during the summer of 1973. As is shown rain is approximately five times higher in S concentration than snowfall. This is true both for remote stations and stations close to S sources. Notice that even though the SO_4-S concentration is high enough to indicate a pH of 3 to 4 in pure water, most rains in this region are rich in cations, resulting in near-neutral pH readings. It must be noted that, once again, the S concentration in rainfall is insignificant in terms of the total daily emissions of gaseous S in Alberta. The results in Table 2 are for June, July and August, the months which get the majority of rainfall, and as shown those three months get the most S emission in the rainfall. Considering both rain and snow, deposition of S in precipitation is at most 4 to 5 kg/ha annually near emission sources, and at least 1 to 2 kg/ha in areas remote from sources.

Rain became strongly acid when intercepted by forest trees exposed to S emissions (Baker, Hocking and Nyborg, 1973). The increased acidity of the intercepted rain in exposed areas was accompanied by increased SO_4-S content (Nyborg, et al., 1975). Table 3 shows the

Table 3. Sulphur deposition by rain and by spruce throughfall

Location	Sulphur Deposition (kg/ha/Month) Rain	Throughfall
Controls (2 sites)	0.1	0.2
*Exposed (3 sites)	0.7	2.6

*Within 8 km of oil sand extraction plant.

deposition of S in both rain and throughfall at controls and exposed sites. Deposition of S in throughfall was only 0.2 kg/ha/month at remote controls, but was 2.6 kg/ha/month at exposed sites. Apparently S gases were absorbed on trees and then washed off by intercepted rain and this is one of the main ways S is deposited in Alberta forests.

2. ACIDIFICATION OF SOIL AND AMOUNT OF SULPHUR DEPOSITION BY DRY FALLOUT

The pH of soils after being kept in containers under closed canopies is shown in Figure 2. In an area of more than 1,000 square km

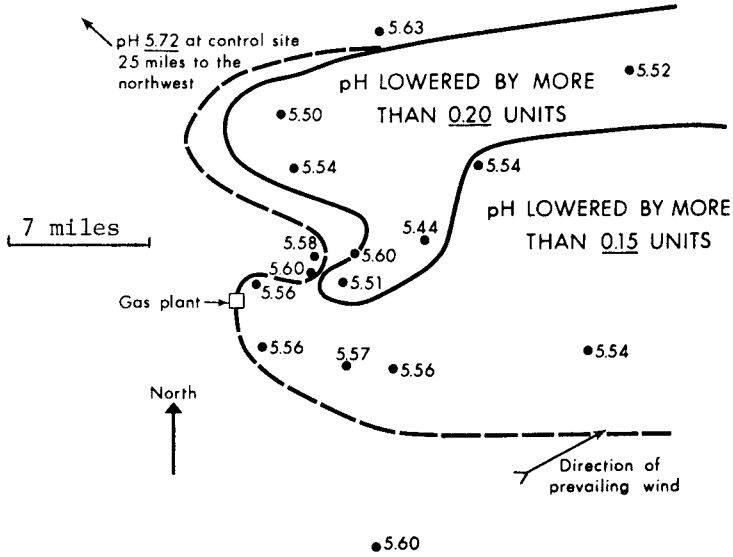

Figure 2. The pH of two soils (0-12 cm depth) under closed canopies for three months in southern Alberta. Control pH = 5.72

downwind from a gas processing plant in Southern Alberta, the pH was depressed by at least 0.15 units in a period of three months. Figure 3

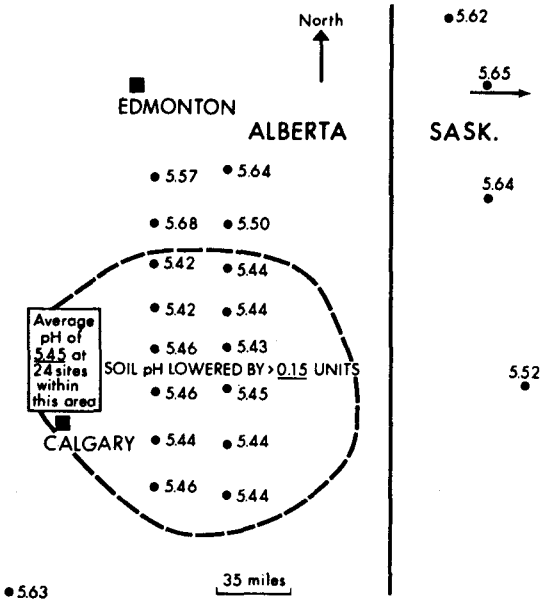

Figure 3. Average pH of top 5 cm of two soils under closed canopies for three months in 1973, in central Alberta and Saskatchewan

gives results of pH depression of soils under closed canopies for the central region of Alberta for the same three month period. Within an area of 25,000 square km the pH was depressed on approximately 0.15 units. One-half of the S emissions in Alberta are emitted upwind from this study area.

Table 4 gives results of pH determination on soil containers under

Table 4. The pH of two soils exposed to the atmosphere for 3 months in 1973 at stations from different areas of Alberta and Saskatchewan

Location	Major Vegetation	Number of Stations	Size of Area in Which Stations Located (Km^2)	Average pH of Soil 0-1 cm	Average pH of Soil 0-5 cm
Remote Controls	Prairie & Forest	4	--	5.50	5.64
Exposed Sites					
Waterton Plant	Prairie	18	1,200	5.43	5.46
Central Alberta	Prairie	36	25,000	5.40	5.45
Ram River Plant	Forest	8	500	5.26	5.55
Oil Sand Plant	Forest	2	--	5.17	5.54

closed canopies after three month exposures in prairie and forested areas. It is seen that pH depression in the forested sites is only half as great as that in prairie sites. Nevertheless, considering the cumulative pH depression over a period of several years, soil forests may be seriously acidified. Our technique was setting bare soils in containers that were on a shelf 0.5 m above the ground and the experimental soils were therefore probably more exposed to SO_2 than were natural soils. However, this experiment demonstrates that soils will be acidified by SO_2 emission, regardless of the exact rate in natural soils.

Table 5 shows the amount of SO_4-S gained by bare uncovered soil.

Table 5. Sulphur brought down in rain and gained by bare soil from June 1 to September 1 at stations near a gas processing plant

Location of Station		SO_4-S (km/ha)	
Direction	Distance From Plant (km)	In Rain	Gained by Soil
Directly Downwind	2	2.0	20.1
	6	1.5	12.1
	10	1.3	10.3
Not Directly Downwind	5	1.8	8.0
	11	1.0	5.4
	11	1.4	3.8

This amount is up to ten times as much detected in rainfall. At the six stations located 11 km or less from a gas plant, the soils gained from 3.8 to 20.1 kg/ha of SO_4-S. However, some soils store little or no SO_4-S from S emission, but instead they covert SO_4-S to forms that can be found in analysis for total S. An example is shown in Table 6 from four stations. Calculating from the S content of crop and the SO_4-S content of the soil, the soil and crop apparently gained from 15 to -2 kg/ha of S emissions. However, using the same calculation but using total S rather than SO4-S, the gain of the soil was 53 to 13 kg/ha. On this soil most of the S emissions do not remain as SO_4-S. Further, crops grown on the soil took up only 1 to 2 kg/ha of S when fertilized with 22 kg/ha of S which was not recovered as SO_4-S in the soil.

An experiment was conducted with a controlled chamber containing an atmosphere with 24 parts per billion (ppb) of SO_2 (Table 7). This laboratory experiment verifies field results on the absorption of SO_2 by soils and the consequent depression of pH. After 30 days of

Table 6. The SO_4-S and total S in a cropped soil kept in containers 3 months at stations near a gas processing plant

Distance from gas plant(Km)	Crop uptake of S (kg/ha) NPK*	NPKS*	Change in SO_4-S of soil during cropping (km/ha)	Gain in total S by non-S fertilized soil and plants (kg/ha)
2	11	13	+3	47
6	8	9	-2	12
16	8	9	+1	37
37	**	**	+15	53

* The NPK treatment received nitrogen, phosphorus, and potassium fertilizers. The NPKS treatment received in addition sulphur at a rate of 22kg S/ha in form of Na_2SO_4.

** Plants were not grown in containers at this station.

Table 7. Effect of exposed to 24 ppb of SO_2 for 30 days on soils, spruce bark, forest litter, and water (Temperature 20°C, relative humidity, 40%)

Material	Soluble SO_4-S (ppm) Control	Change on Exposure	Total S (ppm) Control	Change on Exposure	pH Control	Change on Exposure
Soils						
Chernozemic	3.2	+ 8.0	187	+16	6.04	-0.13
Luvisolic	3.0	+ 9.0	174	+18	5.86	-0.10
Luvisolic + 5% $CaCO_3$	7.4	+14.5	182	+30	0.21	-1.23
Spruce Bark	54.2	+30.0	--	--	--	--
Forest Litter	46.7	+35.6	--	--	--	--

exposure to 24 ppb of SO_2, two soils which were kept in 1-cm deep in open containers increased their SO_4-S content by 8 or 9 ppm. However, the total S of the soils had increased by twice as much, demonstrating that soils can convert SO_2 into a non-sulphate form. Also, the pH of soils decreased by approximately 0.1 units. Bark and forest litter exposed at the same time gained about 30 ppm of SO_4-S. This experiment shows that SO_2, at concentrations not much above those found downwind from emissions, is absorbed by soils at a surprisingly high rate.

A preliminary experiment on absorption of SO_2 by live sphagnum was conducted in the field. The sphagnum was obtained from an area remote from SO_2 emissions, placed in pots and set out at six sites.

Table 8. The soluble sulphate content of the top 2.5 cm of live sphagnum moss set out for 8 weeks at 4 stations near an oil sand plant and at 2 control stations

Distance and Direction of Stations from Plant	Soluble SO_4-S (ppm) of Top 2.5 cm of Moss
Exposed Sites	
2 km East	96
4 km East	100
8 km East	98
8 km South	122
Control Sites	
24 km SW	46
54 km SW	43

After eight weeks moss gained about 50 ppm of soluble SO_4-S at sites near a SO_2 emission source as compared to control sites.

3. OTHER WAYS OF DEPOSITION OF SO_2 EMISSION

Absorption of S by a free water surface kept under a closed canopy was measured at each station in 1974. The absorption of S varied from 4 to 15 kg/ha per six months (the season of open water). In forested areas absorption by water was low in heavily treed sites and higher in open sites. These measurements would best be made over bodies of water so wind is restricted. Nevertheless, the crude measurements do indicate that over open waters there is more S deposited by absorption of SO_2 than there is deposition of S in rainfall.

Preliminary measurements were made in 1974 of the S fallout in dry particulates. In Central Alberta at six sites the S fallout averaged 0.28 pounds S/acre/week (equal to 0.32 kg S/ha/week), and little or none at sites remote from emissions in Saskatchewan (Figure 4). In Central Alberta and S fallout by dry particulates was 3.5 times the deposition of S by rainfall.

GENERAL DISCUSSION

In Alberta rain and snow are usually not strongly acid, and deposit not more than 4 kg S/ha annually. When the ground is covered with snow (about five months of the year) the SO_2 emissions mostly drift out of Alberta because the snow pack contains only about 0.5 kg S/ha. However, for the rest of the year there are several ways other than rainfall in which SO_2 emissions are deposited--direct absorption

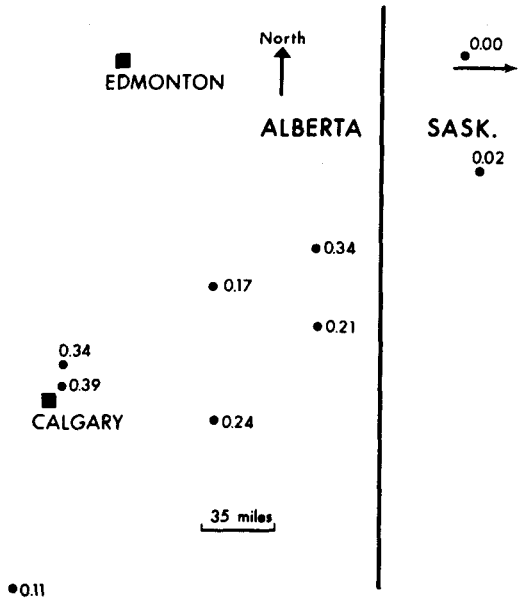

Figure 4. Apparent amount of sulphur deposited as particulates, in central Alberta and Saskatchewan (lb. S/acre/week)

by soils and water, intercepted rainfall by trees, and fallout of particulates containing S. Our estimate is that as much as 50 kg S/ha are deposited for 20 to 30 km downwind from large single emission sources. A small but measurable depression in soil pH accompanies the increase in S content of soils.

The acidification of soils is a long term effect of SO_2 emission. The acidification accumulates year after year, and soils remain acid even after SO_2 emissions have ceased. Soils can be returned to their pH only by application of lime.

Assume that in Alberta S from emissions is deposited mostly locally for 7 months of the year when the ground is free of snow. If the S was deposited on 2,000,000 ha it would average a rate of 50 kg S/ha. Considering the buffering ability of Alberta soils, the deposition of 50 kg S/ha annually would result in a drop in pH of 0.5 to 1.5 units in the top 15 cm of soils after a period of 10 to 20 years. Returning the soils to original pH would need about 2 tonnes of lime/ha. Agricultural soils are easily limed by spreading the lime and working in. It may not be practical to lime Alberta forest soils, because lime usually needs to be worked into soils under our conditions of low rainfall.

Unfortunately, the problem of acidification of soils in Alberta by SO_2 emissions is not all that simple (Nyborg et al., 1973; Hocking and Nyborg, 1974). We do not know what proportion of emitted S is deposited as H_2SO_4 as compared to neutral salts. The amount of S gained by soils from SO_2 emissions can be determined only by total S

analysis which is a rather imprecise method. The depression in soil pH from exposure to SO_2 emissions for a year is at most 0.1 to 0.2 units, which is less than natural temporary shifts in soil pH with seasonal or yearly changes in biological activity. Consequently, results on rate of soil acidification by SO_2 emission are only approximate.

ACKNOWLEDGEMENTS

This work was supported by the Alberta Environmental Research Trust, and Canada Atmospheric Environment Service.

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ACIDITY OF OPEN AND INTERCEPTED PRECIPITATION IN FORESTS AND EFFECTS ON FOREST SOILS IN ALBERTA, CANADA

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ABSTRACT

Emissions of sulphur dioxide appear to have an acidifying effect on grossfall (open rainfall), throughfall, stemflow and soil solution at sites near major sources. Resulting effects on soil chemistry include elevated extractable acidity and aluminum and depressed exchangeable bases, especially calcium and magnesium.

These changes are mostly in the incipient phases in the study area.

INTRODUCTION

Approximately half a million tons of SO_2 are emitted annually into the atmosphere throughout Alberta, mostly as a result of residual inefficiency of sulfur recovery from sour (H_2S containing) natural gas. An earlier paper in these proceedings describes the regional effects of these emissions on acidity of precipitation (Nyborg, Crepin, Hocking, and Baker 1976).

Several large point sources of SO_2 are located in forested areas where they have strong local influences (Baker, Hocking and Nyborg 1973). Preliminary laboratory studies showed that solution and transformation of sulfur compounds in the soil is likely to greatly influence the solubility, mobility and distribution of soil minerals and nutrients (Baker, in press).

This article reports early field data on chemistry of rainfall from two localities in Alberta affected by SO_2 emissions, and effects on forest soils from one of those localities.

METHODS

One locality surrounded two major sulfur-extraction natural gas treatment plants near Rocky Mountain House, Alberta (lat. 52° 20' N, long. 115° 20' W), referred to as RMH, and is an area where soil studies are progressing. The other locality surrounded a processing plant on the Athabasca Oil Sands of northeastern Alberta near Fort McMurray (lat. 56° 50' N, long. 112° 5' W), and will be referred to as the GCOS area.

Experimental sites were located at varying distances from the SO_2 sources. Each site was equipped with plastic rainfall traps that included units to collect grossfall (uninterrupted rain), stemflow, and three throughfall (dripping off foliage) collection units. Collections were made throughout the growing season at weekly intervals or after each major rain event. Fallen snow was collected once from each site during the winter. All samples were analyzed for pH and sulfur content after storage at 1°C for varying periods.

At the RMH sites, soil was sampled from the litter surface (L-F-H), and at 0-5 cm, 5-15 cm and the 15-30 cm depths in the autumn when the soils were very wet. Samples were stored in plastic bags in cold rooms (1°C) until analyzed (for four months).

Field-moist samples were used in all analyses. Eight grams of moist L-F-H and 16 grams of moist mineral soils (approximately equivalent to 4 and 12 grams on an oven dry basis) were first extracted alternately with 25 ml each of warm (40°C) water and 1 n KCl, until 250 ml of leachate was collected. Each addition of water or salt was allowed to completely drain (one hour) before the addition of the next. Extraction was carried out using a V-shaped funnel equipped with a quantitative filter paper and a hardened #50 Whatman filter disc on the surface of the sample. These water-KCl extracts were analyzed for pH, exchangeable acidity, Al, Ca, Mg, Mn, Fe, N, and P.

Following the KCl extraction, selected samples from sites near to and distant from the SO_2 source were sequentially further leached with 100 ml each of (40°C) 0.5 n NaF, 0.1 n NaOH and 0.5 n H_2SO_4 (after Jackson, 1958), for P and N determinations. Aliquots were digested with concentrated H_2SO_4 and a Cu catalyst. No attempt was made to differentiate between organic and inorganic phosphorus and nitrogen. Evaluations were made of the total amounts removed by the various extractants.

Measurements for pH and KCl-extractable acidity were carried out on an automatic Metrohm E436 potentiograph. Titrations were done with 0.04 n $Ca(OH)_2$. The normal and a differentiated titration curve was carried out for each extract. Measurements of Al, Ca, Mg, Mn and Fe in KCl were made using a P.E. Atomic Absorption equipped with a digital concentration readout. Total phosphorus content in each of the four extracts was determined by the molybdate method using ascorbic acid as a reducing agent. Nitrogen evaluations were obtained by distillation

of the digested extracts into boric acid and titrated to pH 4.7 with standard H_2SO_4 using a dead-stop Radiometer titrator.

Where sulfur was determined, the Dean modification (Dean 1966) of the method of Johnson and Nishita (1952) was used.

RESULTS

The pH values of grossfall, throughfall and stemflow for each major rainfall event of the 1974 growing season are shown in Fig. 1 for 3

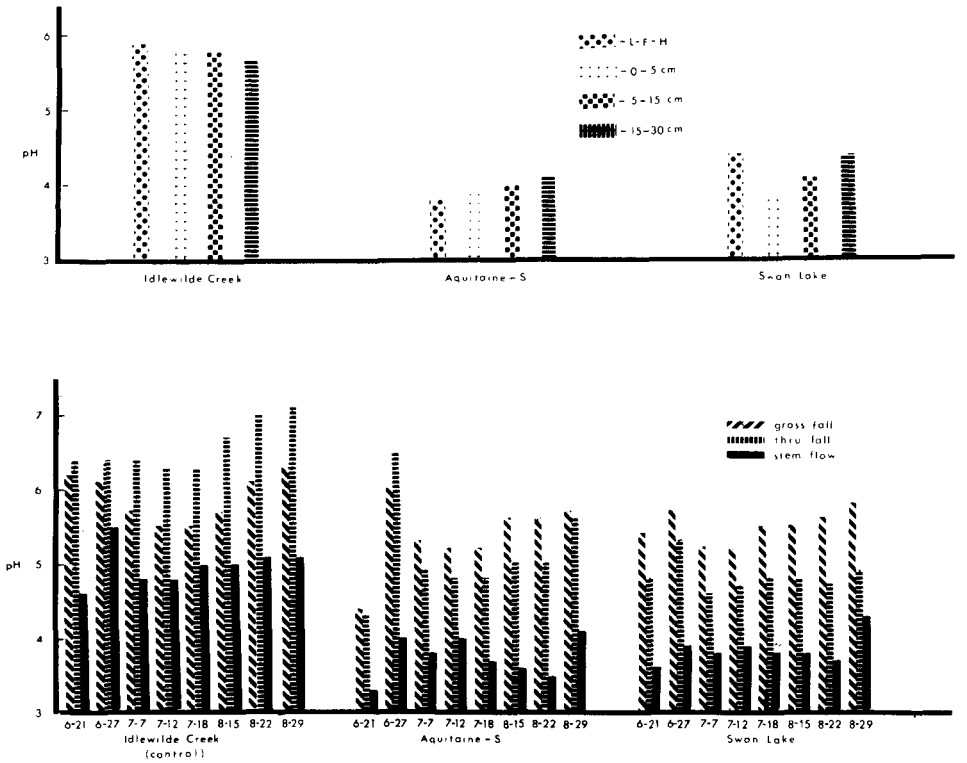

Figure 1. Change in pH of gross fall, thru' fall and stem flow solutions from control and S-contaminated sites during the 1974 sampling period; soil pH values (KCL extracts) for corresponding sites are also given.

representative sites in the RMH area, one distant and two relatively near the SO_2 source. Included in Fig. 1 are pH values of KCl extracts from various soil layers of the given test sites. Average pH values of throughfall and stemflow for the entire season are shown in Fig. 2 for sites near the SO_2 source in the RMH area, and are given in Table 1

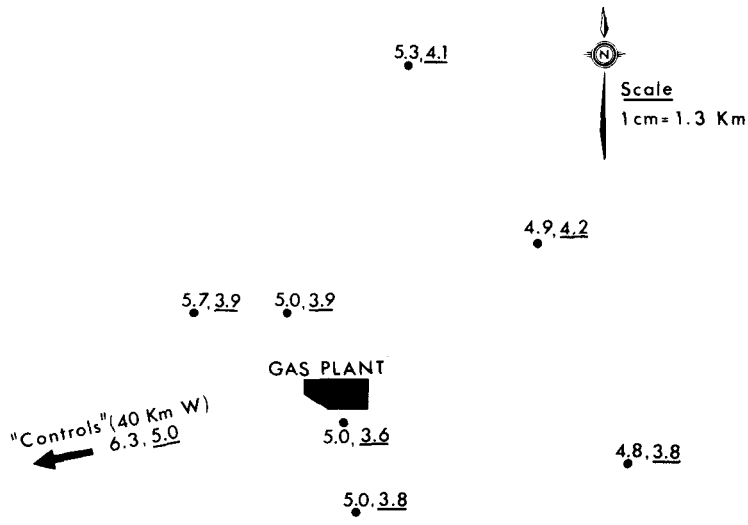

Figure 2. Average throughfall and stemflow (underlined) pH, June 15 - September 5, 1974, of selected sites in the RMH area.

Table 1. Average pH of Grossfall and Spruce Stemflow During July - September, 1974; for sites in the GCOS area.

Site	Distance (direction) From SO_2 source (km)	pH	
		Grossfall	Stemflow
Controls (2)	24,56 (SW)	6.4	6.4
GCOS - 1	3.2 (NW)	6.5	4.7
GCOS - 2	8 (NW)	6.5	4.7
GCOS - 4	2.2 (E)	6.0	5.3
GCOS - 5	3.8 (E)	6.0	4.8
GCOS - 6	9 (E)	6.2	4.5

for sites in the GCOS area. Table 2 gives the sulfur content of the season's rains in the GCOS area, converted to S deposited in Kg/ha/ month. The pH and the sulfur content of snow from the two areas, are shown in Table 3.

Table 2. Sulfur Deposited by Grossfall and by Spruce Throughfall*, GCOS area, during the 1974 growing season (July - September)

Site	Distance (direction) From SO_2 Source (km)	S Deposited (kg/ha/month)	
		Grossfall	Throughfall
Control - 1	56 (SW)	0.11	0.22
Control - 2	24 (SW)	0.11	0.33
GCOS - 1	3.2 (NW)	0.66	1.3
GCOS - 2	8 (NW)	0.55	3.2
GCOS - 3	8 (S)	1.2	4.1
GCOS - 3A*2	8 (S)	1.2	0.88

*1 Data for stemflow not given owing to lack of a quantitative factor for conversion.

*2 Aspen

Notable in the rainfall data are the consistently lower pH values of intercepted rain than open rain, and the seasonal trend (Fig. 1) towards slightly higher values from an initial minimum.

Data for the constituents of the soil leachates are presented in Tables 4 and 5 for individual sites in the RMH area. Averaged for sites distant from the main SO_2 source, the most prominent features of the data are that for KCl extractable and exchangeable Al which are much higher in high exposure/impingement sites than in distant ones (Fig. 3 & 4).

Values for the ratio between exchangeable Al : extractable bases are plotted against soil pH, for samples of mineral soil, in Figure 4; showing a strong trend of reduced pH for greater Al : base ratio.

DISCUSSION

Notable in the rainfall data (Fig. 1) is the trend towards increasing pH in successive events through the season. Also, although not as acidic as near some heavily industrial areas, the pH of intercepted precipitation, especially stemflow, is consistently much lower than open grossfall. The contained sulfur also is significantly greater.

TABLE 3. Soluble Sulfur Content and pH of Snow

Direction and distance (km) of site from source	Sampling Date (1974)	S in Snow Kg/ha	pH of Snow
GCOS area			
S, 4.8	February 22	0.17	5.2
S, 9.6	February 22	0.53	4.8
NW, 3.2 (on river ice)	February 22	0.66	5.2
SW, 56	February 22	0.36	5.2
E, 2.4	April 10	0.22	5.0
E, 4	April 10	0.23	5.4
SW, 24	April 10	0.28	5.2
RMH area			
N, 1.0	April 4	0.34	5.0
N, 12.8	April 4	0.22	5.2
NW, 6.4	April 4	0.30	5.0
S, 1.0	April 4	0.83	4.8
S, 4.0	April 4	0.23	5.4
SE, 11.7	April 4	0.23	5.4
SE, 20	April 4	0.15	5.2
E, 1	April 4	0.50	4.9
NE, 9.6	April 4	0.50	4.9
NE, 24	April 4	0.25	5.2
Northern Saskatchewan ("Control")	February 9	0.11	5.0

Included in Fig. 1 are pH values of KCl extracts from various soil layers of the given test site. Comparing soil extract pH values with those of stemflow, grossfall and throughfall, suggest that the acidic nature of these solutions, particularly near the SO_2 source, is having an acidifying effect on the soil, especially in the two surface layers of soil.

The minimum pH value of rain the first-sampled event of the season, perhaps is due to a greater portion of surface-absorbed SO_2 being collected in the first sampling period. Within any sampling date, there seems to be a positive relationship between grossfall and throughfall, i.e. an increase or decrease in the pH of grossfall is usually accompanied by an increase or decrease in throughfall. This relationship is

Table 4 - Phosphorus and nitrogen, in mg/kg, removed sequentially by various extractants from soils sampled at sites near to and distant from the SO_2 source, RMH area.

		Phosphorus					Nitrogen				
		KCl	NaF	NaOH	H_2SO_4	Total	KCl	NaF	NaOH	H_2SO_4	Total
Idlewilde Ck.	L-F-H	60	150	881	110	1201	969	1584	1565	391	4509
(distant from SO_2 source, 32 Km W.)	0-5 cm	70	22	59	28	179	25	189	253	66	533
	5-15 cm	58	3	14	14	89	47	41	100	50	238
	15-30 cm	1	8	26	66	101	23	59	112	43	237
	Total	189	183	980	218	1570	1064	1873	2030	550	5517
Radiant Ck.	L-F-H	47	164	225	138	574	2020	1186	1899	319	5424
(distant from SO_2 source 38 Km W.)	0-5 cm	3	97	194	62	356	230	551	950	76	1867
	5-15 cm	5	56	84	57	202	221	353	409	64	1047
	15-30 cm	3	42	61	34	160	152	188	294	41	675
	Total	58	359	574	291	1292	2623	2278	3552	500	9013
Average for distant sites	L-F-H	54	157	553	124	888	1495	1385	1732	355	4967
	0-5 cm	37	60	127	45	269	128	370	602	71	1171
	5-15 cm	32	30	49	36	147	134	197	255	57	643
	15-30 cm	2	25	44	50	121	88	124	203	42	457
	Total	125	272	773	255	1425	1845	2076	2792	525	7238
Aquitaine-S	L-F-H	13	158	147	29	347	748	928	1336	136	3148
(near SO_2 source 1 Km S.)	0-5 cm	9	26	31	14	80	187	211	216	57	671
	5-15 cm	5	10	23	10	48	139	84	161	43	427
	15-30 cm	5	7	23	12	47	45	25	146	31	247
	Total	32	201	224	65	522	1119	1248	1859	267	4493
Aquitaine-N	L-F-H	272	181	171	92	716	2423	1842	3483	576	8324
(near SO_2 source 8 Km N.)	0-5 cm	7	93	96	63	250	105	331	397	50	883
	5-15 cm	5	38	73	49	165	90	108	176	43	417
	15-30 cm	20	7	15	39	81	23	54	43	27	147
	Total	303	320	355	243	1212	2641	2335	4099	696	9771
Swan Cl.	L-F-H	53	117	112	42	324	906	816	1115	215	3052
(near SO_2 source 14 Km S.)	0-5 cm	1	46	72	40	159	46	254	320	65	685
	5-15 cm	1	27	61	40	129	135	192	155	32	514
	15-30 cm	9	9	14	17	49	22	44	48	32	146
	Total	64	199	259	139	661	1209	1308	1638	344	4499
Swan Lk.	L-F-H	73	146	90	32	341	1575	1208	1422	299	4504
(near SO_2 source 18 Km SE.)	0-5 cm	2	50	82	33	167	116	314	331	66	827
	5-15 cm	1	94	85	51	231	46	316	209	66	637
	15-30 cm	nil	54	74	46	174	nil	240	227	79	546
	Total	76	344	331	162	913	1737	2078	2189	510	6514
Average for near sites	L-F-H	103	151	130	49	433	1413	1199	1839	307	4758
	0-5 cm	5	54	70	38	167	114	278	316	60	768
	5-15 cm	3	42	61	38	144	103	175	175	46	499
	15-20 cm	9	19	32	29	89	23	91	116	42	272
	Total	120	266	293	154	833	1653	1743	2446	455	6297

Table 5. Acidity, exchangeable cations and pH of 1 n KCl extracts for soils sampled at sites near to and distant from the SO_2 source, RMH area.

Sites		KCl Ext. pH	Acidity - meg/100 g KCl Ext. to pH ± 5.5	Acidity - meg/100 g KCl Ext. to pH ± 8.2	Cations - meg/100 g Al	Ca	Mg	Fe	Mn	Total* bases	Al / bases	Ca/Mg
Idlewilde Ck.	L-F-H	5.9	0.4	2.8	1.3	66.7	9.2	0.5	0.1	76.5	0.017	7.3
(distant from SO_2 source, 32 Km W.)	0-5 cm	5.8	0.2	0.5	0.2	15.0	2.1	nil	nil	17.1	0.012	7.1
	5-15 cm	5.8	0.1	0.5	0.2	6.5	1.9	nil	nil	7.5	0.027	6.5
	15-30 cm	5.7	0.1	0.5	0.2	10.6	1.8	nil	nil	12.4	0.016	5.9
Radiant Ck.	L-F-H	5.9	0.8	3.8	1.4	43.8	6.9	0.5	0.2	51.4	0.027	6.3
(distant from SO_2 source, 38 Km W.)	0-5 cm	4.7	0.8	1.3	0.9	11.8	2.1	nil	0.1	14.0	0.064	5.6
	5-15 cm	4.7	1.0	1.7	1.1	10.2	2.1	nil	nil	12.3	0.089	4.9
	15-30 cm	5.0	0.3	0.5	0.5	14.9	2.9	nil	nil	17.8	0.028	5.1
Ricinus	L-F-H	6.1	nil	1.3	0.4	29.7	5.1	nil	nil	34.8	0.011	5.8
(distant from SO_2 source, 32 Km SE.)	0-5 cm	4.8	0.3	0.7	0.6	6.8	1.5	0.1	nil	8.4	0.071	4.5
	5-15 cm	5.0	0.2	0.5	0.3	10.3	2.0	nil	nil	12.3	0.024	5.2
	15-30 cm	4.9	0.1	0.5	0.4	9.7	2.5	nil	nil	12.2	0.033	3.9
Jack Fish LK.*	L-F-H	6.1	nil	1.9	1.2	47.8	8.6	nil	0.1	56.5	0.021	5.6
(distant from SO_2 source, 78 Km NNW)	0-5 cm	5.5	nil	0.6	0.3	8.9	1.8	nil	nil	10.7	0.028	4.9
	5-15 cm	4.9	0.1	0.6	1.1	3.6	1.0	0.2	nil	4.8	0.229	3.6
	15-30 cm	4.5	0.4	0.8	0.7	2.8	0.8	0.1	nil	3.7	0.189	3.5
Average for four distant sites	L-F-H	6.0	0.3	2.4	1.1	47.0	7.5	0.3	0.1	54.9	0.019	6.3
	0-5 cm	5.2	0.3	0.8	0.5	10.6	1.9	nil	nil	12.5	0.044	5.5
	5-15 cm	5.1	0.4	0.8	0.7	7.7	1.4	nil	nil	9.1	0.092	5.1
	15-30 cm	5.0	0.2	0.6	0.5	9.4	2.0	nil	nil	11.4	0.067	4.6
Aquitaine-S	L-F-H	3.8	3.6	5.8	2.5	22.4	3.1	2.4	1.3	29.2	0.086	7.2
(near SO_2 source, 1 Km S.)	0-5 cm	3.9	3.6	4.6	3.5	6.3	1.4	0.4	0.2	8.3	0.422	4.5
	5-15 cm	4.0	4.6	5.7	4.4	6.6	2.0	0.1	nil	8.7	0.506	3.3
	15-30 cm	4.1	4.8	5.8	4.6	9.7	3.2	nil	nil	12.9	0.357	3.0
Gulf	L-F-H	4.5	1.8	5.5	1.2	33.9	6.4	0.1	0.5	40.9	0.029	5.3
(near SO_2 source, 1 Km SW.)	0-5 cm	4.4	1.7	2.9	2.8	10.6	3.0	0.2	nil	13.8	0.203	3.5
	5-15 cm	4.7	0.6	0.9	0.8	3.1	1.0	0.1	nil	4.2	0.190	3.1
	15-30 cm	4.5	0.5	0.9	0.6	3.3	1.0	nil	nil	4.3	0.140	3.3
Pr. Ck. Camp	L-F-H	5.8	nil	2.3	0.4	51.2	6.5	nil	0.2	57.9	0.007	7.9
(near SO_2 source, 12 Km NW.)	0-5 cm	4.6	0.6	1.1	0.7	17.3	2.6	nil	nil	19.9	0.035	6.7
	5-15 cm	4.4	1.4	2.3	1.7	12.7	2.6	0.1	nil	15.4	0.110	4.9
	15-30 cm	4.7	0.3	0.8	1.3	10.4	2.2	0.3	nil	12.9	0.101	4.7
Pr. Ck. Ran. Sta.	L-F-H	4.0	4.0	6.9	2.3	15.1	3.6	0.1	0.8	19.6	0.117	4.2
(near SO_2 source, 13 Km N.)	0-5 cm	4.0	5.1	6.2	6.0	1.4	0.4	nil	nil	1.8	3.333	3.5
	5-15 cm	4.9	0.3	0.7	0.3	4.3	1.0	nil	nil	5.3	0.057	4.3
	15-30 cm	4.6	0.6	1.1	0.7	13.6	3.4	nil	nil	17.0	0.041	4.0

Table 5. Continued

Sites		KCl Ext. pH	Acidity - meg/100 g KCl Ext. to pH ≒ 5.5	Acidity - meg/100 g KCl Ext. to pH ≒ 8.2	Cations - meg/100 g Al	Ca	Mg	Fe	Mn	Total* bases	Al / bases	Ca/Mg
Aquitaine-N	L-F-H	4.7	2.5	5.9	1.5	34.5	7.3	0.6	3.3	45.7	0.033	4.7
(near SO_2 source, 8 Km N.)	0-5 cm	4.2	1.5	2.4	1.4	7.2	1.0	0.1	0.1	8.4	0.167	7.2
	5-15 cm	4.1	2.0	2.9	2.1	4.5	0.7	0.2	nil	5.4	0.389	6.4
	15-30 cm	4.2	2.3	3.4	2.6	9.7	2.6	0.1	nil	12.4	0.210	3.7
Swan Ck.	L-F-H	4.3	1.8	4.7	1.1	23.7	4.2	0.5	1.9	30.3	0.037	5.6
(near SO_2 source, 14 Km S.)	0-5 cm	4.6	0.4	1.2	0.5	13.0	2.5	nil	0.1	15.6	0.032	5.2
	5-15 cm	4.5	2.0	2.6	1.8	7.7	1.5	nil	nil	9.2	0.196	5.1
	15-30 cm	4.6	1.0	1.5	0.9	6.6	1.2	nil	nil	7.8	0.115	5.5
Swan Lk.	L-F-H	4.4	2.3	5.7	1.4	25.1	5.4	0.8	2.1	33.4	0.042	4.6
(near SO_2 source, 18 Km SE.)	0-5 cm	3.8	8.1	10.1	7.5	5.3	1.5	0.2	0.1	7.1	1.056	3.5
	5-15 cm	4.1	4.7	5.8	4.3	7.0	1.5	nil	nil	8.5	0.506	4.7
	15-30 cm	4.4	0.9	1.6	1.0	6.7	1.5	nil	nil	8.2	0.122	4.5
Average for seven near sites	L-F-H	4.5	2.3	5.5	1.5	29.4	5.2	0.6	1.6	36.8	0.050	5.6
	0-5 cm	4.2	3.0	4.1	3.2	8.5	1.8	0.1	0.1	10.5	0.750	4.9
	5-15 cm	4.4	2.2	3.0	2.2	6.4	1.5	0.1	nil	8.0	0.280	4.5
	15-30 cm	4.4	1.5	2.2	1.7	8.6	2.2	nil	nil	10.8	0.155	4.1

* excluding Al

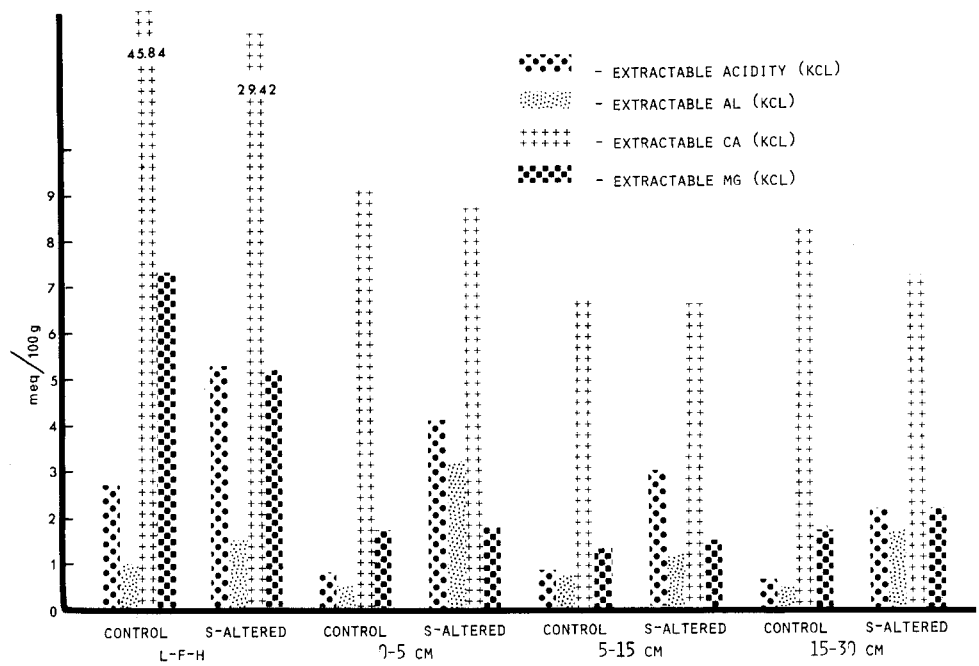

Figure 3. Effect of S-products on certain soil characteristics.

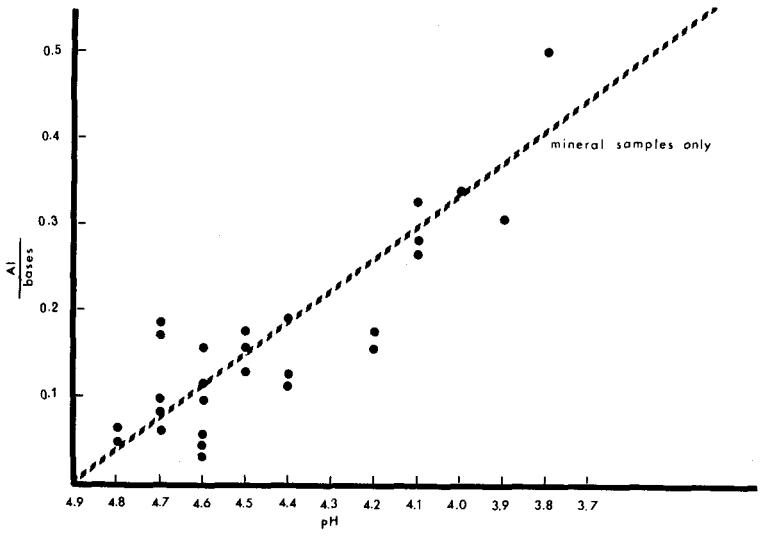

Figure 4. A plot indicating the general relationship between pH and the Al/bases (mainly Ca + Mg) ratio.

not seen in the pH of stemflow and suggests that the acidic nature of bark may play as great or greater role in the pH of stemflow as surface absorbed SO_2. With both throughfall and stemflow, the leaching of organic acids from vegetation likely contributes to the acidity of these solutions. Greater acidity of grossfall should create conditions for greater leaching of organic acids.

There is a general trend for grossfall and throughfall pH values to increase over the sampling season which suggests that with frequent summer rains there is little chance for SO_2 accumulation in the atmosphere or on the surfaces of foliar material. This feature is not seen in the pH values of stemflow throughout the sampling season and may confirm the suggestion that acid groups leached from bark surfaces may be more responsible for the acidity found in stemflow.

The basis for sequential extraction of P and N lay in the hypothesis that if SO_2 fallout increased the acidity of the soil solution, there would be greater solubility and mobility of soil constituents, particularly phosphorus, which is normally considered fairly immobile (Fried and Broeshart, 1967). In addition, if solubilization of phosphorus-bearing constituents took place, the released phosphorus should be found in association initially with aluminum, and, as the soil pH decreased further, in association with iron. Work presently in progress in this laboratory indicates that, for forest soils, the extractants used remove phosphorus fractions which differ somewhat from aerated cultivated soils, as originally suggested by Jackson (1958). This sequential leaching approach should be useful in detecting shifts in distribution of soil phosphorus between different cationic species, especially Al and Fe.

Current data (Table 4) show that both phosphorus and nitrogen are concentrated in the litter surface (L-F-H horizon) and thus the source of much of these constituents probably is organic. This fact should make any effect of SO_2 on the distribution of soil-P more easily detectable. Generally, NaOH removed more phosphorus and nitrogen than the other extractants, suggesting alkaline hydrolysis and liberation of organically bound phosphorus, particularly from the L-F-H horizon. In mineral soils, phosphorus may be removed by anion exchange, hydroxyl ions liberating phosphates bound to aluminum and iron (Fried and Boeshart, 1967).

Mineral soil samples from sites near the SO_2 source show KCl extracts with much higher exchangeable aluminum values than soils from distant sites. This suggests that the acidifying effect of SO_2 in the soil solution brought about a modification of the cation composition of the soil exchange complex and that Al^{3+} is much more prominent in SO_2 contaminated soils. There is in fact, a consistent relationship between the aluminum content of the KCl extract and acidity, both to pH 5.5 and pH 8.2 (unpublished preliminary results) than between acidity and pH, suggesting that pH alone may not be a reliable parameter to describe changes in soil acidity.

CONCLUSIONS

After two years of studies, data show that SO_2 appears to be having an acidifying effect on grossfall, throughfall, stemflow and soil solution at sites near major sources. Potassium chloride extractable acidity and aluminum are greater in soils suspected of SO_2 contamination, while exchangeable bases (especially calcium and magnesium) are lower. The acidifying effect of SO_2 at present, is not as obvious on soil anionic constituents as that on soil cationic constituents.

Nitrogen and phosphorus cycling are vitally linked with forest growth. Increased soil acidification could ultimately bring about the removal of these from the root zone or create conditions whereby these elements would be chemically or physically fixed so as to be unavailable for stand use.

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CHEMICAL AND BIOLOGICAL RELATIONSHIPS RELEVANT TO THE EFFECT OF ACID RAINFALL ON THE SOIL-PLANT SYSTEM

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ABSTRACT

This paper deals with problems of measuring acidity in rainfall and the interpretation of these measurements in terms of effects on the soil-plant system.

Theoretical relationships of the carbon-dioxide-bicarbonate equilibria and its effect on rainfall acidity measurements are given. The relationship of a cation-anion balance model of acidity in rainfall to plant nutrient uptake processes is considered. It was concluded that average H^+ concentration calculated from pH measurements is not a satisfactory method of determining H^+ loading from rainfall unless the rain is consistently acid. Cation-anion balance or titration methods should be more reliable.

The flux of H^+ ions in soil systems due to plant uptake processes and sulfur and nitrogen cycling is considered. H^+ is produced by oxidation of reduced sulfur and nitrogen compounds mineralized during decomposition of organic matter. Plant uptake processes may result in production of either H^+ or OH^- ions. Fluxes of H^+ from these processes are much greater than rainfall H^+ inputs, complicating measurement and interpretation of rainfall effects. The soil acidifying potential due to the oxidation of the NH_4^+ in rainfall is examined, with the conclusion that acidity from this source is of a similar magnitude to direct H^+ inputs common in rainfall.

I. INTRODUCTION

Recently evidence has been accumulated supporting the assumption that in some areas the acidity of rainfall has been increasing in recent years as a result of man's activity. This increase has been assumed to

be largely due to increased atmospheric inputs of SO_2 from anthropogenic sources (Likens, 1972; Likens and Bormann, 1974). Various investigators have called attention to possible adverse effects of the acidity on terrestrial and aquatic ecosystems.

Several important aspects of this problem may not have received adequate attention in the scientific literature. It is not the purpose of this paper to support or to contest the validity of the hypothesized adverse ecological effects due to acid rainfall. Rather, the information and concepts presented here are intended to be useful in the formulation of testable hypotheses and to provide a firmer basis for future experiments designed to measure these ecological effects.

II. CARBON DIOXIDE-BIOCARBONATE EQUILIBRIUM IN RAINFALL

Various investigators have recognized the importance of the carbon dioxide-bicarbonate system in determining the pH of otherwise neutral rainwater (Barret and Brodin, 1955; Pearson and Fisher, 1971; Likens and Bormann, 1974). Unfortunately many of the reporting practices and interpretations found in the literature suggest that this system is not adequately taken into account. Observed bicarbonate levels of rainfall are best understood by considering the equilibrium with atmospheric carbon dioxide. Perhaps a short explanation will be useful to workers concerned with rainwater chemistry and its ecological implications.

The generally accepted standard atmospheric CO_2 concentration is approximately 316 parts per million (ppm) or a partial pressure of 3.16×10^{-4} atmospheres. The reactions of CO_2 and water can be represented by (1) and (2) below and these are summed to obtain (3).

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \qquad (1)$$

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^- \qquad (2)$$

$$CO_2 + H_2O \rightleftarrows H^+ + HCO_3^- \qquad (3)$$

The logarithms to the base 10 of the equilibrium constants at 25°C for (1) and (2) are given by Sillen and Martell (1964) as -1.46 and -6.35 respectively. These are summed to obtain log K of -7.81 for (3), and the equilibrium expression is given by (4).

$$\frac{[H^+][HCO_3^-]}{[CO_2]_g} = 10^{-7.81} \qquad (4)$$

The $[H^+]$ and $[HCO_3^-]$ are the ion activities in moles per liter and are considered to be identical to concentration in this very dilute system. The $[CO_2]_g$ refers to the partial pressure of CO_2 in atmospheres.

If we restrict the system to stmospheric CO_2, $[CO_2]_g$ becomes 3.16×10^{-4} and (4) can be rearranged to (5).

$$[H^+]\ [HCO_3^-] = 10^{-11.31} \qquad (5)$$

In a pure water system where no source of HCO_3^- is available other than from CO_2, and assuming the system to be sufficiently acid so that the direct hydrolysis of water will be insignificant in comparison to the $[H^+]$ ion derived from the CO_2 equilibrium process, the $[H^+]$ concentration must equal $[HCO_3^-]$. Therefore, from (5) above we can write:

$$[H^+]^2 = 10^{-11.31}$$

$$[H^+] = 10^{-5.65}$$

Thus, we expect a pH of 5.65 (and $pHCO_3$ of 5.65) for pure rainwater in equilibrium with atmospheric CO_2 at 25°C. The concentration of H^+ and HCO_3^- would be 2.2×10^{-6} moles per liter and with a rainfall of 1 meter annually, the "loading" would be 2.2×10^{-3} moles per square meter per year. Hydrogen ion loading values in this range are not meaningful as the concentrations within the soil system are controlled by the CO_2 partial pressure in the soil. If rainfall or soil solution is more acid than pH 5.65 for reasons other than the effect of CO_2, the $[H^+]$ term in Equation (5) increases and the $[HCO_3^-]$ decreases. Bicarbonate concentrations decrease to insignificant levels between pH 5 and 4, and in more acid systems CO_2 partial pressures become unimportant in controlling pH.

In basic or near neutral solutions in equilibrium with CO_2, the HCO_3^- ion is very important. From the dissociation of water at 25°C we obtain Equation (6).

$$[H^+] = \frac{10^{-14}}{[OH^-]} \qquad (6)$$

Substituting (6) into (5) above we obtain (7).

$$\frac{[HCO_3^-]}{[H^+]} = 10^{2.69} \qquad (7)$$

Equation (7) states that the concentration of HCO_3^- in equilibrium with atmospheric CO2 will be $10^{2.69}$ or 490 times that of OH^-. This is a very important relationship and explains why we would not normally

expect to encounter a highly alkaline rain while acid rain is common. Alkaline earth cations entering the atmosphere as oxides, i.e., CaO, Na_2O, MgO etc., on encountering water droplets would be hydrated to hydroxides. The hydroxides will be rapidly converted to bicarbonate, and at equilibrium 490 bicarbonate ions will be present for each hydroxyl. This provides an effective buffer and prevents highly alkaline conditions from occurring at the ionic concentrations found in rainfall.

A convenient form of Equation (5) above is shown in (8).

$$[HCO_3^-] = 10^{pH-11.31} \qquad (8)$$

Equation (8) shows clearly that, for a system in equilibrium with atmospheric CO_2 at any given pH, the HCO_3^- concentration is fixed or, conversely, for any HCO_3^- concentration the pH is fixed. If data are reported that do not fit this relationship the system may not have been in equilibrium with a CO_2 partial pressure of 3.16×10^{-4} atmospheres. The graphical presentation in Figure 1 over the range usually encountered in rainfall samples shows clearly that alkaline rainfall could only occur in the presence of very high bicarbonate levels. In most cases the HCO_3^- ion may be regarded as the alkaline component of rainfall rather than the OH^- ion. When rainfall containing HCO_3^- enters an acid soil, the bicarbonate acts as a base, each HCO_3^- reacting with 1 H^+ ion to form CO_2 and H_2O as shown by the reverse of equation (3).

The above discussion ignores the carbonate ion. This need not concern us here, because the mole fraction of dissolved carbon in the CO_3^{2-} forms is negligible at the pH values considered. As pH increases, CO_3^{2-} increases. If pH values above about 8.5 were encountered, this ion would become significant.

Changes in CO_2 partial pressure during sample collection and storage could significantly affect pH and bicarbonate measurements on many rainwater samples. For illustration, I have plotted in Figure 2 the HCO_3^- and pH values for a series of rainwater samples reported by Egner and Eriksson (1955a, 1955b). The reported pH values are generally about 0.5 unit lower than would be consistent with a CO_2 concentration of 300 ppm but are generally much more consistent with 1000 ppm CO_2. The 1000 ppm level could easily exist in confined collection vessels or storage containers, but there is no way to be certain that this is the cause of the discrepancy. Granat (1972) has reported a similar and consistent effect in a large number of samples. He suggests that it is due to the presence of undissolved materials that yield the major ions commonly found in rainfall upon dissolution, but he does not suggest any compounds with the necessary properties.

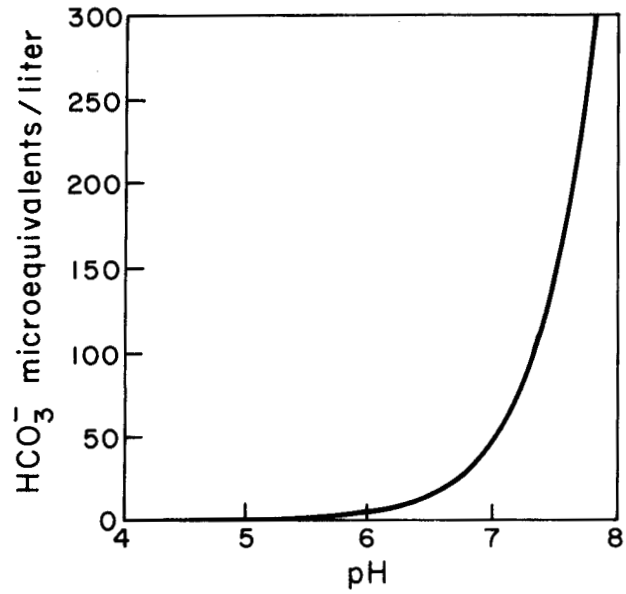

Figure 1. The relationship between pH and HCO_3^- activity in equilibrium with atmospheric CO_2, (316 ppm).

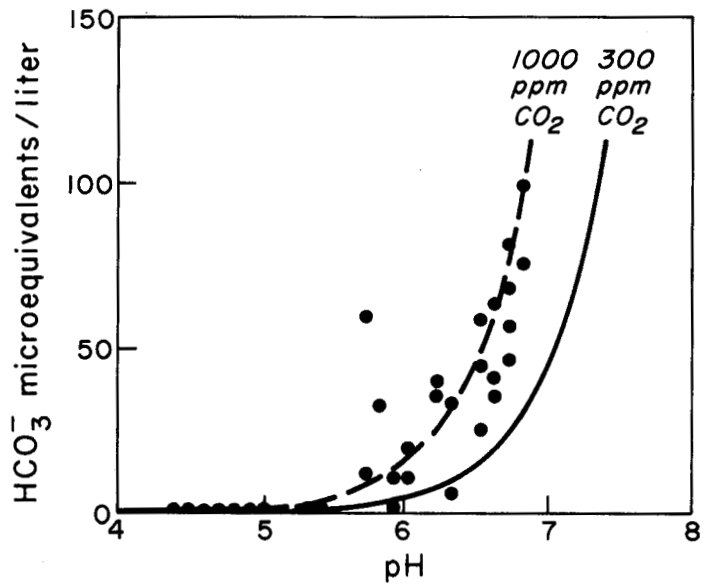

Figure 2. Plot of the pH and HCO_3^- levels reported by Egner and Eriksson (1955b, data set D501.).

In practice few errors will result from pH measurements at unknown CO_2 concentrations if the rainfall is consistently acid. However, if non-acidic events are interspersed with acid events, the errors could be substantial. The diagram shown in Figure 3 should prove useful in

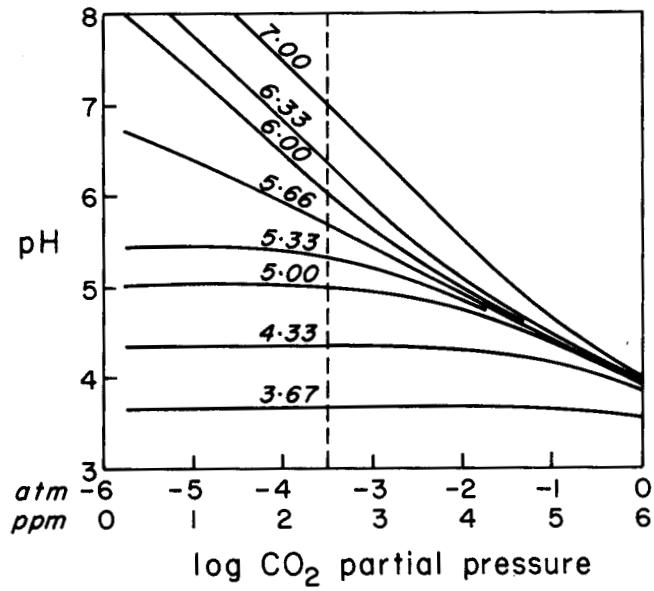

Figure 3. Diagram showing the effects of varying CO_2 partial pressure on pH. Dotted line indicates 316 ppm CO_2 and numbers refer to pH at 316 ppm CO_2.

this regard. It is developed by utilizing the principle that the net alkalinity b is independent of CO_2 partial pressure, and in systems where the CO_3^- ion is negligible, is defined by (9).

$$b = [OH^-] + [HCO_3^-] - [H^+] \qquad (9)$$

Rearranging (9):

$$[HCO_3^-] = b - [OH^-] + [H^+]$$

Substituting for $[HCO_3^-]$ in (4) above, replacing $[OH^-]$ by $10^{-14}/[H^+]$, and rearranging we obtain (10).

$$[H^+]^2 + [H^+]b - 10^{-7\cdot81}\ [CO_2] - 10^{-14} = 0 \qquad (10)$$

For any combination of pH and CO_2 partial pressure, $[OH^-]$ and $[HCO_3^-]$ may be calculated by means of (4) and (6) and b calculated from (9). To construct figure 3 arbitrary pH values were selected and the values

of b determined for 316 ppm CO_2. The lines were then generated by calculating $[H^+]$ as a function of $[CO_2]$ using (10).

No significant effects due to CO_2 partial pressure variations would be expected where the lines on Figure 3 are horizontal. In general the CO_2 pressures of interest are in the range of 300 to 1000 ppm, but higher values may occur. From the graph we see that with samples below pH 4.33 no effects occur within the range of interest, but at pH 5.0 CO_2 pressures above 1000 ppm would depress measured pH. With samples above pH 5.00 the error due to variations in CO_2 becomes unacceptable.

Several methods might be employed to minimize possible errors. First, I suggest that reported pH values should be those taken only after equilibration with known CO_2 partial pressures. This would assure uniformity between samples and provide a uniform basis for comparing data from different investigations. This equilibration is particularly important with samples above pH 5.0. Secondly, H^+ ion loadings per unit area should not be calculated by simply determining total H^+ from pH and volume measurements. The long-term effects on soil systems are more likely to be related to the net H^+ loading over time. This would be the difference between H^+ and titratable alkalinity or, in practical terms, H^+ minus HCO_3^-. The HCO_3^- represents the alkaline component of the rainfall so in order to estimate net H^+ loading from pH measurement, any HCO_3^- must be subtracted from the total H^+ found. This method has been used by Granat (1972). If all major cations and anions are determined, a method of calculating net acidification using anion-cation balances as discussed in the next section should be considered.

III. CATION-ANION BALANCE IN RELATION TO ACID RAINFALL

An important property of solution systems, whether soil solution or rainfall, is that electrical neutrality is maintained. The chemist analyzing precipitation or stream water utilizes this property when he checks his results to ascertain whether the cations found equal the anions. If the difference exceeds normal analytical uncertainty, either an analytical error has been made or some important constituent has not been determined.

This property may be utilized effectively in determining the acidity of rainfall in the absence of pH measurements, provided the major cations and anions have been accurately determined. The major anions other than HCO_3^- involved in the system are NO_3^-, Cl^-, and SO_4^-. Major cations commonly encountered are Ca^{2+}, Mg^{2+}, Na^+, K^+, and NH_4^+. If the anions exceed the cations, electrical neutrality of the system

is maintained by H^+ ions and the system is acid. This is the situation we would expect when acidification occurs due to H_2SO_4 and HNO_3 formed from SO_x and NO_x gases in the atmosphere. Excluding HCO_3^- and H^+, the excess of anions over cations on an equivalent basis may be used to estimate net acidity as shown by (11).

$$e = 2\,[SO_4^{2-}] + [NO_3^-] + [Cl^-] - 2\,[Ca^{2+}] - 2\,[Mg^{2+}] - [K^+] - [NH_4^+] \quad (11)$$

where: e = excess acid in moles per liter (-e = alkalinity).

For certain ecosystem effects this measurement may be more appropriate than direct H^+ measurements. For instance, the long-term effects of soil acidification are probably more appropriately considered in terms of a deficit of basic cations than in terms of H^+ ions directly. If the excess anions in acid rainfall are mobile, they will be leached from the soil in association with bases from the exchange complex, resulting in base depletion and acidification. Some soils, particularly those that are acid and highly weathered, exhibit significant anion exchange properties. In these soils anion mobility is reduced, and an excess of acid anions over basic cations may not result in base depletion. This condition is discussed more fully in relation to the sulfur system in Section IV.

If the basic cations in rainfall exceed the anions, the deficit would be made up by OH^- ions in solution if no CO_2^- was present. In the atmosphere, the OH^- ions are rapidly converted to HCO_3^- as explained above. At any rate, the excess of basic cations over anions (excluding HCO_3^-) should be an appropriate measure of the ability of the rainwater to increase the base status of the lithosphere or hydrosphere.

In practice rainfall acidity measurements derived from anion minus cation calculation should correspond very closely to values obtained by subtracting HCO_3^- from H^+ derived from pH measurements. Rainwater at pH 5.0 contains 10 micromoles H^+ per liter and 100 micromoles per liter at pH 4.0. Cation levels are generally of the same order of magnitude, so measurements that give acceptable accuracy of the cations and anions in this range should also combine to give acceptable estimates of net acidity or alkalinity. Occasionally rainwaters may be encountered with ionic concentrations of the order of several thousand microequivalents per liter. Cation-anion balance may not give acceptable values for acidity of the initial rainfall in these cases as the total ion content is much higher than the H^+ concentration and relatively small analytical errors would drastically affect the estimated acidity. Unfortunately, when higher concentrations are present, direct pH measurements may also be a poor indicator of the effect of the water on the acid base relationships of the soil due to the increased probability of incomplete ionization of acids or bases.

In order to examine the validity of this relationship, a data set was selected from the literature and H^+ ion loading calculated by the anion minus cation method. The observed vs. predicted values were then compared by linear regression. For the data of Pearson and Fisher (1971), the relationship obtained using all 37 points was: Y = 9.24 + .758 X with a correlation coefficient (r) = .826; where Y is the observed H^+ minus HCO_3 in millimoles per square meter per year and X is the anions minus cations in milliequivalents per square meter. It was also noted that a good deal of the scatter resulted from a few coastal points where high Na^+ and Cl^- levels appeared to be erratic. When the coastal points were excluded the least squares regression equation for the remaining 30 observations was; Y = 5.71 + 0.90 X with a correlation coefficient (r) of 0.900. This relationship is shown in Figure 4. A similar comparison was made using data given by Egner

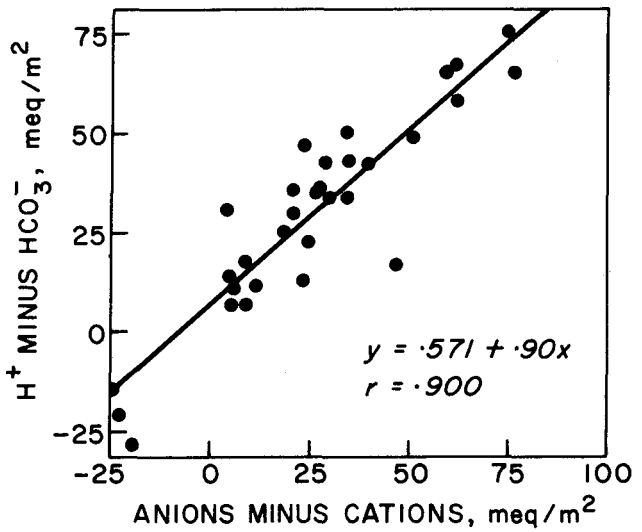

Figure 4. Relationships between net acidity as calculated by anions (excluding HCO_3^-) minus basic cations, and observed H^+ minus HCO_3^- for data set reported by Pearson and Fisher (1971). Coastal stations were not included.

and Eriksson (1955b). In this case the least squares regression equation was Y = 0.12 + 0.571 X with a correlation coefficient (r) of 0.750; where Y is observed H^+ minus HCO_3^- and X is calculated from anions minus cations. One location extremely high in Na^+ and Cl^- was excluded. This case is interesting because most of the values are negative, i.e. the samples were effectively basic. The bulk of the

scatter appears to arise from the negative values. Whether this reflects analytical errors or is due to other causes is not known. It is entirely possible that the anion minus cation values more accurately reflect the net H^+ loading of the system than the H^+ minus HCO_3^- values.

Granat (1972) has proposed a model for calculating acidity of rainfall from the concentration of the individual ions as follows:

$$a = 2\ ([SO_4^{2-}] - \frac{27.6}{457}\ [Na^+] + [NO_3^-] - [NH_4^+]$$

$$b = \frac{1}{2}([K^+] - \frac{9.7}{457}\ [Na^+]) + ([Mg^{2+}] - \frac{55.6}{457}\ [Na^+])$$

$$+ ([Ca^{2+}] - \frac{10.0}{457}\ [Na^+])$$

$$e = a - 2b$$

Where: a = amount of available acid
b = amount of base expressed as moles of carbonate
e = excess acid in moles per liter (-e = alkalinity)

This model assumes that all sodium in rainfall is of marine origin. The fraction of the SO_4^{2-}, K^+, Mg^{2+}, and Ca^{2+} assumed to be of marine origin is equal to the concentration of sodium times the ratio of the respective ion in sea water to the concentration of sodium in sea water. The model is apparently intended to represent the net acidity or alkalinity of rainfall assuming it to be an aqueous solution or suspension formed from sea salts, sulfuric acid, nitric acid and ammonia. Implicit in the model is the assumption that the ratio of Cl^- to Na^+ is the same in rainfall as in sea water. Granat shows that the model is reasonably accurate in predicting the net acidity or alkalinity of rainfall.

It may not be readily apparent to the casual reader, but this model is actually a form of the strong acid anion minus basic cation method of calculating acidity shown in equation (11). The models are identical if the molar ratio of Cl^- to Na^+ in the rainfall is 1.19, the ratio found in sea water. Deviations of acidity or alkalinity calculated by Granat's model from measured values should be equal to the difference between measured Cl^- concentration and an estimated Cl^- concentration determined by multiplying the Na^+ concentration by 1.19.

The concept of cation-anion balance and electrical neutrality of the system is also useful in considering acid-base relationships of plant uptake of ions. In order to maintain electrical neutrality in the system, the plant must either take up equal amounts of cations and anions on an equivalent basis or, if the amounts are unequal, it must release to the solution an amount of ions equal to the difference and of the same charge as the excess. A reasonable conceptual model of

this effect is that the plant gives off H^+ ions equal to the excess of cations over anions taken up, and indeed this seems to be the case (Fried and Broeshart, 1967 p. 97). The converse of this is that an excess of uptake of anions over cations is balanced by a release of OH^- ions which appear in the media as HCO_3^- due to the presence of CO_2.

Most plants take up more anions than cations, but this may be reversed if the bulk of the nitrogen uptake occurs as NH_4^+ rather than NO_3^-. Variations of a magnitude sufficient to cause major differences in the acidity relationships of the media may occur. Healthy plants usually contain substantially lower quantities of the usual anions, i.e. NO_3^-, Cl^-, SO_4^{2-}, and $H_2PO_4^-$, than of the basic cations. This results from the reduction of SO_4^- and NO_3^- to reduced forms of S and N which are utilized in the protein structure. The excess of basic cations are electrically balanced by organic anions formed in the plant. During the breakdown of the dead plant material, these basic salts of organic acids may be hydrolyzed. The bases are removed and leached as bicarbonates and the remaining litter is acidic due to the presence of these organic acids. If the pH lowers to the point that bicarbonates can no longer exist, this mechanism of leaching is no longer operative. Bases then can only leach in conjunction with the above anions or by chelation with certain organic complexes.

The acid base relationship of this soil-plant system is complex. It does not seem justified to regard this in terms of a simple input-output system of H^+ ions; the cation-anion balance and acidity relationships of the whole soil-plant system must be considered. Apparently one critical research need, in terms of evaluating ecological effects of acid rainfall, is to synthesize present knowledge of the acidity and cation-anion relationships into an overall model from which testable hypotheses can be developed. Some important aspects of this system are considered in more detail in the following sections.

IV. ACIDITY RELATIONSHIPS OF THE SULFUR CYCLE

Possible effects of sulfur inputs from anthropogenic sources on soil-plant systems are an important aspect of the acid rainfall problem. As it would seem desirable to consider possible effects from the standpoint of the total sulfur cycle, a brief description of the acidity relationships of this cycle appears appropriate.

While sulfur may be present in a variety of forms in plant tissue and residues, it is mostly in reduced (S^{2-}) form. The bulk of the sulfur is found in the amino acid units of the various proteins. Microorganisms that break down plant residue and soil organic matter may utilize the reduced sulfur in the organic material or, in some

cases, may utilize sulfate sulfur from the surrounding media. At any rate, the organic sulfur compounds are transformed to reduced or incompletely oxidized forms such as sulfides, elemental S, thiosulfates etc., (Starkey, 1966). These reduced or incompleted oxidized compounds are then oxidized to sulfate by aerobic chemautotrophs. The oxidation of the reduced sulfur from the soil organic matter to the sulfate form will inevitably be accompanied by the release of two H^+ ions for each sulfur atom oxidized. This general reaction may be represented by equations (12) and (13) for sulfide and elemental sulfur:

$$H_2S + 2\ O_2 \rightarrow 2H^+ + SO_4^{2-} \qquad (12)$$

$$S + 3/2\ O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-} \qquad (13)$$

In Figure 5, the oxidation of organic sulfur to SO_4^{2-} is shown as releasing 2 H^+ ions. H_2S may also act as an acid, but the dissociation constants are such ($pK_1 = 7.24$, $pK_2 = 14.92$) that it would be largely non-ionized in acid soil systems.

If we assume the SO_4^{2-} released is rapidly taken up by plants, the acid formed by the oxidation will be balanced by the release of 2 OH^- (or HCO_3^-) ions from the plant in the uptake process (Figure 5). The net change in H^+ ions for the overall process in the soil is zero (2 H^+ and 2 OH^- ions formed), and no change in acidity results. The consideration of the OH^- ions released by the plant as a result of uptake of anions is an essential point. However, it cannot be validly considered in isolation, but must be considered as a part of the total cation-anion balance of nutrient uptake and plant processes.

Plants apparently take up sulfur almost entirely as the sulfate ion but, as noted previously, the preponderance of sulfur in the plant is in the reduced form. Sulfate is reduced to the S^{2-} form within the plant prior to its incorporation into the structure of the plant in the sulfur containing amino acids. This reduction results in the removal of 2 H^+ (Figure 5) ions according to a reaction that may be considered the reverse of (12) above. The consumption of 2 H^+ ions at this point balances the loss of 2 OH^- ions, (which may be considered as equivalent to formation of 2 H^+ ions) during the uptake of sulfur.

The total H^+ ion production and consumption of the sulfur cycle (Figure 5) is balanced and no net change in acidity should result. While the cycle represents a drastic simplification of the sulfur oxidation-reduction processes in the system, the acidity relationships should be basically valid.

The anaerobic reduction of sulfate to sulfide (Figure 5) requires low oxygen levels and a fixed carbon energy source, as it is carried out by heterotrophic anaerobic organisms. High concentrations of sulfide compounds may accumulate in flooded soils where sulfate is

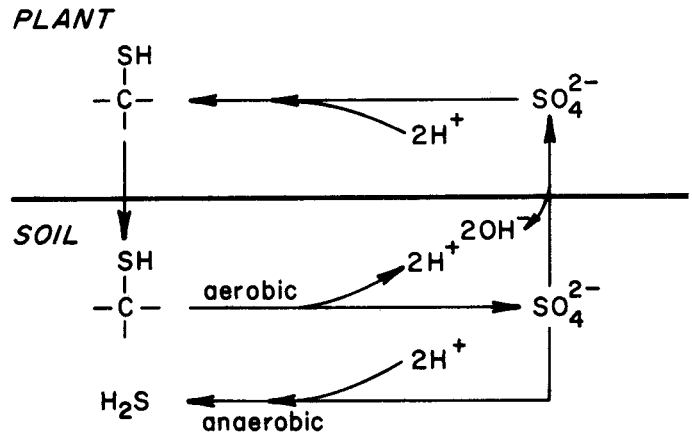

Figure 5. Simplified sulfur cycle showing acid formed or consumed by the various processes.

continually replenished, such as river deltas. This process tends to produce neutral or basic soils as H^+ ions are consumed. Drainage of these soils results in rapid acidification due to H^+ produced during the oxidation of S^{2-} to SO_4^{2-}.

While the sulfur cycle is inherently balanced as far as acid production and consumption are concerned, it does provide some potential for leaching of bases and subsequent development of soil acidity. This arises because lags may occur between oxidation to sulfate and uptake of the sulfate ion. If sulfate ions accumulate, there is a concomittant increase in H^+ formed in the oxidation of reduced sulfur to sulfate. The H^+ ions replace basic cations on the clay and organic matter complexes, and these bases may be leached from the soil in association with the SO_4^{2-} anion. The quantification of any acceleration of this loss of cations that may be due to acid rainfall is a critical aspect of the assessment of possible ecological effects that may result.

In neutral or acid soils sulfate ions may remain in the soil solution or become adsorbed on soil particles. Various conceptual models have been proposed but for our purposes it is most useful to consider this adsorption to be an anion exchange phenomenon. Soil particles are generally negatively charged but some positive charges exist as the result of the amphoteric nature of soil organic matter

and broken bonds on the edges of the clay lattices. As soils become acid, the alumino-silicates tend to decompose as represented by equations (14-16).

$$Al(OH)_3 + H^+ \rightleftarrows Al(OH)_2^+ + H_2O \quad (14)$$

$$Al(OH)_2^+ + H^+ \rightleftarrows Al(OH)^{2+} + H_2O \quad (15)$$

$$Al(OH)^{2+} + H^+ \rightleftarrows Al^{3+} + H_2O \quad (16)$$

According to this model most reserve acidity in soils does not consist of H^+ ions adsorbed on negatively charged soil colloids but exists in the form of monomeric Al^{3+} and positively charged hydroxy aluminum complexes and polymers. These positive charges neutralize negatively charged colloids or adsorbed anions such as SO_4^{2-}. As soils become more acid their cation exchange capacity decreases due to neutralization of negative charges by this mechanism. The increase in positive charges with acidification increases the capacity of soils to adsorb anions such as sulfate (Harward, Chao, and Fang, 1962; Harward and Reisenaur, 1966). Apparently as acidity increases due to anthropogenic sulfur inputs, the ability of the soil to hold the sulfate ion through the adsorption mechanism would also increase.

If reduced sulfur such as elemental S° is added to an aerobic soil system, we can expect oxidation to SO_4^{2-} by soil organisms releasing $2H^+$ ions. When rainfall containing H_2SO_4 enters the system, the H^+ ions are supplied directly. If the rainfall contains a mixture of H_2SO_4 and H_2SO_3(Brosset, 1973), the pH of the rainfall would not be as low as for a similar concentration of H_2SO_4 alone, due to the lower dissociation of H_2SO_3 but the H_2SO_3 would undoubtedly be oxidized to H_2SO_4 when temperature and moisture conditions are favorable. Thus, the net effect on the acidity of the soil system would be the same of H_2SO_3 as for H_2SO_4.

Recent data of Nyborg et. al., (1973) indicate that direct soil absorption of SO_2 may be substantial. This would also result in H_2SO_3 formation in the soil.

From the above we see that the net increase in acidity per mole of sulfur added is identical for S^0, SO_2, H_2SO_3, or H_2SO_4. However, if he SO_4^{2-} is rapidly absorbed by the plant systems, the resultant release of OH^- ions (Figure 5) would tend to balance the extra acidity.

Sulfur loads calculated from the data of Pearson and Fisher (1971) for the northeastern U. S., tend to be in the range of 8 to 15 kg ha^{-1} yr^{-1}. Jonsson and Sundberg (1970) give a value of 9 kg ha^{-1} yr^{-1} for the Swedish forests. Values of this magnitude could probably be absorbed by most agricultural ecosystems as they are in the same general range as harvest removals of sulfur. In forest ecosystems a

a long-term build up of sulfur in soils, plants, and litter might be expected. If loading is greater than the capacity of the ecosystem to utilize or store sulfur, leaching losses will probably occur, bases will be lost in conjunction with the SO_4^{2-}, and the soil will become more acid.

The above discussion refers specifically to inputs of sulfur that are not balanced by basic cations. If rainfall inputs of sulfate are accompanied by similar amounts of basic cations, i.e., Na^+, Ca^{2+}, Mg^{2+}, or K^+, little change in soil acidity would be expected. Over long periods of time, however, if the distribution of these input ions is different than the distribution of ions in the soil solution and in equilibrium with exchangeable cations in the soil, a shift in the cation equilibria could occur.

The capacity to utilize additional sulfur is often closely related to the nitrogen cycle. Nitrogen sulfur ratios of most plant proteins will be in the range of 12:1 to 16:1, while ratios in soil organic matter tend to be of the order of 8:1 or 10:1 (Stewart and Whitfield, 1965). When nitrogen being taken up by plants is largely derived from soil organic matter, the growth limiting nutrient is more likely to be nitrogen than sulfur. The sulfur mineralized will usually be sufficient for utilization of the nitrogen mineralized. However, if nitrogen comes from an outside source such as fixation of atmospheric nitrogen or nonsulfur containing fertilizers, the probability of sulfur deficiency is substantially increased. Sulfur responses in agriculture are generally found on legume crops such as alfalfa and clover or on crops where heavy nitrogen fertilizer applications are made using fertilizer materials that do not contain sulfur. In forest ecosystems where nitrogen fixation is rapid such as in alder stands, there is a definite possibility that anthropogenic sulfur inputs would result in accelerated growth. In such systems the removal of sulfur as a growth limiting factor would probably increase productivity. It is even possible that sulfuric acid in rainfall would not result in increased soil acidity due to the balancing effect of the OH^- ions given off by the plant in the uptake of SO_4^{2-}.

Mature timber stands or other systems in which nitrogen is supplied largely from internal cycling are less likely to be sulfur limited. If the capacity of these ecosystems to utilize sulfur inputs is exceeded, the probability of deleterious effects from sulfuric acid in rainfall would be increased.

Finally, the effect of sulfur inputs on base rich soils should be considered. Such soils are generally found in arid areas, but occasionally occur under humid or subhumid conditions. These soils are virtually 100% base saturated, i.e., all cation exchange positions are occupied by bases, and they generally contain free alkaline earth carbonates. The acid-base relationships of the sulfur cycle here are identical to those discussed above except for the effect of excess

acid. Free carbonates result in a large buffering capacity. Acid rainfall high in sulfate ion would dissolve calcium carbonate, and sulfates would tend to accumulate and precipitate out as gypsum.

Gypsum cannot ordinarily be considered toxic as many productive soils naturally contain gypsum crystals, but changes in plant communities might occur on soils that did not normally contain gypsum. Also many calcareous grassland soils have an acidic layer a few centimeters thick near the surface. Acid rainfall or SO_2 sorption would be expected to intensify this layer. The possible ecological effects of these changes are unknown.

V. ACID-BASE RELATIONSHIPS OF THE NITROGEN CYCLE

In light of the recent interest in the effect of anthropogenic sulfur inputs on the acid-base relationship in soil-plant systems, it is appropriate to call attention to the role of the nitrogen system in this regard. From an overall ecosystem point of view, the nitrogen cycle can be expected to release or consume much greater quantities of H^+ ions than would be involved in the sulfur cycle. Also the contribution of nitrogen compounds to the potential of rainwater to acidify soil systems may be much greater than generally recognized. Plant uptake of nitrogen occurs in both the NH_4^+ and NO_3^- forms. Factors that determine the relative uptake in each of these forms include the nature of the plant and the presence or absence of conditions favorable to the oxidation of NH_4^+ to NO_3^- in the soil system.

While plants may contain many types of nitrogen compounds, the major portion of the nitrogen is found in the structural proteins. This nitrogen is in the N^{3-} oxidation state, the same as is found in NH_3, NH_4^+ and soil organic nitrogen. When plants take up nitrogen in the NH_4^+ form, no change in oxidation state in the system is required. Starting with the soil organic component in Figure 6, we consider the release of N to be a simple deamination of $-CNH_2$ to NH_3 with no change in acid-base status required. This NH_3 will require 1 H^+ ion to ionize as NH_4^+.

The uptake of NH_4^+ by a plant results in the release or exchange of an H^+ ion so the net change in acidity for the soil system is zero. The acid-base relationships in the plant are relatively simple when nitrogen is taken up in the NH_4^+ form. One H^+ is released in the conversion to NH_3 or $C\text{-}NH_2$. This balances the H^+ ion released in the uptake process so the net change is again zero. The acid-base relationship of the cycle appears to balance as one would intuitively expect.

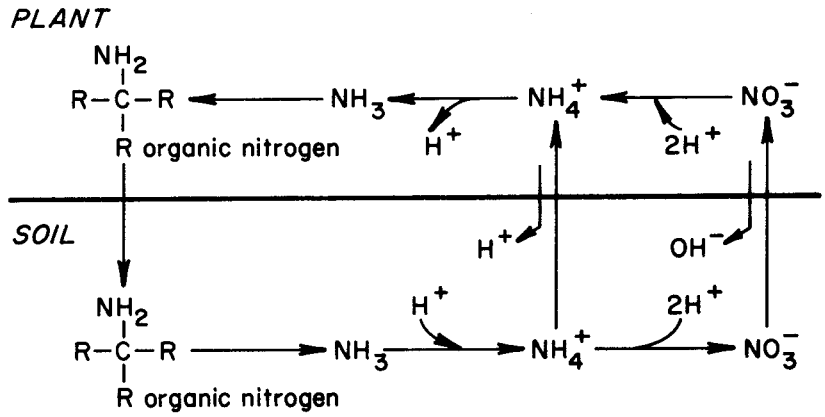

Figure 6. Simplified nitrogen cycle showing acid formed or consumed by the various processes.

The system becomes more complex when we consider the oxidation of NH_4^+ to NO_3^- and the subsequent uptake of the nitrate ion. The oxidation of NH_4^+ to NO_2^- and subsequently NO_3^-, releases a total of $2H^+$ ions, as shown below:

$$NH_4^+ + 3/2\ O_2 \rightarrow 2H^+ + NO_2^- + H_2O \qquad (17)$$

$$NO_2^- + 1/2\ O_2 \rightarrow NO_3^- \qquad (18)$$

These transformations are carried out in the soil largely by chemautotrophs, step (a) by organisms of the genus *Nitrosammonas* and (b) by *Nitrobacter*. The subsequent uptake of NO_3^- releases 1 OH^-, which balances one half the acidity released in the oxidation. The other half is balanced by the H^+ utilized in the protonation of NH_3. Again, we find the net change in the soil is zero and the system balances, provided the cycle is completed by plant uptake.

The plant transformations may be regarded as the reverse of those found in the soil. Two H^+ ions are consumed in the reduction of NO_3^- to NH_4^+ by the nitrate reductase enzyme system. One of these is balanced by the loss of an H^+ to form NH_3 prior to the amination. The other is balanced by the release of the OH^- that occurred during the uptake of NO_3^-, as an OH^- lost by the plant is equivalent to the formation of an H^+.

Even though the overall system can be considered balanced, the nitrogen cycle offers potential mechanisms for losses of bases and acidification of the soil system. When mineralization occurs followed by the oxidation of NH_4^+ to nitrate, the H^+ ions formed will replace a basic cation on the cation exchange complex. This basic cation is then subject to leaching in conjunction with the NO_3^- ion. If conditions

allow any build-up of NO_3^-, the potential for leaching exists when water passes through the profile. Most natural ecosystems tend to maintain low nitrate levels as the nitrates formed are rapidly taken up by the plants.

Some interesting questions arise when one considers the potential acidity relationships of mineral nitrogen inputs in precipitation. Any anion taken up by a plant will cause the release of an OH^- ion, so nitrate could be considered as resulting in a basic reaction. The highly mobile nitrate ion is rapidly absorbed by the plant, and Pearson and Fisher (1971) note that stream loads of mineral N are less than precipitation inputs. Even though this possible basic effect may be valid, one must be cautious in the interpretation of this effect in isolation from the rest of the cation-anion system.

Perhaps the most interesting aspect of the nitrogen cycle in relation to rainfall acidity involves the ammonium ion. If the NH_4^+ falling in precipitation is oxidized in the soil to the nitrate form, 2 moles of H^+ will be formed for each mole of NH_4^+ oxidized. The data of Pearson and Fisher (1971) show that this effect may be substantial. Table 1 shows values of the mean ionic concentration and loading for Mays Point, New York in 1966, calculated from their data. The NH_4^+

Table 1. Average ionic loading and composition for rainwater collected at Mays Point, New York in 1966 (Pearson and Fisher, 1971).

Cations	Milligram Equivalents* $meter^{-2} \cdot year^{-1}$	Microgram Equivalents* $liter^{-1}$
Ca^{2+}	35.7	45.9
Mg^{2+}	11.7	15.0
Na^+	8.1	10.4
K^+	3.1	4.0
NH_4^+	15.1	19.4
H^+	34.9	44.8
Anions		
SO_4^{2-}	87.9	113.0
Cl^-	10.5	13.5
NO_3^-	2.7	3.5

*Data as shown by Pearson and Fisher was in units of tons per square mile per day. Precipitation totaled 78 centimeters.

value of 15.1 milliequivalents of NH_4^+ per square meter at this location also happens to be the mean value for all locations and years that they report. They report an H^+ loading of 34.9 milliequivalents per year which would correspond to a mean value of 44.8 microequivalents per liter with a total precipitation of 78 centimeters. This mean H^+ concentration results in an "average pH" of 4.35. If 2 moles of H^+ are released in the oxidation of each mole of NH_4^+ to NO_3^- the oxidation of 15.1 milliequivalents of NH_4^+ to NO_3^- will result in the release of 30.2 milliequivalents of H^+ per square meter, an amount very similar to the 34.9 milliequivalents reported as the direct input from H^+ loading.

Another example of the possible significance of the effect of acidification due to oxidation of NH_4^+ can be seen from data shown by Likens (1972) and Likens and Bormann (1974). Likens (1972) calls attention to an apparent shift from NH_4^+ to NO_3^- as the dominant form of inorganic nitrogen in New York since about 1945. Likens and Bormann (1974) note increasing acidity of rainfall over the same period as evidenced by pH values of about 4.0 at present. No direct pH measurements are available for the early samples, but they are inferred to be higher due to the recorded presence of bicarbonates and from their reaction to methyl orange indicator. The data are presented in graphical form, but apparently a value of 0.9 milligrams NH_4^+ per liter is representative of the bulk of the observations prior to 1945, with a few values above 3.0. The release of 2 H^+ ions per mole on oxidation of 0.9 milligrams NH_4^+ per liter would release 0.106 milligrams H^+ per liter.

Data from six collection stations in this area in 1970-71 (Likens 1972) averaged 0.48 milligrams NH_4^+ per liter or 0.053 milligrams H^+ per liter on oxidation. The direct H^+ input for these samples was 0.105 milligrams per liter or an "average" pH of 3.99. These data clearly illustrate the importance of the NH_4^+ component to the capacity of rainfall to acidify soils. It should also be recognized that if the high NH_4^+ contents of the pre-1945 samples are indeed representative of rainfall from that era, the potential to acidify soils would have been substantial even though the rainfall was apparently not acid.

When ammonium is taken up directly by the plant, acidification still occurs due to the H^+ given off by the plant in the uptake process. The magnitude of this effect is often underestimated. In the past many experiments showing poor growth in solution and pot cultures when ammonium was used as a nitrogen source were interpreted as a toxic effect of NH_4^+ ion when in fact the toxicity was caused by acidity developed in the medium. Carnation producers had long considered NH_4^+ as an unsuitable source of nitrogen, but it has been shown that they do well when NH_4^+ is used if $CaCO_3$ is added to prevent acidification (Schekel, 1971).

Ammonium inputs, whether oxidized to nitrate or not, can thus be shown to have an acidifying effect. While it is probably extreme to consider the total potential acidification as representing two moles H^+ per mole of NH_4^+, the effect should be recognized in our evaluation of the effect of rainfall acidity.

If ammonium inputs are important, it may be well to consider their source and distribution. In past years, many measurements of nitrogen inputs in rainfall were made for the purpose of evaluating their agricultural significance. Results vary widely, and it is impossible to accurately evaluate whether the variation is due to contamination and analytical inaccuracies or actual variation in amounts. It has been noted that the results quite consistently show a 2:1 ratio of ammonium to nitrate N (Stevenson, 1965), but the results of Pearson and Fisher (1971) show widely varying ratios both between locations and between years at a single location.

Atmospheric ammonia levels vary widely. Sources of ammonia often widely quoted include industrial, atmospheric fixation (electrical and photochemical), and volatilization from land surfaces. Recently Luebs, Davis, and Laag (1973) have shown much higher atmospheric concentrations of NH_3 in a dairy area in California than in a control area. They also claimed NH_4^+ inputs in the precipitation in the dairy area to be three times that of the control area. Hutchinson and Viets (1969) have reported high ammonia absorption by traps near feedlot operations. Thus, the possible effects of high concentrations of livestock must be considered as well.

Atmospheric NH_3 reacting with sulfuric acid aerosols would form ammonium sulfate and bisulfate salts. The resultant solution would be much less acidic than aerosols not neutralized by NH_3, yet the system would retain the capacity to acidify soils as shown by the mechanisms discussed above. Therefore, the neutralization of acid aerosols by atmospheric NH_3 may not reduce the capacity of the rainfall to acidify soils.

In conclusion, it probably is not possible at the present time to predict quantitatively the effect of nitrate and ammonium on the capacity of acid rainfall to acidify the soil system. On theoretical grounds we could expect substantial effects, and evaluation of this contribution should be included among the goals of future research on the acid rainfall problem.

VI. SUMMARY

A number of chemical and biological considerations relevant to understanding the effects of rainfall acidity on soil-plant systems have been discussed. The following points are particularly important and should be thoroughly understood by researchers engaged in acid rainfall investigations.

A. Due to the effect of atmospheric CO_2 the basic component of rainfall exists largely as HCO_3^-. If samples are above pH 5.0, pH measurements are subject to serious errors due to fluctuations in CO_2 partial pressure.

B. The potential of rainfall to acidify soil or waters is characterized by its containing more acid anions than basic cations. This excess of anions can be an appropriate measure of the capacity of the rainfall to contribute to the acidity of soil systems.

C. The acidity of a plant growth medium is affected by the relative uptake of cations and anions by the plants growing in the medium. The overall effect of acid rainfall is not only the effect of H^+ ions added to the system but may also reflect the relative plant uptake of the various ions added to the system.

D. In the natural sulfur cycle H^+ ions are continually being formed and consumed by various biological processes. An important aspect of the acid rainfall question involves the effect of additional sulfur loading on these processes.

E. Soil nitrogen transformations normally involve a substantial production and consumption of H^+ ions. This flux of H^+ ions is much larger than that involved in sulfur transformations or the input from acid rainfall. Measurement of the effects of H^+ inputs from outside the system may be complicated by this larger flux due to normal nitrogen transformations.

F. The oxidation of ammonium to nitrate by aerobic chemautotrophic bacteria results in the production of acid. Oxidation of the ammonium contained in rainfall may result in an H^+ in acid rain. The consideration of this process substantially complicates the interpretation of rainfall induced H^+ loading.

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SHORT-TERM EFFECTS OF A SIMULATED ACID RAIN UPON THE GROWTH AND NUTRIENT RELATIONS OF *PINUS STROBUS*, L.[1]

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ABSTRACT

Acidified precipitation may affect the productivity of forests by altering the availability of plant nutrients of by affecting the ability of trees to absorb and assimilate those nutrients. In this study, the short-term effects of simulated acid rain (pH range 5.6 - 2.3) upon the growth and nutrient relations of Eastern White Pine seedlings (*Pinus strobus*, L.) grown in a sandy loam soil were examined. Soil chemistry, soil leachate chemistry, seedling tissue chemistry, and seedling productivity were monitored.

In spite of increased leaching of cations from the soil, resulting in near depletion of available K^{+1}, Mg^{+2}, and Ca^{+2} at pH 2.3, seedling productivity increased with acidity through the 20-week experimental period. Foliar nitrogen concentrations indicate that fertilization with NO_3^{-1}, added to the rain as HNO_3, may have caused the growth increase. Implications of cation losses and NO_3^{-1} fertilization are discussed.

The potential effects of acid precipitation on forest ecosystems are numerous and wide-ranging. Recent investigations suggest that mounting inputs of hydrogen ion via rainwater may cause: 1) A decrease in the pH and base saturation of forest soils (5) resulting from increased leaching of metallic cations from exchange surfaces (6); 2) An increase in foliar leaching from the forest canopy (4, 10); 3) Abnormal morphogenesis of, and injury to, plant tissue, especially leaves (2, 9); and 4) A reduction in forest productivity (1, 3, 7). The consequences of mounting inputs of SO_4^{-2}, NO_3^{-1}, and Cl^{-1}, the primary anions associated with acid rain, have received little attention.

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[1]A contribution of the Hubbard Brook Ecosystem Study supported by grants from the National Science Foundation.

In the past, these effects have been studied, for the most part, individually. As a result, compounded stresses and relationships between stresses may have gone unnoticed and unmeasured. In this paper, we describe an integrated study of some of the effects of a simulated acid rain upon the growth and nutrient relations of Eastern White Pine seedlings (*Pinus strobus*, L.) grown in a sandy loam soil. Soil chemistry, soil leachate chemistry, seedling tissue chemistry, and seedling productivity are examined.

METHODS

On October 18, 1973, each of 125 three-inch plastic pots containing 180 ± 6 grams of sandy loam soil* were planted with four white pine seeds. The seed was collected from a single tree located in northwestern Connecticut. The pots, placed on a greenhouse bench under 3,000 Lux of supplimentary incandescent lighting (16 hr/day), were regularly irrigated with distilled water. No fertilizers were applied. Two weeks after seedling emergence, each pot was thinned to one seedling, and the population was randomly divided into five subsets of 25 plants.

Beginning on December 3, 1973 and continuing for the next 20 weeks, each subset was subjected to one weekly six-hour artificial acid rain adjusted to one of the following pH's: 5.6 ± 0.6, 4.0 ± 0.1, 3.3 ± 0.1, 3.0 ± 0.0, and 2.3 ± 0.0. To simulate the anion composition of rainfall in central New Hampshire, "rains" were solutions of sulfuric, nitric, and hydrochloric acids in the proportion by chemical equivalents, SO_4^{-2} (66%), NO_3^{-1} (24%), Cl^{-1} (10%). Analytical grade acids and glass distilled water were used. Rain drops (0.5 - 0.8 mm in diameter) were produced with a stainless steel rain nozzle. The seedlings, placed on a turntable, rotated slowly through the "rain" with each pot receiving approximately 190 ± 5 mls of solution per treatment (190 mls/week = 4.2 cm/week in comparison to an average of 2.5 cm of rain falling weekly in the northeastern U.S.). During treatment, plants were illuminated with 4300 Lux of fluorescent light.

Soil Leachate Chemistry: Four pots from each subset of 25 were randomly selected for soil leachate analysis. During every other treatment (beginning on the first week) leachate flowing from the bottom of these pots was collected, weighed to the nearest gram, and analyzed to determine K^{+1}, Mg^{+2}, and Ca^{+2} concentrations (atomic absorption

*Physical Characteristics: Sand: 86%, Silt: 10%, Clay: 4%. Loss on ignition: 2.6%. Cation Exchange Capacity: 0.50 meq/10g soil.

analysis) and pH (electrometric analysis). A pot containing neither soil nor seedling, a control, was monitored identically. Net losses per treatment of K^{+1}, Mg^{+2}, and Ca^{+2} (mg) were calculated for each monitored pot by subtracting control cation losses from gross leachate losses.

At the conclusion of the experiment, the ten bi-weekly leaching losses were summed for each pot and doubled to estimate the total amount of each cation leached from each pot during the 20 treatments. Means and standard deviations for estimated total losses of the three metallic cations were calculated for each pH level and t-tests were computed between all treatment level pairs to detect significant differences in leaching. Differences were considered significant when $p \leq 0.005$.

Seedling productivity: Following the 20 treatments, the pine seedlings were examined for tissue damage and then harvested. Their roots were washed. The lengths of all fascicled needles of five randomly-selected seedlings from each subset were measured. Total plant weight and total needle weight were determined for each seedling following oven drying at 90°C. Means for each subset were subjected to t-tests to detect significant differences ($p \leq 0.005$) in productivity between pH levels (Fig. 1).

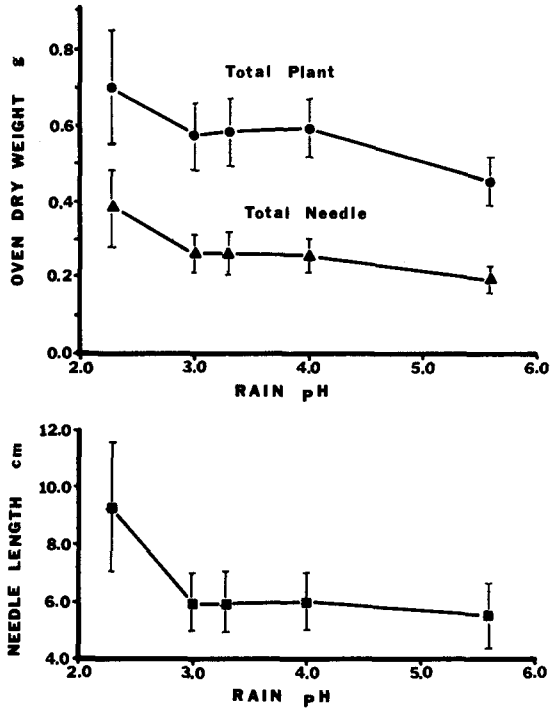

Figure 1. Seedling productivity as affected by rain chemistry. Mean oven dry total plant weight, mean oven dry total needle weight per plant, and mean fascicled needle length are shown.

Tissue Chemistry: Needles from the seedlings of each treatment level were pooled and two subsamples from each were analyzed for K^{+1}, Mg^{+2}, and Ca^{+2} using an H_2O_2 - H_2SO_4 digestion and atomic absorption analysis. Kjeldahl nitrogen concentrations were determined with the Kjeldahl digestion technique. Stem and root tissue were similarly pooled, subsampled, and analyzed. Nutrient concentrations and

corresponding tissue weights were used to calculate mean weights of K^{+1}, Mg^{+2}, Ca^{+2}, and Kjaldahl N, assimilated per plant in each treatment level.

Soil Chemistry: The soil from each treatment was pooled and analyzed (two replicates) to determine pH (electrometric analysis), exchangeable K^{+1}, Mg^{+2}, and Ca^{+2}, (ammonium acetate extraction), Kjeldahl nitrogen (Kjeldahl digestion), and nitrate-nitrogen (phenol-disulfonic development (8)). A sample of untreated soil was also analyzed.

"Rain", leachate, soil, and tissue chemistry data were compiled into partial nutrient budgets for the five treatment levels (Figs. 3a - 3f). Estimates of soil weathering inputs of K^{+1}, Mg^{+2}, and Ca^{+2} were calculated using the following equation.

Weathering Input = Loss from Soil - Input to Soil - Declines in Exch. Cations = (Soil Leachate + Tissue Assimilation) - (0.0 input of cations) - (Initial - Final Exchangeable Cations)

RESULTS AND DISCUSSION

Growth analyses indicate that short-term productivity of the White Pine seedlings significantly increased as concentrations of H_2SO_4, HNO_3, and HCl were increased in the artificial rain. Total plant weight and total needle weight were significantly lower at pH 5.6 than at all higher acidities, and all growth measures were significantly higher at pH 2.3 than at all other levels (Fig. 1). No significant growth differences were observed in the pH range 4.0 to 3.0. The relationship between assimilated Kjeldahl nitrogen (Fig. 3f) and productivity (Fig. 1) through the five pH levels suggests that fertilization with HNO_3-nitrogen may have been an important growth determinant.

Tissue damage, necrotic needle segments up to 2 mm long, appeared on all seedlings exposed to pH 2.3 "rains". No other seedlings displayed visible injury. Decreases in growth over the 20-week period did not coincide with leaf damage, but continued destruction of photosynthetic tissue may, in the long run, affect reductions in productivity.

Gordon(2) showed needle dwarfism (needles growing to only one half their normal length) in pines resulting when developing foliage was misted with H_2SO_4 solutions adjusted to pH's below 4.0. Our work produced quite different results (Fig. 1). It is unclear why stunting did not result from our acid treatments. Increased needle growth was probably caused by NO_3^{-1} fertilization.

Figure 2 conceptualizes nutrient flow through and within our plant-

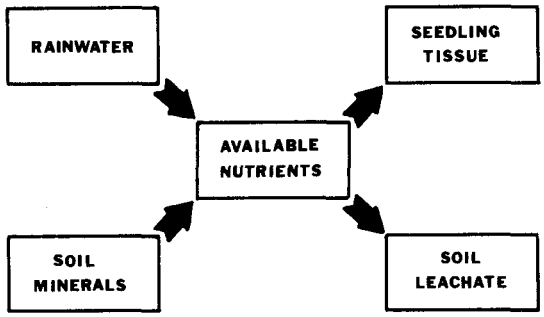

Figure 2. A simple model of nutrient flow through and within the plant-soil systems. Five nutrient reservoirs and the major fluxes between them are shown.

soil systems. Cation flux centers about the pool of exchangeable cations held at polar binding sites on soil particles and free within the soil solution. Additions may be made to this pool via "rainwater" input and soil mineral weathering. The pool may be decreased through plant uptake and leaching outputs. Figures 3a - 3f indicate that patterns in K^{+1}, Mg^{+2}, Ca^{+2}, and N flow through our systems were altered in several ways as the acid concentration of the "rain" was increased.

Inputs of H^{+1}, SO_4^{-2}, NO_3^{-1}, and Cl^{-1} were of course increased with rain acidity. Figure 3a shows the total input of nitrogen per pot for the 20 treatments increasing logrithmically through the pH range. No K^{+1}, Mg^{+2}, or Ca^{+2} were added with "rain".

Figure 3. Effects of rain chemistry upon the nutrient pools and nutrient flows through and within the plant-soil systems.

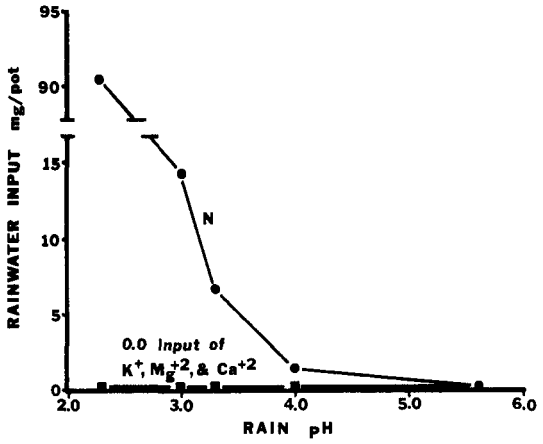

Figure 3a. Total inputs of N, K^{+1}, Mg^{+2}, and Ca^{+2} with rainwater after 20 treatments.

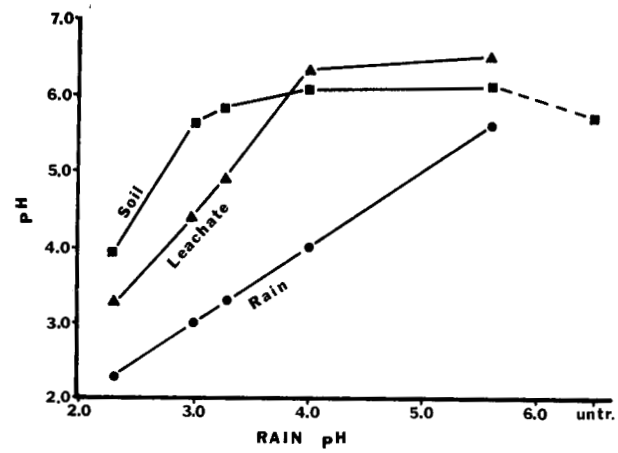

Figure 3b. Mean pH of rain and soil leachate through the 20 week experimental period, and soil pH before and after the 20 weeks (Untr = untreated soil).

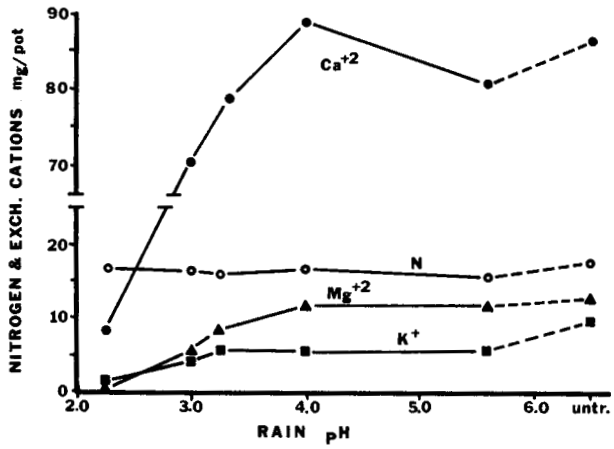

Figure 3c. Exchangeable cations and Total N before and after the experimental period. (Untr = Untreated soil).

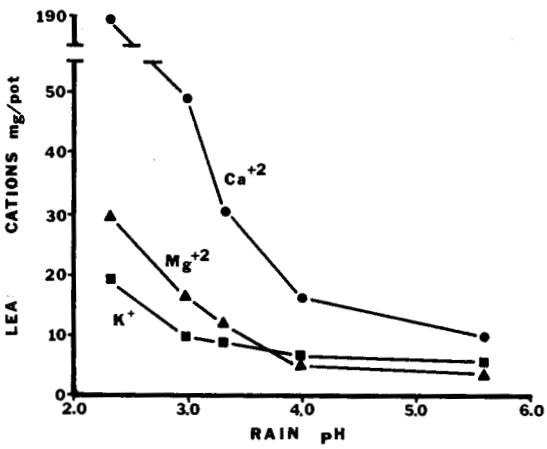

Figure 3d. Estimated total leaching losses of K^{+1}, Mg^{+2}, and Ca^{+2} after 20 treatments.

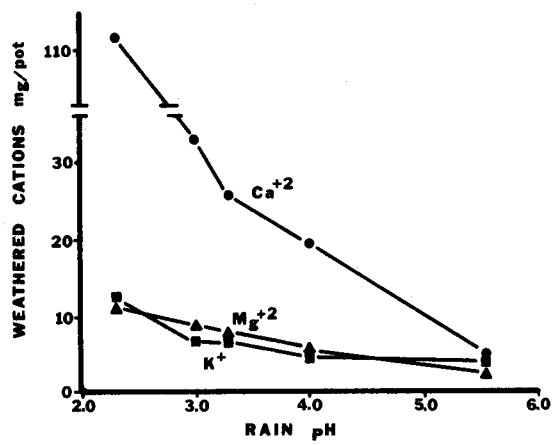

Figure 3e. Estimated weathering inputs of K^{+1}, Mg^{+2}, and Ca^{+2} over the 20-week experimental period.

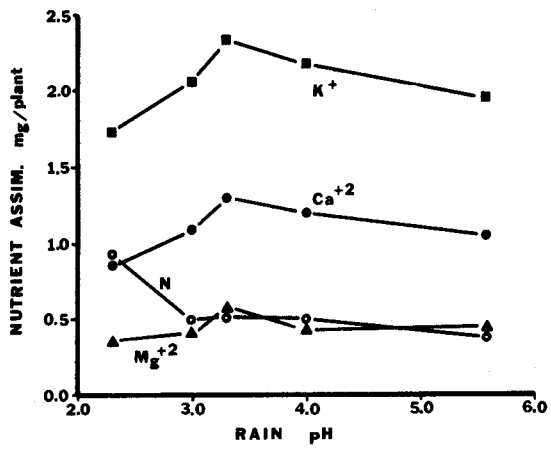

Figure 3f. Seedling assimilation of K^{+1}, Mg^{+2}, Ca^{+2}, and N measured at the end of the experimental period.

Although we did not employ titration to precisely measure H^+ exchange processes within the soil, our pH determinations of "rain", soil, and leachate (Fig. 3b) suggest the importance of this mechanism. pH differences between "rainwater" and soil leachate indicate uptake of H^+ by the soil via cation exchange and/or neutralization of acids by basic compounds in the soil occurring at all treatment levels, but increasing with "rain" acidity. Declines in soil pH provide further evidence for H^+ uptake via exchange.

Mean leaching losses of K^{+1}, Mg^{+2}, and Ca^{+2} continuously rose with rain acidity (Fig. 3d). T-tests indicate that for Mg^{+2} and Ca^{+2}, leaching losses significantly increased with each increase in the H^+ concentration of the rain. Significant increases in the leaching of K^{+1} were observed at pH's of 3.0 and below. Two mechanisms involving hydrogen ions may underlie these trends: 1) H^+ exchange with cations held on soil binding sites; and 2) Acid induced weathering of soil minerals.

Measurments of exchangeable cations retained by the soil following the 20 treatments (Fig. 3c) suggest that at pH's of 4.0 and above, losses via leaching and plant uptake were balanced by weathering inputs. No continuous declines below values for untreated soil are evident in this range. At pH 3.3, decreases in exchangeable Mg^{+2} occurred. At pH 3.0, exchangeable K^{+1}, Mg^{+2}, and Ca^{+2} decreased to between 54% and 84% of their respective mean concentrations at higher pH's, and at pH 2.3, exchangeable cation concentrations decreased to very low levels. Depletions of available cation reserves may have resulted from saturation of exchange sites with H^{+} and subsequent decrease in the ability of the soil to hold nutrient cations and/or a situation of leaching outputs outpacing weathering inputs. Soil Kjeldahl nitrogen appeared to be unaffected by rain acidity. Soil nitrate-nitrogen levels were undetectible (less than 0.01 µg/g soil) in all treatments. The water-soluble nitrate was apparently rapidly leached from the pots by the "rain".

Estimated weathering inputs of K^{+1} and Mg^{+2} rose continuously but linearly with logarithmic increases in the acidity of the simulated rain (Fig. 3e). Three to four-fold increases coincided with 1500-fold increases in "rain" acidity (pH 5.6 to pH 2.3). Weathering of Ca^{+2} responded more logarithmically with an approximate 22-fold increase over that pH range.

The greatly accelerating weathering rates estimated for Ca^{+2} raise several questions. How long might supplies of weatherable Ca^{+2} last? Were these reserves seriously depleted at pH 2.3 over the 20 week period? We made no direct measures to answer these questions. However, the steady declines in the leaching losses of Ca^{+2} from Week 5 through Week 19 (Fig. 4) may suggest concurrent declines in Ca^{+2} weathering,

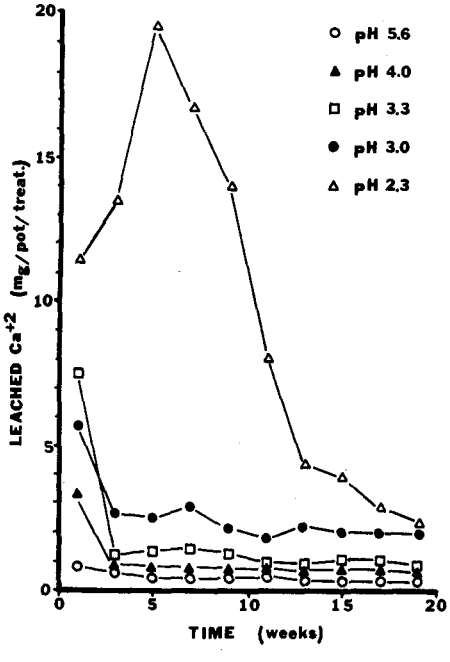

Figure 4. Weekly leaching losses of Ca^{++} through the 20-week experimental period.

and accordingly, decreases in the supplies of weatherable Ca^{+2}. (Similar temporal patterns were observed for K^{+}, and Mg^{+2} leaching.) It must be stressed that this evidence in only circumstantial. Declines in exchangeable Ca^{+2} and in the base saturation of the soil measured at pH 2.3 might also promote the pattern of decreasing Ca^{+2} leaching.

Nutrient assimilation by the pine seedlings showed some relationship to precipitation chemistry. Organic nitrogen levels in the plant tissue (lowest at pH 5.6 and highest at pH 2.3) probably reflect NO_3^{-1} levels in the rainwater. Amounts of assimilated K^{+1}, Mg^{+2}, and Ca^{+2} vary with plant weight through the pH range 5.6 - 3.0, indicating fairly uniform concentration in plant tissue. At pH 2.3, however, decreased amounts of assimilated cations resulted in spite of increased plant weight. Stem and leaf concentrations of the three measured cations dropped to between 1/2 and 2/3 of concentrations at lower acidity levels. These declines may be results of the low levels of available cations in the pH 2.3 soils, and/or major increases in foliar leaching expected at this treatment level (10).

An over-all effect of our pH 2.3 acid "rain" was to produce, after 20 weeks, an acid soil, quite low in supplies of exchangeable cations and, perhaps, weatherable cations. Declines in seedling assimilation of these nutrients at pH 2.3 resulted. Despite these trends, seedling productivity increased with rain acidity during the 20-week period. High nitrate inputs through rainwater were probably responsible. Nitrogen, however, can only stimulate growth when adequate supplies of all essential nutrients are present. The low levels of available K^{+1}, Mg^{+2}, and Ca^{+2} at pH 2.3 apparently did not become limiting during the 20-week treatment period, but questions are raised concerning how much longer decreasing cation supplies may have supported growth. We feel that the increased productivity of the pine seedlings noted at pH 2.3 may have been a short-term phenomenon.

SUMMARY AND CONCLUSIONS

1. 125 Eastern White Pine seedlings, individually potted in sandy loam soil, were randomly divided into five treatment groups of 25 plants. Each group was subjected to 20 weekly treatments with a simulated acid rain adjusted to one of the following pH's: pH 5.6, pH 4.0, pH 3.3, pH 3.0, and pH 2.3. "Rains" were solutions of sulfuric, nitric and hydrochloric acids. Soil leachate was collected during treateents and subsequently analyzed. Soil chemistry, seedling tissue chemistry, and seedling productivity were measured at the end of the 20-week period.

2. Monitoring of "rain", soil, and leachate pH's indicated uptake of H^{+} by the soil, probably through ion exchange mechanisms. Marked soil pH declines were measured after 20 weeks of treatment at pH 2.3.

3. Leaching of Mg^{+2} and Ca^{+2} steadily increased with "rain" acidity through the pH range 5.6 - 2.3. K^{+1} losses did not increase until the "rain" pH was lowered to 3.0 and 2.3.

4. Declines in exchangeable K^{+1}, Mg^{+2}, and Ca^{+2} were measured at pH's of 3.0 and below. Greatly depleted levels of exchangeable cations were found at pH 2.3.

5. Estimated weathering inputs of K^{+1}, Mg^{+2}, and Ca^{+2} steadily increased with "rain" acidity through the pH range 5.6 - 2.3. Ca^{+2} inputs rose most dramatically with a 22-fold increase over that pH range.

6. Declines in cation leaching (at pH 2.3) through time suggest that supplies of weatherable K^{+1}, Mg^{+2}, and Ca^{+2} may have been greatly reduced by the 20 pH 2.3 treatments.

7. K^{+1}, Mg^{+2}, and Ca^{+2} assimilation by the seedlings was fairly constant through the pH range 5.6 - 3.0. Declines were observed at pH 2.3. Nitrogen assimilation, fairly constant from pH 5.6 to 3.0, rose significantly at pH 2.3, probably as a result of high NO_3^{-1} inputs with rainwater.

8. Seedling productivity increased significantly with rainwater acidity. Lowest growth was measured at pH 5.6, and the greatest growth at pH 2.3. NO_3^{-1} fertilization probably caused this trend.

9. Nitrogen can only stimulate growth when supplies of available cations are adequate. Increased leaching losses of K^{+1}, Mg^{+2}, and Ca^{+2} and the declines in exchangeable (and perhaps weatherable) cations measured at pH 2.3 raise questions regarding how long declining supplies of available cations might support growth. The accelerated productivity noted at pH 2.3 may be a short-term phenomenon.

10. Foliar damage, observed only at pH 2.3, was not associated with declines in seedling productivity over the 20-week period. Questions are raised regarding the impact of needle injury on long-term growth.

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SULFATE MOBILITY IN AN OUTWASH SOIL IN WESTERN WASHINGTON

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ABSTRACT

The effect of acidic precipitation on cation leaching in a second-growth Douglas-fir ecosystem at the Thompson Research Center is reviewed. Sulfate mobility and soil pH buffering power were tested by applications of heavy doses of sulfuric acid to the study plot. Sulfate at high concentrations proved to be immobilized, presumably by adsorption to soil sesquioxide surfaces. Soil sulfate adsorption was determined at varying sulfate concentrations, and two mechanisms of adsorption are implied by the shapes of the adsorption isotherms.

INTRODUCTION

In a paper given at the American Geophysical Union Annual meeting last April, we reported that acid rainfall and associated sulfate ions accounted for approximately 25% of the yearly cation removal from the Thompson site (Cole and Johnson, 1974). It appeared that sulfate was mobile in the Everett soil whereas hydrogen ions immediately exchanged with metal cations resulting in the transport of sulfate salts out of the system. However, continued sulfate output during periods of zero input suggested that the system had some buffering capacity with respect to sulfate.

Two approaches were taken to determine and characterize the sulfate and pH buffering power of the soil system: (1) the lysimeter study plot was leached with aliquots of sulfuric acid ranging in concentration from 10 to 1000 times higher than that occurring at Cedar River at present, and (2) a series of soil sulfate adsorption studies was conducted in the laboratory.

METHODS

Successive aliquots of 10^{-3}, 10^{-2}, and 10^{-1} N H_2SO_4 followed by distilled water were applied to the soil over the forest floor, A- and B-horizon lysimeter plates such that the forest floor received 1.6 cm and the A and B received 3.2 cm of solution each time for a total of eight leachings. The first two applications were designed to simulate heavier acid loads that the system might experience in the future, and the last application was designed to potentially exhaust the exchangeable cation capital of the soil to 50 cm depth (30000 eq/ha). Incoming precipitation was shielded from the plot during these applications. Solution samples were taken daily following each application and analyzed for pH, specific conductance, HCO_3^-, SO_4^{2-}, Na^+, Ca^{2+}, Mg^{2+}, K^+, and Mn^{2+}. Bicarbonate was done by titration to pH 4.5, sulfate was done on a Technicon Autoanalyzer 11 (method 226-72W), and the cations were done by atomic absorption (I. L. Spectrophotometer 353).

For three months following these applications, solutions from the plot were collected and analyzed, allowing naturally occuring precipitation to fall on it. At the end of this period, soils in the study plot and the surrounding area were sampled and extracted for sulfate by shaking 20 grams of air-dried soil with 100 ml 0.02 N K_2HPO_4 for 30 minutes, a slight modification of the method given by Ensminger (1954).

Soil sulfate adsorption was determined by shaking six replicates of 5 g air dried samples with 25 ml solution for 24 hours. Initial solution sulfate concentration ranged from zero (distilled water) to 10 meq/l.

RESULTS

Figure 1 shows the sulfate concentrations and pH of solutions taken following acid application. All points were shifted to the left so that the lag due to soil moisture storage is approximately accounted for.

It is immediately obvious that acid deposition had a very small effect on sulfate levels in the B-horizon solution, raising them from 0.06 to 0.17 meq/l only after the 10^{-1} N (100 meq/l) application. B-horizon pH apparently began to drop with the 10^{-3} N application. Forest floor and A-horizon leachates showed dramatic increases in sulfate concentrations beginning after the 10^{-3} N acid application. Forest floor and A-horizon solution pH dropped similarly to B-horizon solution pH, but remained at the low levels for longer periods. Forest floor pH appeared to be climbing rapidly back to normal levels toward the end of the study period following a low of 3.83, A-horizon pH rose slowly from a low of 4.31 to 4.64, and B-horizon pH began to drop erratically as

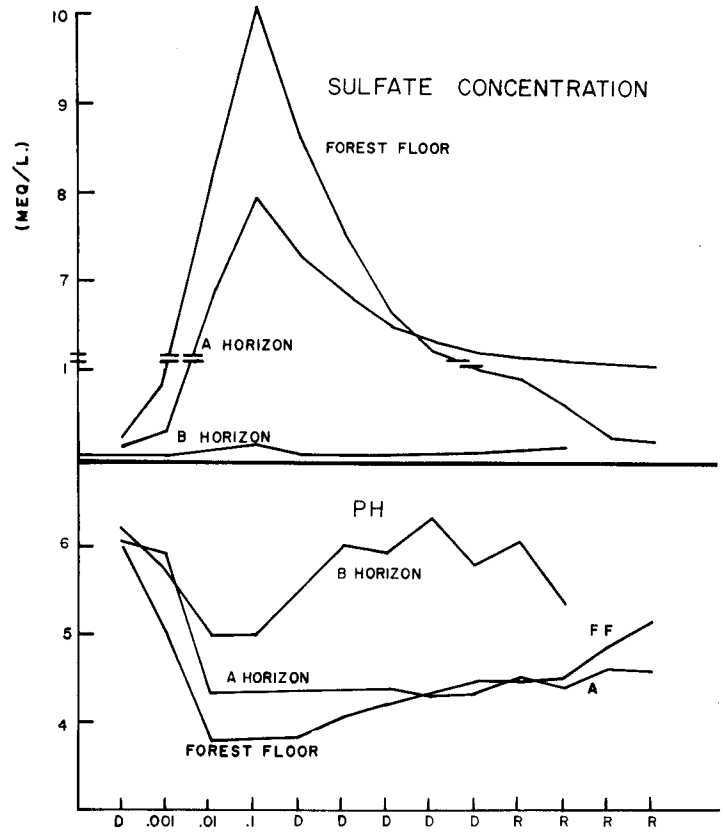

Figure 1. Soil solution pH and sulfate concentration after acid leaching. Normality of applied acid is indicated, D = distilled water leaching, R = natural rainfall leaching.

sulfate concentration rose slightly to 0.095 meq/l. In all cases, the pH drop occurred with the 10^{-3} N acid application and reached a minimum with the 10^{-2} N application.

Table 1 gives the figures for total input, output, and storage for H^+, SO_4^{2-}, and total cations for the various horizons. It is obvious from these data that the hydronium ion is far less mobile in this soil than the sulfate ion, even though pH drops were dramatic. The total H^+ loading should have been sufficient to exhaust all exchangeable cations within this soil section. It is quite conceivable that the higher acid concentrations mineralized some litter, though this was not physically apparent.

The total of H^+, Ca^{2+}, Na^+, K^+, Mg^{2+}, and Mn^{2+} removal was lower than that of SO_4^{2-} probably because of the removal of other cations such as NH_4^+ and Al^{3+} not accounted for. About two-thirds of the calculated total supply of Na^+, Ca^{2+}, and K^+ was removed from the forest floor and

Table 1. H^+, SO_4^{2-}, and total cation budgets after acid leaching from lysimeter data., (eq/ha).

Horizon	Input			Output			Storage		
	H^+	SO_4^{2-}	TC[2]	H^+	SO_4^{2-}	TC	H^+	SO_4^{2-}	TC
Forest floor	17760	17760	0	0.2	16000	10000	17760	1760	-10000
Forest floor +A	35520	35520	0	0.2	15000	11200	35520	20000	-11200
B (50 cm)	0.2	15000	11200	0.0	200	200	0.2	14800	11000

[1]Background concentration factors subtracted

[2]Ca^{2+}, Mg^{2+}, Mn^{2+}, Na^+, and K^+ only. TC = total cations

A-horizon yet virtually none of this cation capital was removed past 50 cm in the B-horizon.

Table 2 gives the results of the sulfate extractions done on the

Table 2. Soil pH and sulfate content of acid-treated (AT) plot and Cedar River (CR) soil (Everett series).

Horizon and depth (cm)	pH		Soil sulfate				Storage in AT soil	
			AT		CR			
	AT	CR	meq/100g	eq/ha	meq/100g	eq/ha	meq/100g	eq/ha
A(4-12)	4.57	5.10	0.74	6,200	0.26	2,200	0.48	4,000
B(12-30)	5.01	5.18	0.78	19,600	0.26	6,500	0.52	13,100
B(30-50)	5.40	5.38	0.86	30,500	0.13	4,500	0.73	26,000
B(12-50)	5.45	5.48	0.80	56,300	0.18	11,000	0.62	45,300
TOTAL				62,500		13,200		49,300

acid treated plot (AT) and the surrounding soil (CR). Most of the sulfate now retained in the Everett soil is held in the A-horizon and the upper 22 cm of the B-horizon, yet acid application resulted in the greatest storage in the lower 20 cm of the B-horizon. This implies that the bulk of the as yet unfilled sulfate adsorption capacity lies in the lower B-horizon. Estimated total sulfate storage from this data is higher than that calculated from lysimeter data, but the relative magnitudes of storage between horizons is clear nonetheless. Acid treatment resulted in pH lowering in the A and upper B-horizon, where net sulfate storage was least, implying that soil hydrogen ion and sulfate ion buffering power are related with respect to sulfuric acid input.

Figure 2 shows the results of the sulfate adsorption study. Sul-

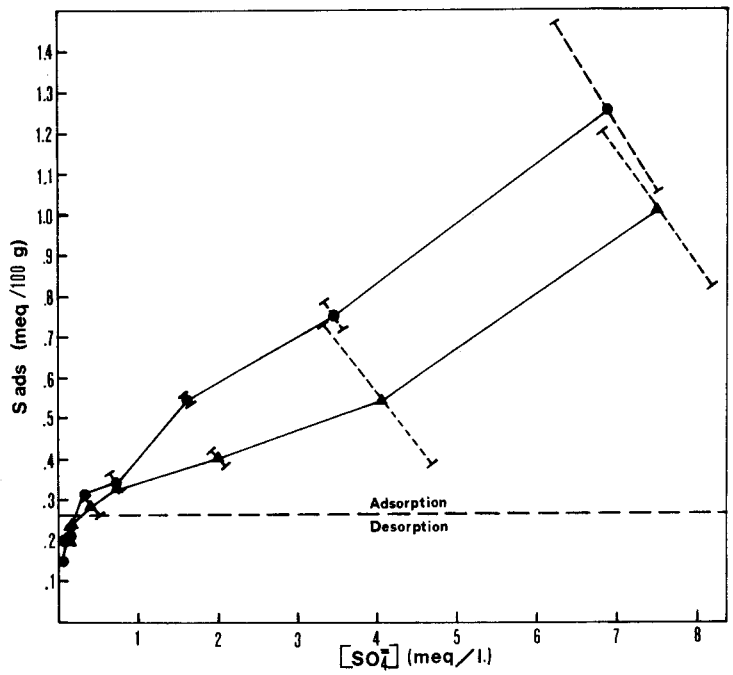

Figure 2. Sulfate adsorption (Sads) on the Everett soil vs equilibrium sulfate concentration [$SO_4^=$]. ▲——▲ = A-horizon, ●——● = B-horizon. Error bars indicate 95% confidence intervals in solution sulfate concentration and calculated sulfate adsorption.

fate adsorbed on soil colloids (Sads) is plotted against equilibrium sulfate concentration in solution. Sulfate adsorbed is calculated from initial minus final solution sulfate concentrations, using 0.26 meq/100g as an initial value for adsorbed sulfate (Table 2). (Soil from the upper 22 cm of the B-horizon was used.) Error bars represent 95% confidence intervals.

B-horizon sulfate adsorption is greater than A-horizon adsorption at a given solution sulfate concentration, but no maximum adsorption value is indicated for either horizon from these data points. The lower portions of both adsorption-desorption isotherms seem to asymptotically approach maxima, but beyond roughly 0.7 meq/l the slopes of the isotherms increase drastically, implying no maximum adsorption value to at least 7.5 meq/l.

Figure 3 shows plots of $[SO_4^{=}]/Sads$ vs $[SO_4^{=}]$ for the lower

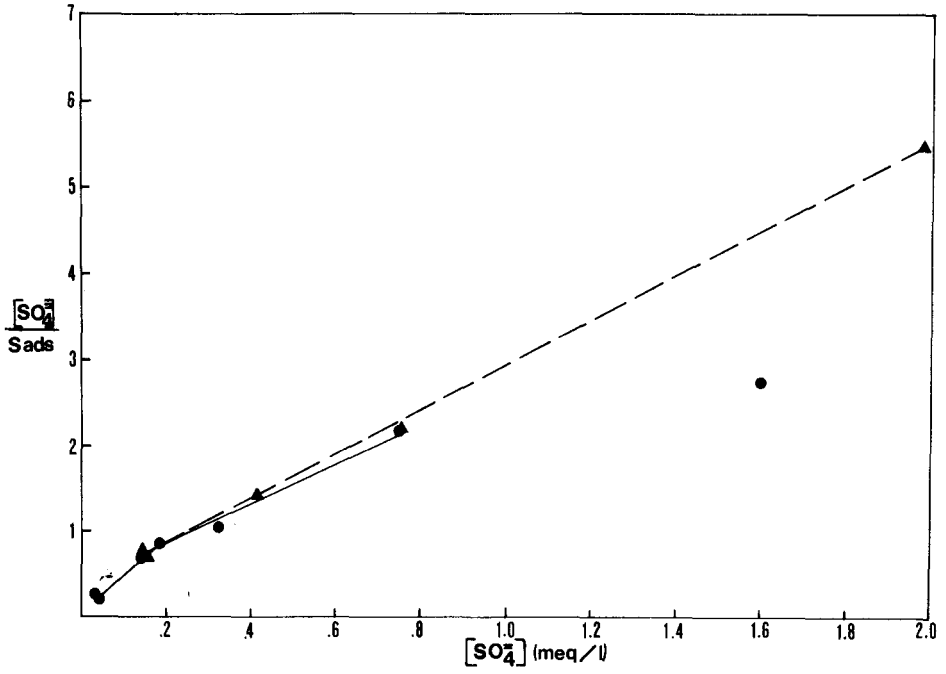

Figure 3. Test of fit to the Langmuir equation. ●——● = A-horizon, ▲——▲ = B-horizon.

portions of the isotherms. A straight line indicates a fit to the langmuir equation,

$$\frac{Sads}{\max Sads} = \frac{b[SO_4^{=}]}{1+b[SO_4^{=}]}$$

where b is a constant and max Sads is the maximum adsorption capacity.

The entire low level portion of A-horizon isotherm fits this equation, and parts of the B-horizon isotherm do.

DISCUSSION

Both the acid leaching experiment and the soil sulfate adsorption studies clearly show that sulfate has limited mobility in the Everett soil. Total sulfate adsorption has been shown to be proportional to the

sesquioxide content of the soil (Chao, et al., 1964; Barrow, et al., 1969). This apparently does not hold true for the Everett soil, however, in that the A-horizon contains 1.4% Fe and 0.23% Al, the upper 17 cm of the B-horizon contains 1.02% Fe and 0.06% Al,and the lower 20 cm of the B-horizon contains 0.93% Fe and 0.118% Al (as free oxides) (Schlichte, 1968).

Sulfate adsorption has been shown to be strongly pH dependent, greater amounts being adsorbed at low pH values (Gebhardt and Coleman, 1974; Harward and Reisenauer, 1966; Chao et al., 1965). This is presumably due to (1) the protonation of hydroxy surfaces, giving them a more positive charge, and (2) the reduction of the concentration of competing OH^- ions. The reduction of A-horizon and upper B-horizon pH during the acid leaching experiment undoubtedly enhanced sulfate adsorption, and greater quantities of sulfate may have remained mobile if neutral sulfate salts rather than acid had been applied.

Various mechanisms of sulfate adsorption have been proposed: Gebhardt and Coleman (1974) suggest that HSO_4^- is adsorbed rather than $SO_4^=$ on the basis of the similarity between sulfate and chloride adsorption isotherms for tropical soils. Aside from the sulfur species adsorbed, two basic mechanisms of adsorption have been proposed; (1) OH^- displacement on sequioxide surfaces (Chao, et al., 1965; Chang, et al., 1963; Gebhardt and Coleman, 1974), and (2) -O- displacement from within sequioxide structures, or "anion penetration" (Chao, et al., 1962; Harward and Reisenauer, 1966). The first mechanism would result in readily exchangeable sulfate, the second in more strongly bound, less available sulfate.

The sulfate adsorption isotherms for the Everett soil indicate that at least two mechanisms or sites of adsorption are at work, in that the low concentration portions of both curves are distinct from the high concentration portions. The low concentration portions, which roughly conform to the Langmuir isotherm, may represent mostly OH^- displacement, whereas the roughly linear high concentration portions may reflect a greater degree anion penetration. Presumably some OH^- adsorption and some anion penetration occurs at any given sulfate concentration.

CONCLUSIONS

Sulfate mobility is limited in the Everett soil, as in others (Harward and Reisenauer, 1966; Bornemisza and Lianos, 1967; Chao, et al., 1962), by the capacity of the soil to adsorb sulfate. Such adsorption probably consists of at least two mechanisms, resulting in both tightly and loosely bound sulfate. Full recovery of high-level adsorbed sulfate can apparently be obtained by extraction with a more highly adsorbed anion such as phosphate, and nearly full recovery of

low-level adsorbed sulfate is indicated by the distilled water extractions (Figure 2).

In considering the possible effects of acidic precipitation on cation removal from a given ecosystem, the mobility of sulfate in the given soil must be considered, or there exists a distinct possibility of overestimating the net transfer of cations due to acid deposition. The data presented here and in a previous paper (Cole and Johnson, 1974) has shown that the ecosystem studied has the ability to buffer and moderate cation losses due to heavy loads of sulfuric acid over short periods, and certain other ecosystems may possess this capacity as well. The long-term effects of sulfuric acid deposition may be another matter; if the soil's ability to adsorb sulfate (and thus prevent increased cation loss) is reached or a new equilibrium level is attained, acid deposition may result in equivalent sulfate salt losses. The fact remains, however, that sulfate, especially in acid form, interacts strongly with soils that have appreciable sesquioxide contents, and the characteristics of this interaction must be known and employed in evaluating and modeling cation losses due to sulfuric acid deposition.

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SOIL ACIDIFICATION BY ATMOSPHERIC POLLUTION AND FOREST GROWTH

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ABSTRACT

In recent years concern has been expressed about the danger of harmful pollution deposits which affect areas at great distances from the emission sources.

The investigation was so designed that a possible reaction in growth resulting from a supposed acidification could be observed as far as possible. A poorer growth development was observed in regions, which are suspected of being more susceptible to acidification than those regions which are presumed to be less susceptible in this respect. We have found no good reason for attributing the reduction in growth to any cause other than acidification.

1. GENERAL

It has long been known that smoke fumes from industries may damage surrounding vegetation. Forests around such local pollution sources often have reduced growth, and may in extreme cases be completely destroyed.

In recent years concern has been expressed about the danger of harmful pollution deposits which affect areas at great distances from the emission sources. In this respect the sulfur compounds have attracted most attention. It appears to be quite clear from observations during the past few decades that a general acidification is taking place in our environment. The sulfur emitted into the atmosphere is brought down to the surface of the earth by rainfall, in the form of sulfuric acid, and causes acidification, which amongst other things, is clearly expressed in the increased acidification of lakes and rivers. Soils are also exposed to sulfuric acid, and it may be suspected that as a result, a longterm impoverishment of the soil will ensue. On soils which are more susceptible to acidification, this results in an

accelerated impoverishment which in its turn may result in a lower growth rate as compared with less susceptible regions. *This hypothetical difference in growth between regions of different susceptibility to acidification is the object of study in this investigation.*

2. MATERIAL

The investigation is limited to Sweden south of 61°N (essentially Svealand and Götaland), i.e. to about 40 percent of the country's productive forest land by area, or about 50 percent of the production.

In this part of the country, two types of region have been selected, primarily on the basis of soil and water chemical conditions (see Section 3), viz. those regions, which are suspected of being *more susceptible* to acidification, as a result of sulfur deposition, than other regions; and those regions which are presumed to be *less susceptible* in this respect. It is possible that these latter regions have remained substantially unaffected by the deposited sulfur.

For the sake of simplicity the more susceptible regions are designated as A regions (acid), and the less susceptible as B regions (basic). The remaining regions, which fall between A and B, have not been utilized in the analysis of the growth reduction.

Growth data are derived from observations carried out by the Department of Forest Survey at the Royal College of Forestry in Sweden. This department collects annually various types of forest information according to a systematic sampling procedure. From some sample trees increment cores are taken (at breast height), i.e. a continuous wood sample from the bark to the pith. On these cores the annual ring widths can be measured, giving a series for each tree of annual increments well defined in time, each one the result of a biological process with many interacting growth factors. The question is whether the deposited sulfur has so far directly or indirectly affected this process, and hence also growth.

The growth comparison according to the above, between the two susceptible types of region, is carried out for everyone of the four groups of material in table 1.

The total number of sample trees processed was 4269. These trees are derived from the sample tree material for the years 1966-1969, and are so selected that they have a breast height diameter over bark of 20-40 cm, and 50-120 annual rings.

Table 1. The material groups

Tree species	Site quality classes according to Jonson [within parentheses: the annual average yield in m^3 (total volume on bark) per hectare during 100 years]	
Scots pine Pinus silvestris	II-III (8-6)	IV-VI (4.5-2.5)
Norway spruce Picea abies	I-II (10.5-8)	III-V (6-3.4)

3. THE BASIS FOR DELIMITATION OF REGIONS DIFFERING IN SUSCEPTIBILITY

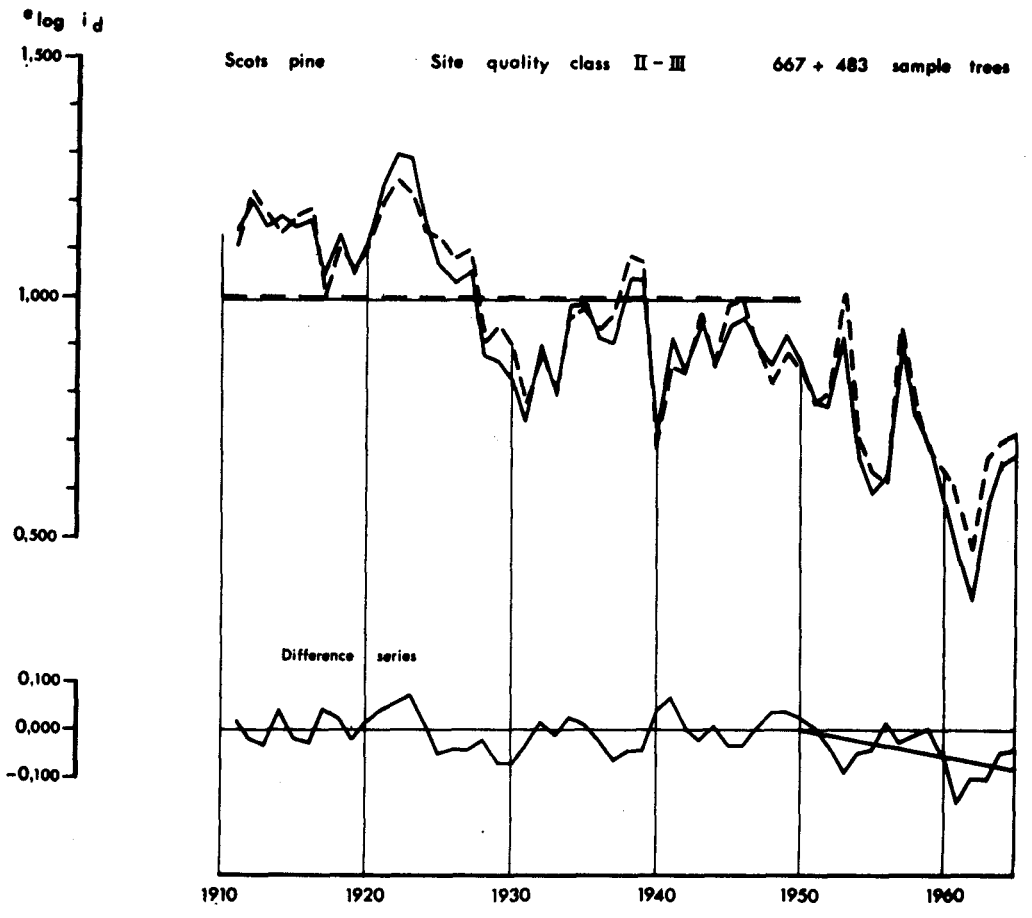
The criteria of selection for regions, which can be suspected to be more or less susceptible to acidification, have been the magnitude of the acid fallout over the country (the average pH value of the precipitation) and information about pH values and ion composition in Scandinavian lakes and rivers in 1965 and 1970 and finally information about the distribution of soil types.

The main emphasis has been laid on the last-mentioned criteria. If, for example, a region consists of precambrian tills of low base status or of glacifluvial sand deposits, and the surface water within the region has both a low pH value and a low cation value, the region has been regarded as more susceptible to atmospheric chemical influence. No numerical ranking into susceptibility classes has been carried out.

The various regions have been delimited and classified by Professor S. Odén.

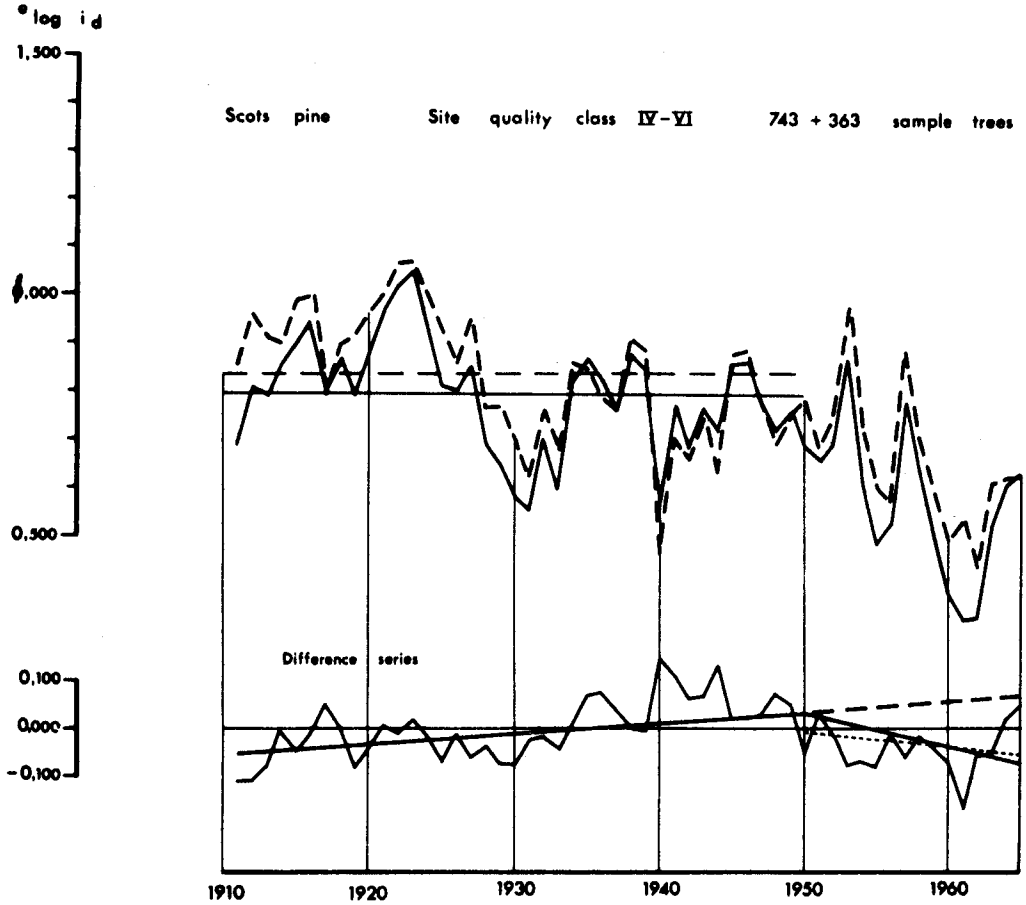
4. STATISTICAL MODELS, CALCULATIONS AND RESULTS

A statistical model was introduced for the annual growth of a tree. This model led to the consideration of averages of logarithmized annual growths, the averages being based on the sample trees from each region and also on the combined region groups (A and B, respectively). The annual difference between the A and B averages was considered as a statistical time series with a trend function. This trend function was represented by a broken linear function composed by one time-linear



Figures 1a and b. Averages of logarithmized double annual ring widths (in mm) for the more susceptible (full line) and less susceptible (dashed line) regions, repectively, and difference series of these average series. The average level during the period 1911-1950 is shown for each series. Two linear trends of the difference series are also drawn. The trend of the acidification component is represented under the two assumptions of individual (full line) and common (dotted line) rate of ageing, repectively, discussed in the text.

The figures before "sample trees" represent the number of sample trees; the first one from the more susceptible regions and the second from the less susceptible regions.



trend, representing the differences in growth level and in rate of ageing, and another time-linear trend starting at a year t_0, representing the possible increasing difference between the two groups of regions in acidification effect on growth. If the regions in group B have not been affected by acidification, the slope of the latter trend component is a measure of the average acidification effect on growth in region group A.

The slope of this acidification component was estimated by the method of least squares, and the standard error of the estimate was estimated (by two methods). As concerns the rate of ageing, each region was given its own rate in the main model, but calculations were also performed under the assumption of a common rate of ageing, the latter implying a time-constant trend component up to the year t_0 in the difference series.

The estimated acidification trends were compared with the estimated standard errors in an assessment of the statistical significance. This led to the following statement: *The observed difference in trends between more susceptible and less susceptible regions could hardly be interpreted as reflecting the statistical uncertainty in the estimates.*

5. CONCLUSIONS

When casual conclusions are to be drawn on the basis of an analysis of non-experimental observations, a situation arises in which no good methods are available.

The risk is that an erroneous explanation will be given of a course of events, even though the facts have been carefully scrutinized.

This investigation was so designed that a possible reaction in growth resulting from a supposed acidification could be observed as far as possible. A poorer growth development was observed in more susceptible regions than in less susceptible. We have found no good reason for attributing the reduction in growth to any cause other than acidification.

The conclusion must therefore be that *acidification cannot be excluded as a possible cause of the poorer growth development, but may be suspected to have had an unfavorable effect on growth within the more susceptible regions*.

The investigation gives only an impression of the order of magnitude of the average annual reduction during the period 1951-1955, for the more susceptible regions in relation to the less susceptible. The values 0.3 and 0.6 per cent have been proposed, in an example, as a reasonable approximation to this relative reduction. The investigation gives no information about the absolute level of the reduction for the two groups, nor about the reduction during a certain year. A difference is assumed between site quality classes, but it could not be statistically established.

In this connection it should be pointed out that during the period 1945-1965, the productivity of the Swedish forests as a whole increased considerably, principally because of more efficient forest management.

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ACID PRECIPITATION AND FOREST VEGETATION

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ACIDIC PRECIPITATION AND FOREST VEGETATION

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Most plants can take up nutrients from the atmosphere as well as from the soil solution. This capacity is especially important in natural ecosystems such as forests and bogs where nutrients from other sources are scarce and where fertilization is not a normal management procedure. Trees develop very large canopies of leaves and branches that extend high into the air. Thus, trees offer a very large surface for deposition and potential assimilation of substances dispersed in the atmosphere.

Air-borne substances that influence plants include: sea spray from oceans and large lakes, dust resulting from wind erosion of soil as well as from volcanic and cosmic sources; gases such as carbon dioxide, ammonia, sulfur dioxide, hydrogen sulfide, methane, etc. released from decomposing organic matter and volcanoes; biogenic particles such as spores, hyphal fragments, and pollen; particulate matter, aerosols, and gases produced by wild fires and controlled burning of agricultural, forest and urban wastes as well as from industrial, agricultural, residential and commercial heating, and transportation operations. Combustion of fossil fuels is the largest anthropogenic source of air-born substances. Some of these substances include beneficial nutrient elements; others are injurious to plants. Many of these substances originate from natural sources; others are pollutants produced by man.

Many of these atmospheric trace constituents are at least partially soluble in water and can thus be absorbed or assimilated by plants when precipitation is intercepted by vegetation. In a typical forest, an average raindrop washes over three tiers of foliage before it reaches the soil. Since some of the substances dissolved in precipitation are beneficial while others are injurious to plant tissues, the net effect of atmospheric trace constituents can be beneficial or injurious depending on the chemical composition of the precipitation, the species of plant on which it is deposited, and the physiological condition and maturity of the plant.

Rain and snow change in chemical composition within as well as between precipitation events (rain or snow storms). Thus a given plant may be subject to beneficial atmospheric influences at one time and to negative influences at another time in its development. Since trees persist for many years or even decades in the same environment, they are subject to very long-term changes in the chemistry of the atmosphere and precipitation.

The effects of acidic precipitation on plants is only one facet of the much larger subject of atmosphere-plant-soil interactions. Acidity in precipitation should be understood as a reflection not only of the amounts of substances yielding hydrogen ions (such as sulfuric, nitric, hydrochloric and organic acids) but also as a reflection of the total ionic balance between all the other cations and anions dissolved in precipitation. For all of the above reasons, the effects of a given "acidic rain" or a prevailing condition of "acidic rains" are very complex, variable in time, and involve significant interactions which are only partially understood. Thus, these effects are not easily resolved into simple generalizations.

Our hope in this brief introduction is to set the stage for the experimental contributions that follow in this section of the Proceedings. We will set forth a few general concepts as well as some theoretical postulations about the effects of acidic precipitation on vegetation. We hope that these ideas will have some value at least as a stimulus for debate and for experimentation that will increase our present meager understanding of acidic precipitation and its effects on vegetation.

POTENTIAL EFFECTS ON VEGETATION

A partial list of potential effects of acidic precipitation on vegetation is given in Table 1. The effects are classified as either direct or indirect although most direct effects will have many indirect consequences as well. Indirect effects mediated through the soil are excluded from Table 1 since they are discussed in the preceeding section of these Proceedings. A decreased rate of growth would be the expected consequence of most of the effects postulated in Table 1.

IMPLICATIONS FROM EXISTING KNOWLEDGE

As indicated in Figure 1, susceptibility to damage by sulfur dioxide varied with the time of day. Guderian (1970) found in red clover a close parallel between degree of injury, apparent photosynthesis, and amount of sulfur accumulated during the day. Since sulfur

Table 1. Potential Effects of Acidic Precipitation on Vegetation

Direct Effects

1. Damage to protective surface structures such as cuticle.

Damage to surface structures may occur due to accelerated erosion of the cuticular layer that protects most foliar organs. It also could result from direct injury to surface cells by high concentrations of sulfuric acid and other harmful substances that are concentrated by evaporation or adherence of soot particles on plant surfaces.

2. Interference with normal functioning of guard cells.

Malfunction of guard cells will lead to loss of control of stomata and thus altered rates of transpiration and gas-exchange processes and possibly increased susceptibility to penetration by epiphytic plant pathogens.

3. Poisoning of plant cells after diffusion of acidic substances through stomata or cuticle.

This could lead to development of deep necrotic or senescent spots on foliar organs including leaves, flowers, twigs, and branches.

4. Disturbance of normal metabolism or growth processes without necrosis of plant cells.

Such disturbances may lead to decreased photosynthetic efficiency, altered intermediary metabolism, as well as abnormal development or premature senescence of leaves or other organs.

5. Alteration of leaf- and root-exudation processes.

Such alterations may lead to changes in populations of phyllosphere and rhizosphere microflora and microfauna, including nitrogen-fixing organisms.

6. Interference with reproduction processes.

Such interference may be achieved by decreasing the viability of pollen, interference with fertilization, decreased fruit or seed production, decreased germinability of seeds, etc.

7. Synergistic interaction with other environmental stress factors.

Such reinforcing interactions may occur with gaseous sulfur dioxide, ozone, fluoride, soot particles, and other air pollutants as well as drought, flooding, etc.

Table 1.--Continued

Indirect Effects

1. Accelerated leaching of substances from foliar organs.

Damage to cuticle and surface cells may lead to accelerated leaching of mineral elements and organic substances from leaves, twigs, branches, and stems.

2. Increased susceptibility to drought and other environmental stress factors.

Erosion of cuticle, interference with normal functioning of guard cells, and direct injury to surface cells may lead to increased evapotranspiration from foliar organs and vulnerability to drought, air pollutants, and other environmental stress factors.

3. Alteration of symbiotic associations.

Changes in leaf- and root-exudation processes and accelerated leaching of organic and inorganic substances from plants may affect the formation, development, balance, and function of symbiotic associations such as mycorrhizae, nitrogen-fixing organisms, lichens, etc.

4. Alteration of host-parasite interactions.

Resistance and/or susceptibility to biotic pathogens and parasites may be altered by predisposing plants to increased susceptibility, altering host capacity to tolerate disease, altering pathogen virulence, etc. The effects of acidic precipitation may vary with: the nature of the pathogen involved (whether a fungus, bacterium, mycoplasma, virus, nematode, parasitic seed plant, or multiple-pathogen complex); the species, age, and physiological status of the host; and the stage in the disease cycle in which the acidic stress is applied -- for example, acidic rain might decrease the infective capacity of bacteria before infection and increase the susceptibility of the host to disease development after infection.

dioxide is taken up through the stomata, injury occurs mainly during the part of the day when the stomata are open. Sulfur also may be taken up through the cuticle, but this is a much slower process.

The physiological condition and maturity of leaves also is important. Sometimes damage is concentrated along tips and margins of leaves, but this may be a simple consequence of the laws of physics -- edges and tips are more exposed to injurious molecules in the air than are the central parts of leaves.

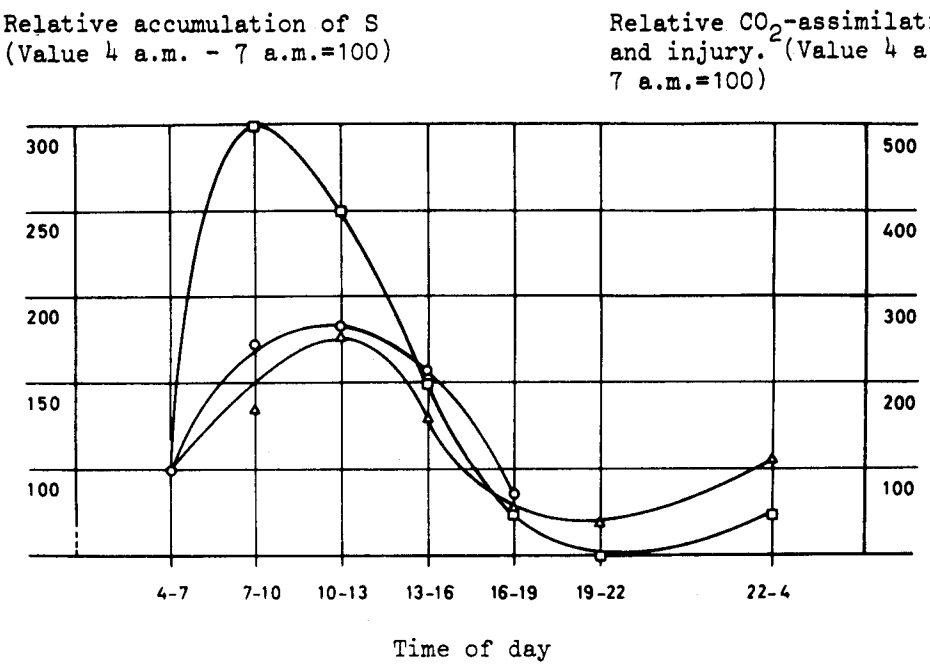

Figure 1. Accumulation of sulfur and degree of injury in red clover during different times of day, compared with apparent photosynthesis. □ degree of injury, o apparent photosynthesis, Δ sulfur accumulation. (Reproduced from Guderian, 1970).

Lichens, which do not have a protective covering of cuticle with stomata, are very sensitive to sulfur dioxide. For the same reason they also may be highly susceptible to the effects of acid rain. Schönbeck et al. (1970) found a very good inverse corelationship between the amount of sulfur dioxide in the air and the amount of living tissue remaining after exposure (Figure 2). Sometimes it is useful to use lichens as very sensitive indicators for air pollution because of the great difficulties of measuring air concentrations of sulfur dioxide in a physiologically meaningful way. Near sources of emission, the concentration of sulfur dioxide during any given 5-minute time interval may differ 2-5 fold from that during the next 5-minute interval (Figure 3). For this reason, a need exists for some type of biological assay, such as can be made by exposing lichens to air pollution over convenient periods of time.

Photosynthesis is very sensitive to air pollution. A strong reducing compound such as sulfur dioxide may affect both the chlorophyll itself and various steps in the photosynthetic process.

It is well known that plants differ greatly in their susceptibility to sulfur dioxide and other poisonous substances (Linzon, 1972). Genetically controlled variation in resistance or susceptibility to the effects of acid rain may likewise be expected both within and among

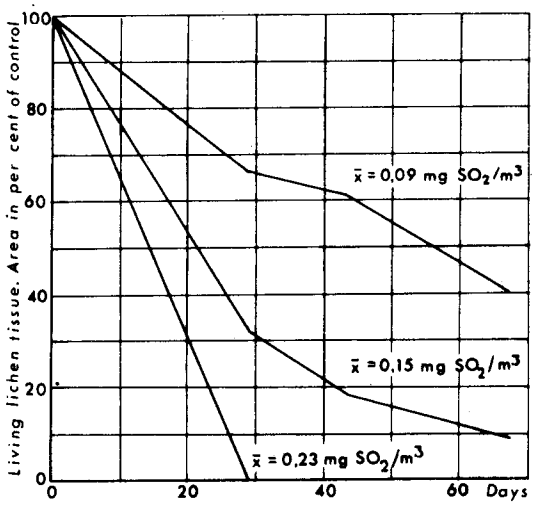

Figure 2. Influence of sulfur dioxide on transplants of a foliose lichen (*Parmelia physodes*) placed in the vicinity of an iron-ore smelter. Sulfur dioxide concentrations were measured according to the method of Stratmann. (Reproduced from Schönbeck et al., 1970).

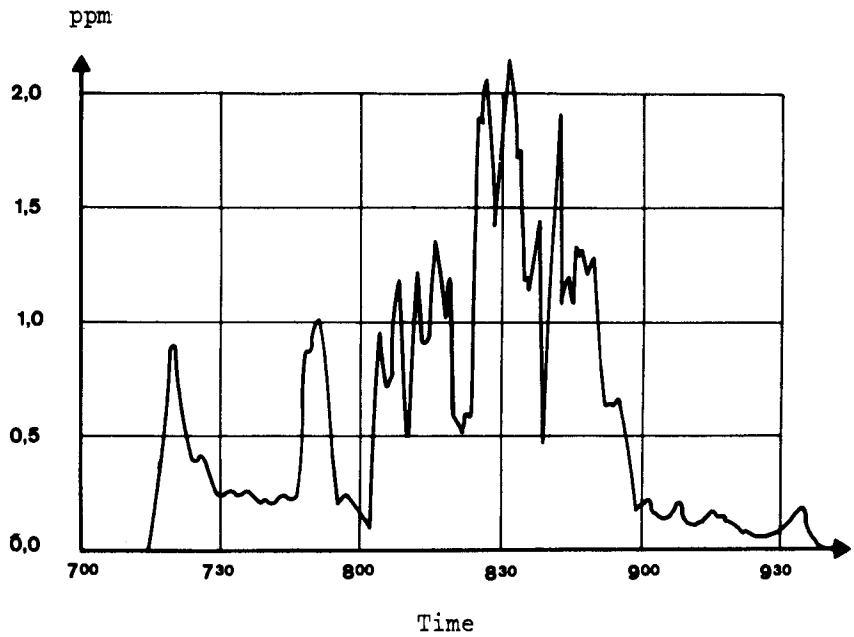

Figure 3. Variation in sulfur dioxide concentration at a station 600 m from cource of emission. (Reproduced from van Haut, 1961).

various species of forest trees. Figure 4 illustrates this variation in sensitivity to sulfur dioxide among various species and selections of woody plants. The concentrations of sulfur dioxide are shown on a logarithmic scale. The marks in the right-hand margin concern plants exposed for very long periods of time. The curved line is an empirical relationship developed by Thomas and Hill (1935) for the first visible

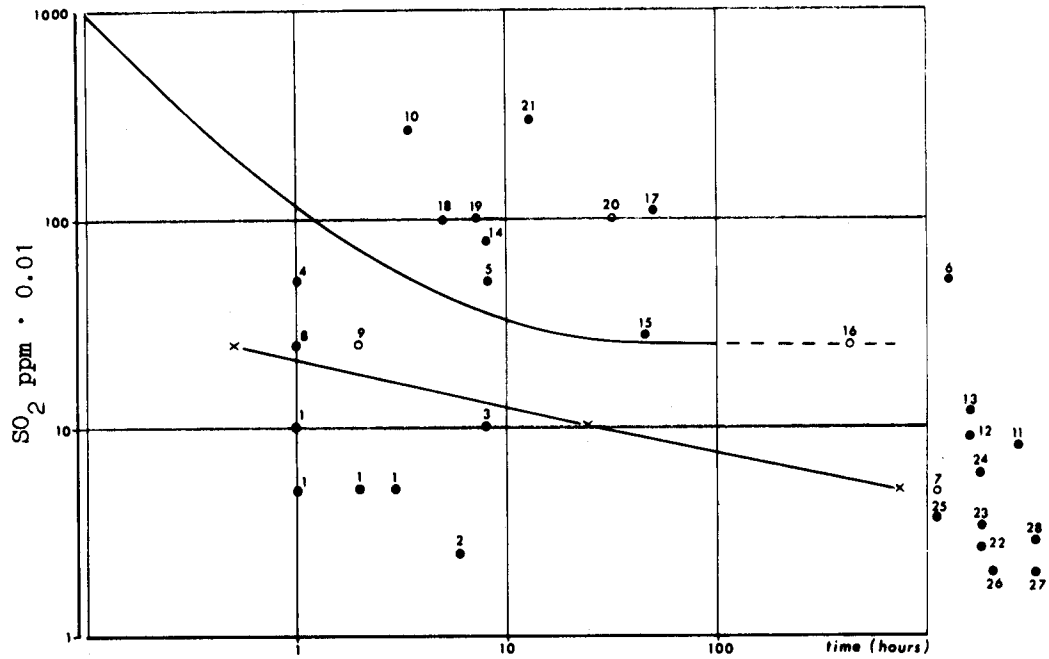

Figure 4. A compilation of values from the literature showing the effects of sulfur dioxide on various species of trees. The curved line represents Thomas and Hill's equation for first noticeable injury in alfalfa. The straight line represents the maximum air-quality standard for sulfur dioxide concentrations in Swedish cities, according to 1972 regulations. The concentration data given in the right-hand margin are for exposure times greater than one month. o noninjured plants, ● injured plants. For further explanation of the numbers in this figure, see the Key to Figure 4 printed below. (Reproduced from Tamm and Aronsson, 1972).

symptom of injury to alfalfa plants. The straight line illustrates the current standard for air concentrations of sulfur dioxide in urban areas of Sweden. The corresponding curve for the United States is somewhat steeper but otherwise not much different. The sensitive plants below the curve are almost all 5-needled pines. Although *Pinus strobus* generally is very sensitive to sulfur dioxide, there is also great genetic variation within this species, as indicated in the Figure. Figure 4 also shows that damage to *Pinus strobus* may be expected even if the current standards for clean air in urban areas in Sweden (and the United States) are strictly observed.

Acidic rain may cause direct injury to (or erosion of) the protective surface structures of plants such as the cuticle. Gaseous sulfur dioxide may not be corrosive enough to damage the cuticle at presently occurring ambient concentrations, but droplets of sulfuric acid in aerosols certainly may have this effect.

Key to Figure 4

Number	Species	Woody plants	Observer
1	Pinus strobus	4-5 week-old needles injured in sensitive clones	Costonis 1970
2	Pinus strobus	Injuries in sensitive clones	Stairs et al. 1970
3	Pinus strobus	Injuries in sensitive clones at fumigation 8 h/per day for 4-8 weeks	Dochinger et al. 1970
4, 5	Pinus strobus	Always injuries	Dochinger et al. 1970
6	Pinus strobus	Injuries	Berry 1964
7	Pinus strobus	No injuries	Jaeger & Banfield 1970
8	Pinus strobus	Injuries	Berry 1967
9	Pinus strobus resinosa banksiana	3, 5 and 7 week-old seedlings without injuries (27°C, 70% RH)	Berry 1971
10	Pinus silvestris	Reduction in photosynthesis. Complete recovery after 48 hours	Vogl & Börtitz 1965
11	Pinus silvestris	No stands in the Ruhr area	Knabe 1971
12, 13	Pinus silvestris	Injured trees die within two or three years	Podzorov 1969
14	Douglas fir	Slight injuries	Thomas 1951
15	Douglas fir	Slight injuries	Thomas 1951
16	Douglas fir	No injuries	Thomas 1951
17	Douglas fir	A few young trees die	Thomas 1951
18	Picea abies	Reduced photosynthesis in late summer, no other injuries	Börtitz 1964
19	Picea abies	Reduced photosynthesis in late summer, no other injuries at fumigation 7 h/per 24 hours during 240 hours	Börtitz 1964
20	Picea abies	No injury in hot weather (stomata closed)	Börtitz 1964
21	Picea abies	Needle necroses	Börtitz 1964
22, 23	Picea abies	Annual mean value, slight injuries	Knabe 1971
24	Picea abies	Annual mean value, severe injuries	Knabe 1971
25	Picea abies	Threshold value for injuries, long-term measurements	Materna 1971
26	Conifers, oak, beech	Thresholdvalue for injuries, mean value	Wentzel 1969
27, 28	Quercus robur Fagus silvatica Larix decidua Pinus silvestris Picea abies	Significant growth reduction at mean value for growing season	

Necrotic spots will develop where high concentrations of acids occur, especially when leaves are exposed to alternate cycles of wetting and drying. In this case, drops of acidic water evaporate leading to an increase in acid concentration and then to local necrotic spots. Similar high concentrations of acids may develop beneath soot particles adhering to plant surfaces.

As indicated in Table 1, if the cuticle and other protective structures are damaged, the plant may be harmed by other environmental and biotic stress factors. For example, loss of control of guard-cell function can lead to loss in control of gas-exchange reactions. Guard cells react, among other things, to changes in the pH of their cytoplasm. Once a plant loses control of its stomata, it will lose control of transpiration, and then may be injured by drought.

A very likely direct effect of air-borne acidic substances is a poisoning effect on metabolic processes within living cells. This requires transport to the cell surface and usually through cell membranes. In vascular plants it also requires diffusion through stomata or through the cuticle. Hence, stomatal frequency and all factors affecting stomata opening are important in determining susceptibility to metabolic poisoning.

Cellular metabolism also may be affected by sulfur and nitrogen oxides without direct evidence of poisoning. Needles of conifers and leaves of deciduous trees often have a shorter functional life-span in polluted areas. In some cases this premature ageing has been accompanied by large accumulations of sulfate in the cells (Lihnell, 1969). Sulfate is much less poisonous than sulfite (Linzon, 1972); in fact, formation of sulfate is a detoxification process in plant cells although accumulation of sulfate still may imply a disturbed metabolism.

Acidic precipitation or acidic substances in the atmosphere may also affect plants by synergistic interactions with various other air pollutants such as ozone or fluoride. Soot particles adhering to plant surfaces may absorb gases from the air and thereby concentrate these substances. The concept of synergistic effects covers a wide range of possibilities. Figure 5 shows the close similarity of distribution patterns for sulfur and lead from atmospheric sources in Scandinavia. Perhaps the concentrations observed to date are not yet great enough to induce synergistic effects on a regional scale, but these and other poisonous substances with potential synergistic effects on living organisms often occur together.

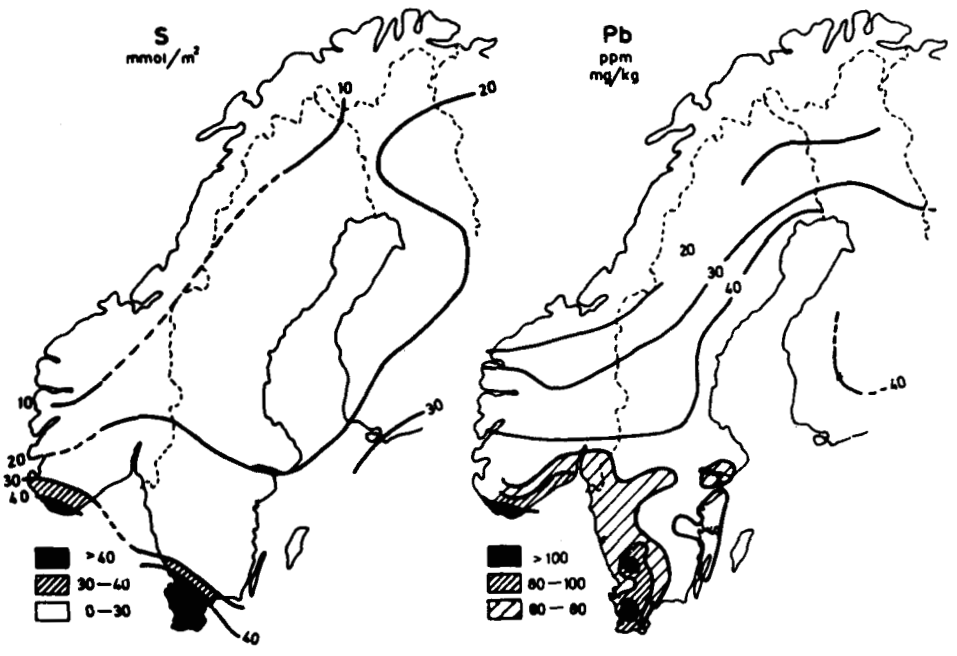

Figure 5. The calculated increase in annual supply of sulfur in precipitation (left) and the lead content of the moss *Hylocomium spendens* in different parts of Scandinavia (right). Note the similar distribution patterns of these two different pollutants. The figures refer to conditions in about 1970. The figures for sulfur are expressed as "excess sulfur" from Granat, 1972, Fig. 5 and for lead from Tyler, 1972. (Reproduced from Malmer, 1974).

In studying the direct and indirect effects of acidic precipitation on plants, it is important to distinguish between local effects and regional ones. The local effects usually are more conspicuous and thus more easily studied. But in some areas of Europe and North America, the regional concentrations of harmful substances in the air are approaching concentrations at which serious long-term effects may be suspected.

In conclusion, it is important to recognize that present knowledge of the effects of acidic precipitation on vegetation is wholly inadequate. Much research is needed to determine the importance of the various potential effects listed in Table 1. We hope that much more complete information about the biological and economic consequences of these effects will become available in the future.

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SOME APPROXIMATIONS FOR THE WET AND DRY REMOVAL OF PARTICLES AND GASES FROM THE ATMOSPHERE

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ABSTRACT

Semi-empirical formulae are presented which can be used to estimate precipitation scavenging and dry deposition of particles and gases. The precipitation scavenging formulae are appropriate both for in- and below-cloud scavenging and comparisons with data indicate the importance of accounting for aerosol particle growth by water vapor condensation and attachment of the pollutant to plume or cloud particles. It is suggested that both wet and dry removal of gases is usually dictated by other than atmospheric processes. Dry deposition of particles to a canopy is shown to depend on canopy height, biomass, vegetative type and mean wind. Two large-scale practical problems are addressed dealing with the relative importance of wet and dry deposition and with the sources which contribute to deposition in a specific location.

Essentially all air pollution is eventually cleansed from the atmosphere by the natural processes generally referred to as precipitation scavenging and dry deposition. The purpose of this report is to present formulae which can be used to approximately describe these cleansing processes. Within the details of the development of these formulae, some unifying features may not be apparent and it may be worthwhile to mention them here. One is that in all cases, whether the removal is by rain, snow, grass, leaves, water surfaces or whatever, the efficiency with which the pollutant is removed from an air stream by an obstacle must be considered. This collection efficiency is usually written as the product of a collision efficiency, defined in Figure 1, multiplied by a retention efficiency. In most cases, out of ignorance, the retention efficiency will be taken to be unity although some comments will be made about the retention of aerosol particles by vegetation and the desorption of gases from liquids. A second unifying feature is that after a collection efficiency has been obtained, it is necessary to sum over all collecting elements to obtain an overall removal rate and usually these integrals must be rather severely

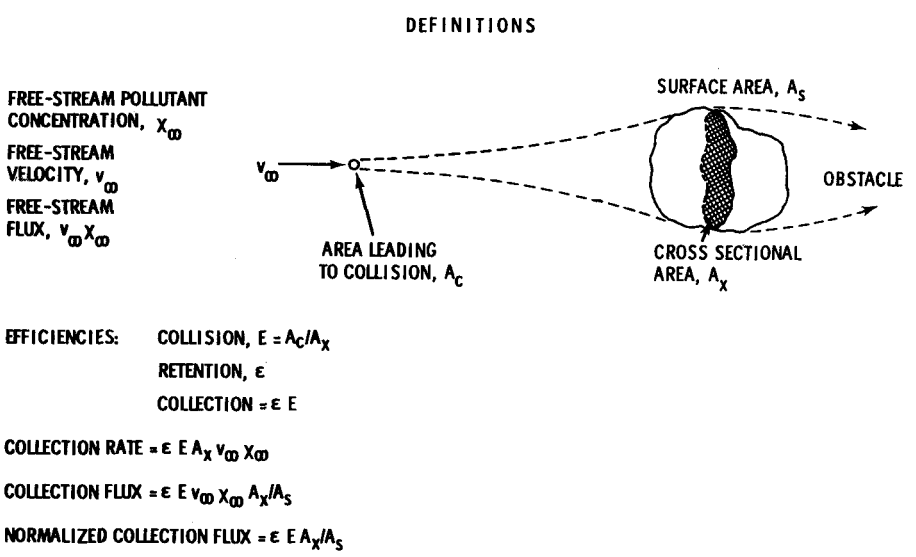

Figure 1. Some definitions. In the sequel the retention efficiency will be taken to be unity.

approximated. A third feature, one that is only beginning to become apparent, is that with further study into the removal processes (accounting for effects such as aerosol particle growth, foliage density within canopies, etc.) the removal rates tend toward simple and rather obvious results, in a sense frustrating the substantial effort devoted to unraveling the complexities. In the closing section of this report some practical applications will be discussed for a few problems which are of current interest. A list of symbols is included as an appendix.

A. PRECIPITATION SCAVENGING OF AEROSOL PARTICLES

By precipitation scavenging or washout is meant the removal of a pollutant from the atmosphere by various types of precipitation such as rain, snow, etc. The obvious abbreviations, rainout, snowout, etc., are also used.* Sometimes it is convenient to distinguish below-cloud scavenging from in-cloud scavenging if the elevation of the pollutant is clearly below or above, respectively, the cloud base. The formulae to be developed are applicable to both cases. The focus in this section will be on washout of particles; then some of the complications associated with gas washout will be mentioned.

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*Readers familiar with earlier precipitation scavenging literature might notice the change in terminology here, recommended at the 1974 International Precipitation Scavenging Meeting. For further details see Slinn (1975a).

1. GENERAL FORMULATION

To describe aerosol particle washout it is convenient to start from a general formulation. Let χda be the amount of contaminant per unit volume associated with particles of radii a to a + da (viz., "a-particles"). Then the evolution of this contaminant is governed by a continuity equation:

$$\frac{D\chi}{Dt} = \nabla\cdot(K\cdot\nabla\chi) - \psi\chi + G\chi - L(\chi) \tag{1}$$

where $D/Dt = \partial/\partial t + \vec{v}\cdot\nabla$ is the usual total time derivative; $\vec{v}$ is the wind field of the air, assumed incompressible; K is the turbulent diffusivity (or, more generally, $K\cdot\nabla\chi$ symbolizes the turbulent flux); ψ is the precipitation scavenging (or washout) rate coefficient; and G and L symbolize gain and loss of contaminant associated with a-particles because of condensation, evaporation, coagulation, etc. Dry deposition could also enter here but it is more convenient to, and later we will, treat it as a boundary condition.

One way to temporarily avoid the many complications in (1) is to take various averages or moments. Thus, if (1) is averaged over all particle sizes it becomes

$$\frac{D\chi_t}{Dt} = \nabla\cdot(K\cdot\nabla\chi_t) - \bar{\psi}(\vec{r},t)\chi_t \tag{2}$$

where the total contaminant density is

$$\chi_t = \int_0^\infty da\chi(\vec{r},t;a) \tag{3}$$

and the particle-average removal rate is

$$\bar{\psi}(\vec{r},t) = \int_0^\infty da\psi(\vec{r},t;a)\chi/\chi_t. \tag{4}$$

To obtain (2) from (1) it has been assumed that turbulence acts on all particles similarly and use has been made of the observation that in all processes contributing to G and L, the contaminant is not lost from the space volume. In turn, if (2) is integrated over a large enough volume of space so that no contaminant is convected from the volume by the wind, then use of the divergence theorem (and $\nabla\cdot\vec{v} = 0$) leads to

$$\frac{\partial Q_t}{\partial t} = -\langle\bar{\psi}(t)\rangle Q_t \tag{5}$$

where the total amount of contaminant present is

$$Q_t = \int d\vec{r}\chi_t(\vec{r},t) \tag{6}$$

and the space- and particle-average removal rate is

$$\langle \bar{\psi}(t) \rangle = \int d\vec{r} \bar{\psi}(\vec{r},t) \chi_t(\vec{r},t)/Q_t. \tag{7}$$

For the case that $\langle \bar{\psi} \rangle$ is time independent then the solution to (5) is

$$Q_t = Q_{t_0} \exp\{-\langle \bar{\psi} \rangle t\} \tag{8}$$

which is a familiar expression used in precipitation scavenging studies.

That the above formalism only temporarily avoids the complexities of (1) is seen when one attempts to evaluate analytically the average removal rates $\bar{\psi}$ or $\langle \bar{\psi} \rangle$; clearly $\psi(\vec{r},a,t)$ and $\chi(\vec{r},a,t)$ must be known. Presumably ψ can be specified (see below) but to obtain χ, apparently (1) must be solved. But if (1) could be solved, there would be no need for the development from (2) to (8). To extricate us from this circuitous development and yet to utilize these coarser descriptions of scavenging, a number of approximations for χ will be introduced. First, though, it is useful to see the accuracy to which ψ can be specified.

2. REMOVAL RATES FOR PARTICLES BY RAIN AND SNOW

Consider first rain scavenging (viz., rainout) of particles. Let the number of a-particles per unit volume be $n(a;\vec{r},t)da$. Then the number of these particles removed per unit volume during dt by drops of radii R to R + dR is

$$N(R)dR\pi R^2 E(a,R) v_t(R) dt \; n(a)da \tag{9}$$

where $N(R)$ is the number distribution function for the raindrops, $v_t(R)$ is their terminal velocity and $E(a,R)$ is the collection efficiency (the collision efficiency multiplied by retention efficiency which herein will be taken to be unity). A suggested semi-empirical expression for the collection efficiency, which accounts for particle diffusion, interception, and inertial impaction, is (Slinn, 1975b)

$$E(a,R) = \frac{4}{Pe}\left[1 + 0.4\, Re^{1/2} Sc^{1/3}\right] + 4\kappa\left[\kappa + \frac{(1 + 2V\kappa)}{(1 + VRe^{-1/2})}\right] + \left[\frac{s - s_*}{s + c}\right]^{3/2} \tag{10}$$

where the symbols are defined in the appendix. Figure 2 shows a plot of (10) with some experimental data.

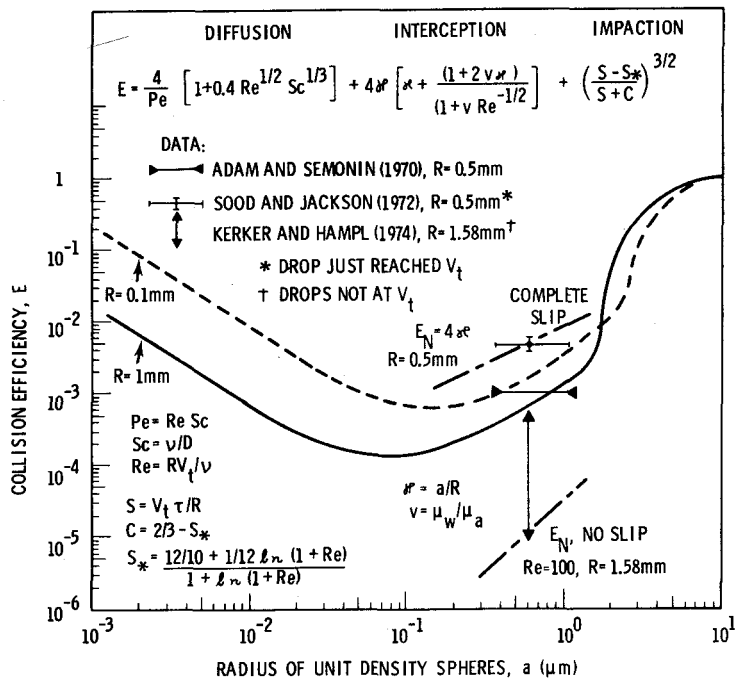


Figure 2. The proposed semi-empirical expression (10) for the collision efficiency between drops and particles as a function of particle size and accounting for diffusion, interception and inertial impaction. See Slinn (1974b) for a possible explanation of the scatter in the data for particles of radii ∿0.5 μm. The diffusion and impaction portions of the curves have sufficient experimental support to consider the corresponding expressions reliable to within a factor of 2 or 3.

The rain scavenging rate is found by integrating (9) with (10) over all drop sizes:

$$\psi_r(a) = \int_0^\infty dR\ N(R) v_t(R) \pi R^2 E(a,R). \tag{11}$$

By comparing (11) with the expression for the rainfall rate

$$p = \int_0^\infty dR\ N(R) v_t(R)\ \frac{4}{3}\pi R^3 \tag{12}$$

and appreciating some of the many uncertainties in the rain scavenging problem (Slinn, 1975b), the author suggests the approximation to (11):

$$\psi_r(a) \simeq \frac{p(\vec{r},t)}{2R_m} E(a,R_m) \qquad (13)$$

where the possible dependence of rainfall rate on position (especially on height within clouds) and on time has been made explicit. In (13), R_m is the volume-mean drop diameter which usually is related to rainfall rate, e.g., for steady frontal rain

$$R_m = 0.35\text{mm}(p/1\text{mm hr}^{-1})^{1/4}. \qquad (14)$$

There is little field data available to evaluate the particle size dependence of ψ_r as given by (13). What data there is, shown in Figure 3, obtained in a plume, 10^3 seconds downwind from a Kraft-process

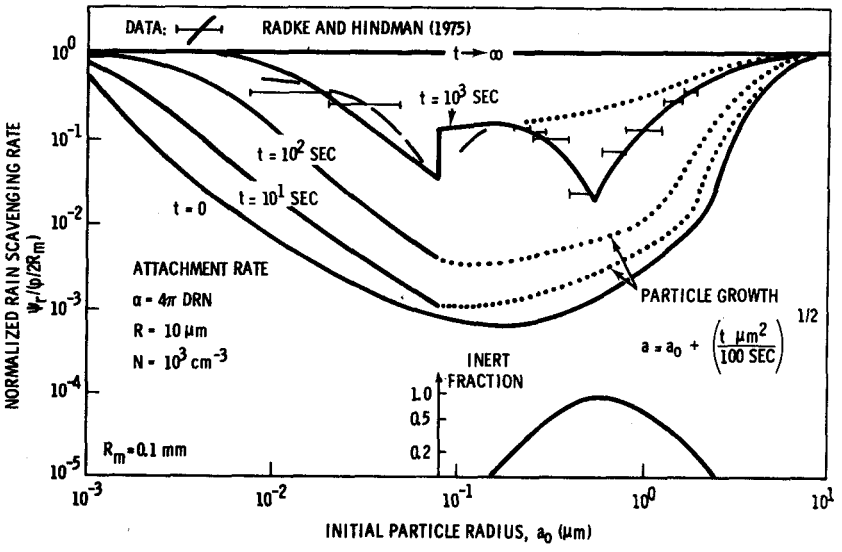


Figure 3. A comparison of the predictions from Equation (13) with experimental data obtained by Radke et al. (1975). Particles smaller than 0.16 μm are assumed to attach to plume droplets (E = 1) at the rate shown. The dotted curve (••••) is obtained assuming that all particles larger than 0.16 μm diameter grow by water vapor condensation, at the rate shown. The solid curve (——) for t = 10^3 seconds is obtained assuming that only some of the particles larger than 0.16 μm grow by water vapor condensation. The inert (non growing) fraction is shown in the inset.

paper mill by Radke et al. (1975) seems to demonstrate the importance of accounting for changes in particle size because of attachment of the particles to plume droplets (and similarly to cloud particles, Slinn, 1974a) and because of water vapor condensation.

In the case of scavenging by ice crystals (viz., snow scavenging or snowout) then the approximations for the removal rate must at the present time be even cruder than those introduced above for rain scavenging. Elsewhere (Slinn, 1975b) the author has suggested

$$\psi_s(\vec{r},t;a) \simeq (10^6 \text{cm/sec}^2)\, \frac{p(\vec{r},t)}{\langle v_t^2 \rangle}\, \mathcal{E}(a,\ell) \qquad (15)$$

where p is the precipitation rate (in rainwater equivalent); $\langle v_t \rangle$ is the average settling speed of the snowflakes; and $\mathcal{E}(a,\ell)$ is the particle/ice crystal collection efficiency in which ℓ is a characteristic dimension of the collecting element in the ice crystal, not necessarily related to the overall size of the ice crystal. A suggestion for $\mathcal{E}$ along with essentially all available data is shown in Figure 4. Calculations based

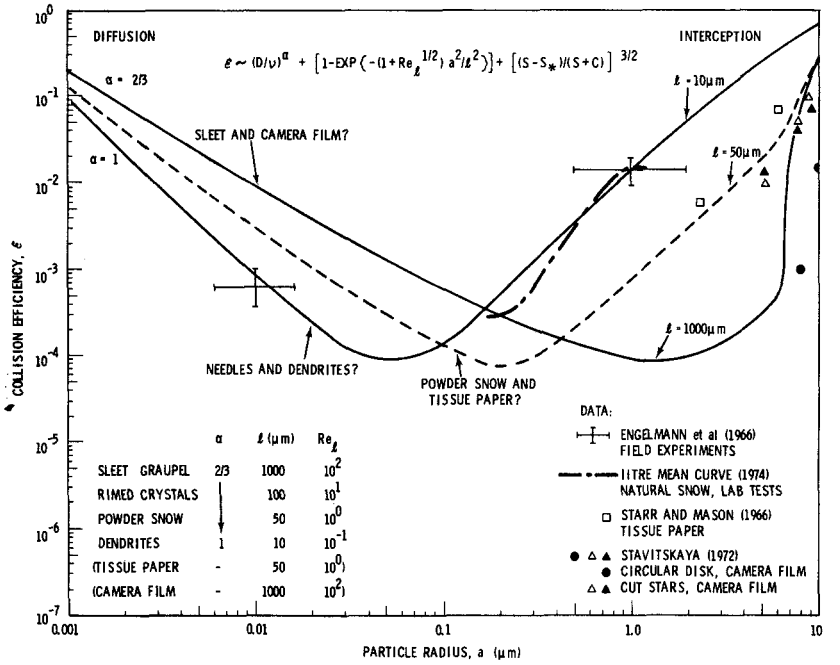


Figure 4. A tentative suggestion for the collision efficiency for particles by snow.

on (15) with data for v_t from Mason (1971) and with $\mathcal{E} = 1$ are shown in Figure 5, as well as some fits to data.

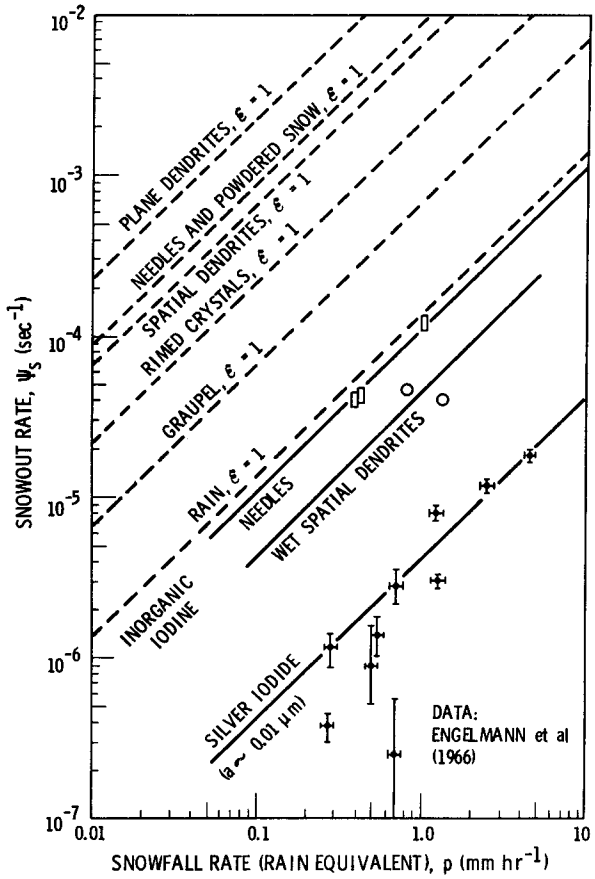


Figure 5. The snowout rate as a function of precipitation intensity as given by (15). The top curves, with $\mathcal{E} = 1$, show the influence of crystal type. The $\mathcal{E}$ values chosen to fit Engelmann et al's. (1966) data were: $\mathcal{E} = 1.3 \times 10^{-2}$ for process-plant iodine scavenged by needles and $\mathcal{E} = 6 \times 10^{-4}$ for AgI particles scavenged by various crystal types, usually powdered snow or spatial dendrites.

3. APPROXIMATIONS FOR PARTICLE- AND SPACE-AVERAGE REMOVAL RATES

Returning now to expressions (4) and (7) for the particle- and space-average removal rates, respectively, it is seen that fairly crude approximations to the air concentration χ would be consistent with the crudeness to which the removal rates, (13) and (15), are known. It should also be mentioned that usually the turbulent diffusion of the contaminant is not known very precisely, rarely to within a factor of two. Here the following approximations are introduced:

• For each chemical species of aerosol present, three portions of the size spectrum are identified, qualitatively as shown in Figure 6 and labelled χ_f (free), χ_g (growing) and χ_h (hosted). Thus

$$\chi = \chi_f + \chi_g + \chi_h \tag{16}$$

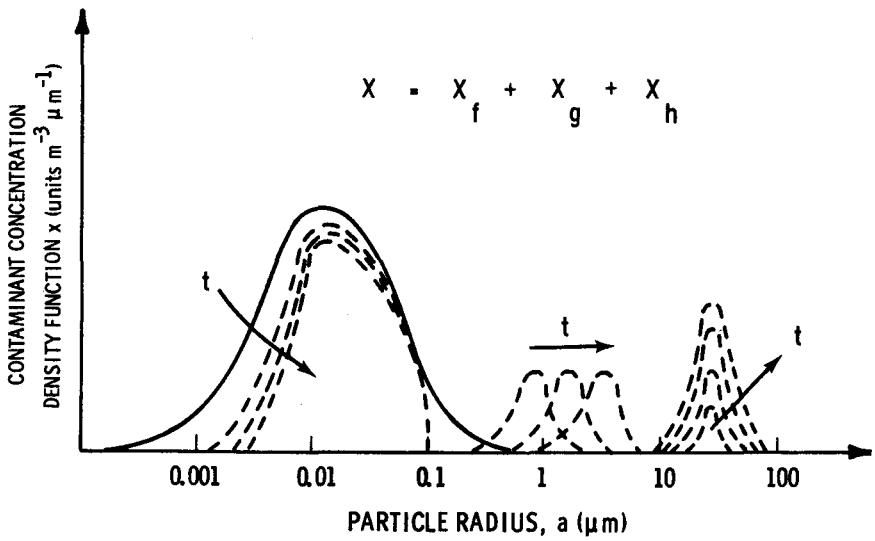


Figure 6. A schematic illustration of the contaminant's assumed distribution among the three particle classes (free, growing and hosted) and their time evolution.

• The evolution of the free particles is approximately governed by

$$\frac{D\chi_f}{Dt} = \nabla\cdot(K\cdot\nabla\chi_f) - \alpha\chi_f - \psi_f\chi_f \qquad (17)$$

where α is the attachment rate, and it is assumed that an adequate approximation to the solution of (17) is

$$\chi_f = \dot{q}_f(a)P(\vec{r},t;K,\vec{v})\ \exp\{-\int_0^s(\alpha + \psi_f)d\tau\} \qquad (18)$$

where $\dot{q}_f(a)da$ is the number of free a-particles released per second, P is some plume model and s is either t or $x/\bar{u}$. Similar approximate solutions are assumed for χ_g and χ_h.

• The radius of the growing particles is assumed known and the host particles (e.g., plume or cloud drops) are assumed to possess the same radius, λ.

• The particle size distribution of χ_f, χ_g and χ_h are assumed to be log normal and integrals over particle sizes are approximated by evaluating the integrands at their mean value.

• It is assumed that the contaminant is distributed among the particles according to

$$\chi(a) = ca^j n(a) \qquad (19)$$

where c is an obvious normalization constant and, for example, j = 3 if the contaminant is just the mass of the particles.

If these approximations and assumptions are used in (4) then the particle-average rainout rate becomes, approximately,

$$\bar{\psi}_r = \frac{P}{2R_m}\left[F_{fo}\exp\{-\int_0^s(\bar{\alpha}+\bar{\psi}_f-\bar{\psi}_r)ds\}\,E(a_{fj},R_m)\right.$$

$$+F_{go}\exp\{-\int_0^s(\bar{\psi}_g-\bar{\psi}_r)ds\}\,E(a_{gj},R_m)+\frac{\bar{\alpha}}{(\bar{\alpha}+\bar{\psi}_f-\bar{\psi}_h)}F_{fo}$$

$$\left.\cdot[\exp\{-\int_0^s(\bar{\psi}_h-\bar{\psi}_r)ds\}-\exp\{-\int_0^s(\bar{\alpha}+\bar{\psi}_f-\bar{\psi}_r)ds\}]\,E(\lambda,R_m)\right] \tag{20}$$

where F_{fo} and $F_{go} = 1 - F_{fo}$ are the initial fractions of the contaminant associated with free and growing particles, respectively, and where

$$a_j = \bar{a}\exp\{(j+\tfrac{1}{2})\sigma^2\} \tag{21}$$

in which $\bar{a}$ is the geometric mean (number) radius and $\sigma = \ell n\bar{\sigma}$ where $\bar{\sigma}$ is the geometric standard deviation, each for the specific class of aerosol. For small time (i.e., for $\bar{\psi}_r t << 1$) or if the difference between any ψ_i and ψ_r is small, for a time independent attachment rate and for j = 3, then (20) with s = t simplifies to the transparent expression for the mass rainout rate

$$\bar{\psi}_r = \frac{P}{2R_m}\left[F_{fo}\exp\{-\bar{\alpha}t\}\,E\{\bar{a}_f\exp(\tfrac{7}{2}\sigma_f^2),R_m\}\right.$$

$$+F_{go}E\{\bar{a}_{go}\exp(\tfrac{7}{2}\sigma_g^2)+(\frac{t\ \mu m^2}{100\ sec})^{1/2},R_m\}$$

$$\left.+F_{fo}\{1-\exp(-\bar{\alpha}t)\}E(\lambda,R_m)\right] \tag{22}$$

in which a specific, particle growth rate has been assumed. Equation (22) is plotted in Figure 7 for the case of the parameters shown and demonstrates the rapid increase in the mass rainout rate both with time and with an increase in the polydispersity of the aerosol (viz $\bar{\sigma}$). For further details on this latter point see Dana and Hales (1975). Expressions similar to (20) and (22) are suggested for snow scavenging; the differences being only in the term outside the braces, [ ], see (15), and with E replaced by $\mathcal{E}$.

There is not yet available sufficient data to test this formulation. Figure 8 shows that data obtained by Burtsev et al. (1970) for the

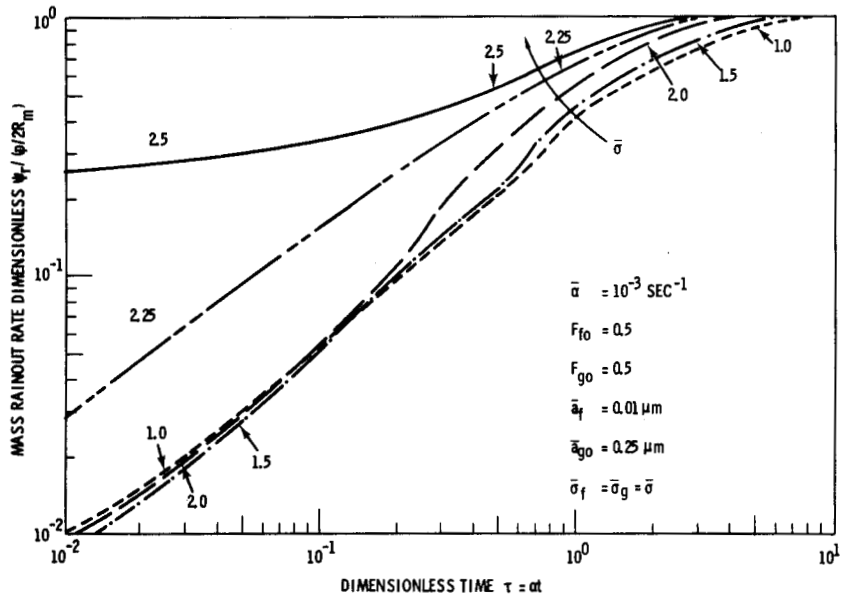


Figure 7. An illustrative example of Equation (22) for the choice of the parameters shown, which illustrates the strong dependence of the mass average removal rate on the polydispersity of the aerosol (reflected in $\bar{\sigma}$) and on the time for attachment and condensational growth.

incloud (convective storm) scavenging of a radioactively tagged aerosol with $\bar{a}$ near 0.1 μm, can be approximately fit ignoring attachment, assuming all particles acted as condensation nuclei and in the available time, grew to about 10 μm diameter drops. The data obtained by Dana and Wolf (1968, 1969, 1970), Figure 9, for removal of total aerosol mass downwind of an 8m tower release, suggests that the soluble tracer did not possess its dry-size when scavenged ($\bar{\sigma}$ is not given) and that a significant portion of the tracer dry deposited in the samplers (Dana, 1972; Slinn, 1974b, 1975b).

To obtain the particle- and space-average removal rates obviously some information is needed about the spatial distribution of the pollutant. Thus for rain scavenging (and similarly for snow scavenging) (7) becomes

$$\langle \bar{\psi} \rangle = \frac{1}{Q_t} \int d\vec{r}\, \frac{p(\vec{r},t)}{2R_m} [E] \chi_t(\vec{r},t) \qquad (23)$$

where [E] represents the term in braces, [ ], in (20), and similarly for snow. If there is some desire to identify the separate contributions from below-cloud (b.c.) and from in-cloud (i.c.) scavenging, then obviously (23) becomes

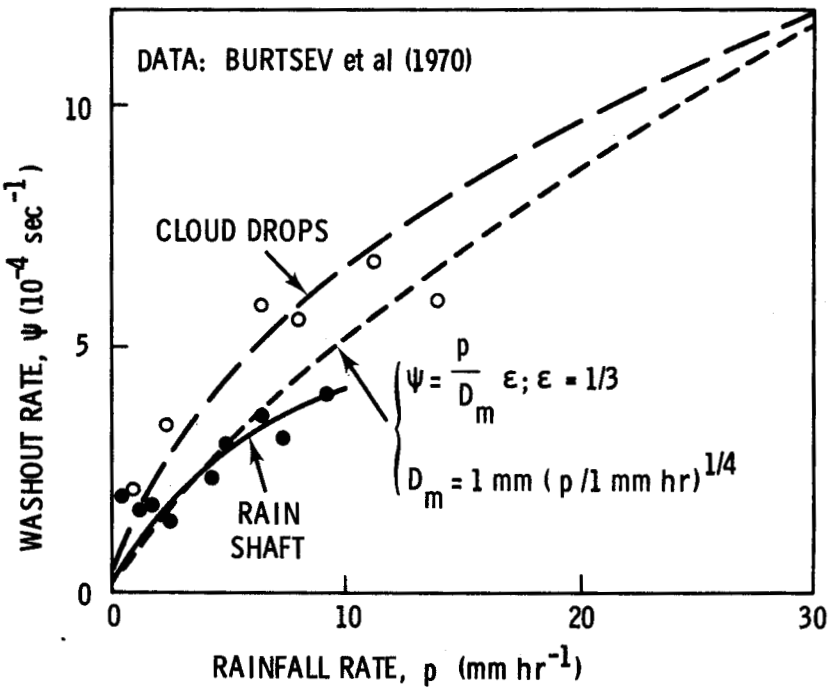


Figure 8. A comparison of theory with experimental data obtained by Burtsev et al. (1970) for the in-cloud scavenging of tracer released into the top of the rain shaft (solid curve) and into the region of "cloud drops" (dashed curve) of a cumulonimbus cloud. The "cloud drops" case probably corresponds to the region of maximum radar reflectivity and it is noted that Burtsev et al.'s description seems to imply that they released AgI seeding material, simultaneously with the release of their radioactively tagged aerosol.

$$\langle\bar{\psi}\rangle = \left(\frac{p}{2R_m}\right)_0 [E]f_{b.c.} + \left\langle\frac{p(z)}{2R_m(z)}\ [E]f\right\rangle_{i.c.} \qquad (24)$$

where f represents the fraction of the contaminant in each location and where it is assumed to be adequate to set the below-cloud values of p and R_m equal to their ground-level values, subscript zero.

It is more useful to obtain estimates for washout ratios, defined as the ratio of the contaminant's concentration in surface level precipitation, κ_0, to its concentration in surface level air, χ_{to}. To obtain this ratio it is noted that the rate of contaminant removal per unit volume is $\bar{\psi}\chi_t$. If the contaminant is distributed fairly uniformly horizontally, then the flux of contaminant to the earth's surface is

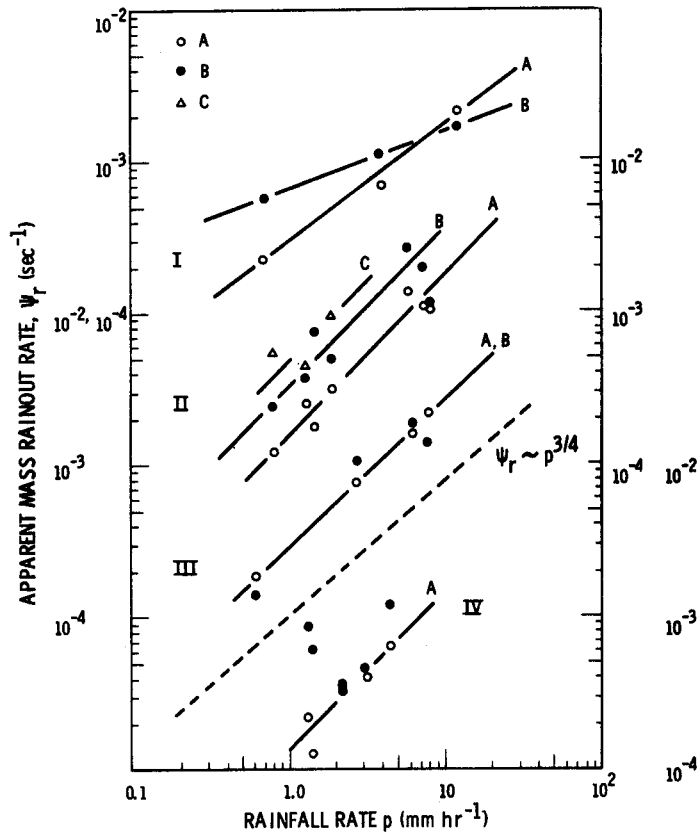


Figure 9. The apparent mass rainout measured during fairly steady rain by Dana and Wolf (1968, 69, 70). A, B and C are arc locations 50, 100 and 150 feet downwind from the release from a 26-foot tower. I: (left-hand ordinate) rhodamine particles, mmd = 11.2 μm; II: (right-hand ordinate) fluorescein particles, mean $a^2\rho_p$ = 35 μm^2 g cm^{-3}; III: (left-hand ordinate) rhodamine particles, mmd = 12. μm; IV: (right-hand ordinate) rhodamine particles, mmd = 4.8 μm.

$\int \bar{\psi}\chi_t dz$. The flux of precipitation to the surface is p_0. Therefore the washout ratio is

$$\frac{\kappa_0}{\chi_{to}} = \frac{1}{p_0 \chi_{to}} \int_{H_1}^{H_2} \bar{\psi}\chi_t dz \qquad (25)$$

where $H_2 - H_1$ spans the heights from which the contaminant is removed.

As with (23), the vertical distribution of χ_t is needed before (25) can be evaluated.

For some special cases, approximations to (25) should be fairly reliable. For example, if the pollutant's concentration is reasonably uniform and essentially constrained within the atmosphere's mixed layer, beneath the cloud base, then for this case of sub-cloud scavenging (25) with (20) or (22), and similarly for snow, leads to

$$\left(\frac{\kappa}{\chi_t}\right)_0 = \frac{[E]\ h}{2R_m} \tag{26}$$

where h is the height of the mixed layer and it is assumed that the mean drop size is invariant beneath the cloud. Another case of interest is if the pollutant is "vacuumed" from the mixed layer by a convective cloud; then one also obtains (26), but in this case, h represents the poorly known height interval $H_2 - H_1$ from which the pollutant is effectively removed. In this case, usually below-cloud scavenging could be ignored, but it would be essential to account for particle growth with E[a(t)].

Although a limited quantity of field data is available, some comparisons with theory are possible. It is seen from (26) that $(\kappa/\chi_t)_o$ is essentially independent of rainfall rate except for R_m's dependence on p. This result is well substantiated by field data (Mahkon'ko et al, 1970; Engelmann, 1970; Gatz, 1975). Figure 10 shows that the magnitude and the particle size dependence of the washout ratios for convective storms as found by Gatz (1975) are reasonably well described by (26), given that neither $\bar{\sigma}$ nor duration of condensational growth is known. For frontal storms, with the typically longer growth times available, one would expect to see less dependence on particle size and indeed one would expect $[E] \to 1$ for most particles (Slinn, 1974a). In this case $(h/2R_m)$ would reflect solely the efficiency with which cloud water is removed from the storm, which usually is the range from 10 to 90%.

B. WET AND DRY REMOVAL OF GASES

In the above, the focus was on wet removal of particles. Here it will be on gases, and it will be seen that there are common simplifying features for both wet and dry removal of gases. In addition, though, there are common features that make predictions extremely difficult, requiring the analysis of a host of interacting chemical reactions. This is generally beyond the present capabilities of the author and therefore will be avoided. The emphasis here will be on the simple aspects of the problem.

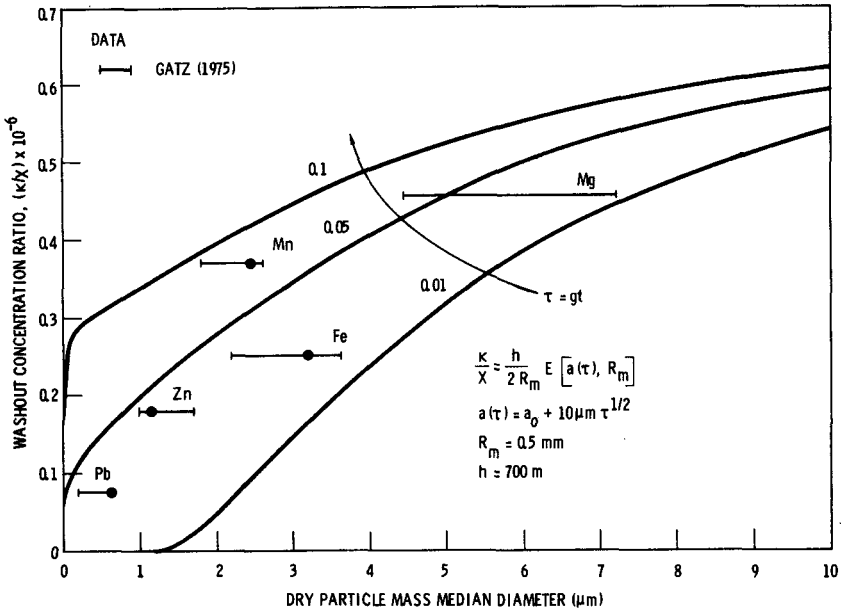


Figure 10. A comparison of predictions of Eq. (26) with the average washout ratios measured by Gatz (1975). The horizontal bars on the data reflect the different mass median diameters (mmd's) found in different cities; the dot on the bar is the mmd measured in the city (St. Louis) near which the washout ratios were measured. τ is nondimensionalized time; g is the unknown particle growth rate; a_o is the dry particle mass median radius, i.e., 1/2 the mmd as given on the abscissa. The choice of the depth of the scavenged volume $h = H_2 - H_1$, was made solely to improve the fit to the data.

Rain scavenging of gases will be considered first. Snow scavenging of gases can generally be ignored unless the gas is dissolved in plume or cloud drops, as appears to be the case for the iodine data shown in Figure 5, or unless the snow is partially melted. Here an impoverished version of the general theory of gas washout (Hales, 1972) will be considered; nevertheless the results obtained are sufficient, with guidance from the general theory, to illustrate the features considered most significant. After these have been presented, a few features of dry deposition of gases will be illustrated.

1. RAIN SCAVENGING OF GASES

For scavenging of gases by rain an expression similar to (1) for each drop size could be written and then integrated over all drop sizes to obtain a total removal rate (Slinn, 1974c); however in most cases

this much detail is not needed as will now be demonstrated. It is assumed here that gas captured by a drop is quickly, well mixed throughout the drop, either because of internal circulation within a large ($\gtrsim$ 1 mm) drop, or because of the relatively small volume-to-surface ratio of a small drop. Let the concentration of the pollutant gas in the drop be c (e.g., in moles ℓ^{-1}). If irreversible chemical reactions during the short raindrop-flight time are ignored, then the gas concentration changes according to

$$v_t \frac{d}{dz}\left(\frac{4}{3}\pi R^3 c\right) = \frac{D}{R}\left[1 + 0.4\ Re^{1/2}Sc^{1/3}\right] 4\pi R^2 (c_{eq} - c) \qquad (27)$$

where the ventilation term (in the [ ] braces) is as in (10) and c_{eq} is the equilibrium concentration of the gas in the drop for the existing air concentration, χ. For some gases, $c_{eq} = H\chi$, where H is Henry's law constant. It is noted in (27) that the driving force is the difference between c_{eq} and the actual concentration, c. For $c > c_{eq}$ the gas can be desorbed from the drop which can lead to some interesting phenomena when drops fall through a distinct plume (Hales, 1972; Slinn, 1974c).

But of more interest here is for the case of a gas fairly uniformly distributed in the atmospheric mixed layer. From (27) it is seen that the e-fold equilibration length is

$$\lambda = \frac{R}{3} \frac{Re}{\left[1 + 0.4\ Re^{1/2}Sc^{1/3}\right]} \qquad (28)$$

Supplying reasonable numerical values in (28) shows that typically, $\lambda = O(1m)$; that is, typically the concentration of the gas in the drop relatively rapidly attains its equilibrium concentration, c_{eq}. This equilibration length scale is of course longer for the unrealistic assumption of a stagnant drop, but even then the time is typically less than 10 seconds (Postma, 1970; Hales, 1972). Consequently, and especially for gases well-mixed in an atmospheric mixed layer whose depth is usually 100 to 1000m, it is reasonable to assume $c = c_{eq}$. This is the simplification alluded to earlier.

The complication is to specify c_{eq}, usually for gases at low air concentrations and usually in drops containing many other impurities. This is the chemistry problem mentioned earlier. Useful discussions and calculations for SO_2, I_2, CO_2 and NH_3 in relatively pure water are given in Junge, 1963; Postma, 1970; and Hales, 1972. However, considering the complications caused by other contaminants, it appears that the best procedure is to measure c_{eq} found in collected rainwater. Here, too, there are problems especially because of simultaneous dry deposition of gases in the rainwater collector and because of the possible desorption of the gas from the water. The latter problem can be and has been overcome in field studies by adding various fixing agents, but then it quickly becomes apparent that to assess the true deposition of gases, the addition of chemical fixing agents is

undesirable since desorption of gases from runoff water may be quite typical. Thus it can be seen that the study of wet removal of gases must give consideration to simultaneous dry deposition and chemical reactions within the ground water. This is considered now and later a few comments will be made attempting to unify the discussion of both wet and dry removal of gases.

2. DRY TRANSPORT OF GASES THROUGH THE ATMOSPHERE

In the case of wet deposition, one usually ignores the transport of the pollution through the atmosphere since obviously the pollution is transported by the precipitation. Further comments on this will be made later in the section dealing with macroscale processes. However, in the case of dry deposition it is essential to evaluate transport through the atmosphere by diffusion since sometimes this can be the rate-limiting stage of the entire dry deposition process. For example, for pollution released from a tall stack on a very stable day, the pollution may not reach the earth's surface for more than 100 km. As interesting as this aspect of the problem is, here it will be ignored. It will be assumed that through the use of some diffusion formula (e.g., Slade, 1968) the near-surface-level air concentration of the pollution (gas or particles) is known. We now address the question: given the pollutant's concentration near the surface collectors (i.e., in the usually, well-mixed, turbulent boundary layer) what is the dry flux to the collectors?

As in the case of wet deposition of gases, the dry deposition flux of gases is usually dictated by the chemistry of dissolution rather than by physical processes in the atmosphere. To see this we review here Chamberlain's (1966) estimate of the flux which the atmosphere can deliver to the surface. It is convenient to write this flux as proportional to the ground-level (or 2 m) air concentration χ_o; the proportionality constant is known as the deposition velocity, v_d. An upper bound (maximum possible value) for v_d is found from an analogy with the momentum flux to the surface, i.e., τ, also written as ρu_*^2 where u_* is known as the friction velocity. The "concentration" of momentum at the 2m height is $\rho \bar{u}_{2m}$. Then a "deposition velocity" for momentum can be written as $\rho u_*^2/(\rho \bar{u}_{2m}) = u_*^2/\bar{u}_{2m}$. Invoking Reynold's analogy, which is strictly appropriate only for smooth surfaces since there is no mass transfer analogy to form (or pressure) drag, we obtain an upper bound for the deposition velocity for a completely-absorbed gas,

$$v_d = u_*^2/\bar{u}_{2m} \tag{29}$$

Typically, with $u_* = 25$ cm sec^{-1} and $\bar{u}_{2m} = 1$ m sec^{-1}, then $u_*^2/\bar{u}_{2m} = 5$ cm sec^{-1}. Actually, since $\bar{u}$ depends linearly on u_* (or v.v.) and both u_* and the roughness height are not nearly so convenient parameters as $\bar{u}$, it is more convenient and may be sufficiently accurate to approximate (29) by

$$v_d = 5 \text{ cm sec}^{-1} \; [\bar{u}_{2m}/1 \text{ m sec}^{-1}]. \tag{30}$$

3. RATE LIMITING PROCESSES FOR BOTH DRY AND WET DEPOSITION OF GASES

Experimental results indicate that the above deposition velocity is rarely attained except for very reactive gases such as I_2. For most gases the flux to the ground or to vegetation is rate-limited by the conversion of the gas to a less volatile compound, by diffusion into the ground water or the ground water's motion, or by passage of the gas through plant membranes. An extreme example of non-atmospheric rate limitation is for the noble gases whose deposition velocity is essentially zero. In the case of gas deposition to lakes or oceans then for reasonably reactive gases, the atmosphere may be rate-limiting since mixing in the water body may promote transfer in the sink. Liss and Slater's (1975) estimates lead them to conclude that the transport to the ocean of SO_2, NH_3, NO_2, SO_3, HCl are limited by atmospheric transport, whereas even to the ocean, the transport of gases such as N_2O, CO, CH_4, CCl_4, CCl_3F, MeI and $(Me)_2S$ are rate-limited by transport in the ocean.

A simple model for dry deposition of gases to a stationary water body (a simulation for soil moisture) may assist toward quantifying the above qualitative comments. With obvious approximations and assumptions, the problem is to solve

$$\frac{\partial \chi}{\partial t} = K \frac{\partial^2 \chi}{\partial z^2} \quad , \qquad \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - kc \; ,$$

$$K \left.\frac{\partial \chi}{\partial z}\right|_{z=0} = D \left.\frac{\partial c}{\partial z}\right|_{z=0} \quad , \qquad c(0,t) = H_0 \chi(0,t) \tag{31}$$

where k is the rate at which the dissolved gas is irreversibly converted to a nonvolatile product and H_o is the overall partion coefficient, the ratio of the total gas in solution (including any ionized component) to the equilibrium air concentration (Postma, 1970). If the initial conditions are $\chi(z,o) = \chi_o$, $c(z,o) = o$ then the solution to the set of equations (31) can be easily found using Laplace transform techniques and yields

$$\frac{v_d}{(K/\pi t)^{1/2}} = \frac{\beta^{1/2} e^{-\kappa} - 1}{\beta - 1} + \frac{\beta(\pi\kappa)^{1/2}}{(\beta - 1)^{3/2}} \exp\{\kappa/(\beta - 1)\}$$

$$\cdot [\mathrm{erf}(\frac{\beta\kappa}{\beta - 1})^{1/2} - \mathrm{erf}(\frac{\kappa}{\beta - 1})^{1/2}] \qquad (32)$$

where $\kappa = kt$ and $\beta = K/(H_o^2 D)$. For $\beta = 1$ the rhs of (32) reduces to $[1 - \{1 - \exp(-\kappa)\}/(2\kappa)]$. For $\beta < 1$, (32) can be written in terms of Dawson's integral. Equation (32) is plotted in Figure 11 and

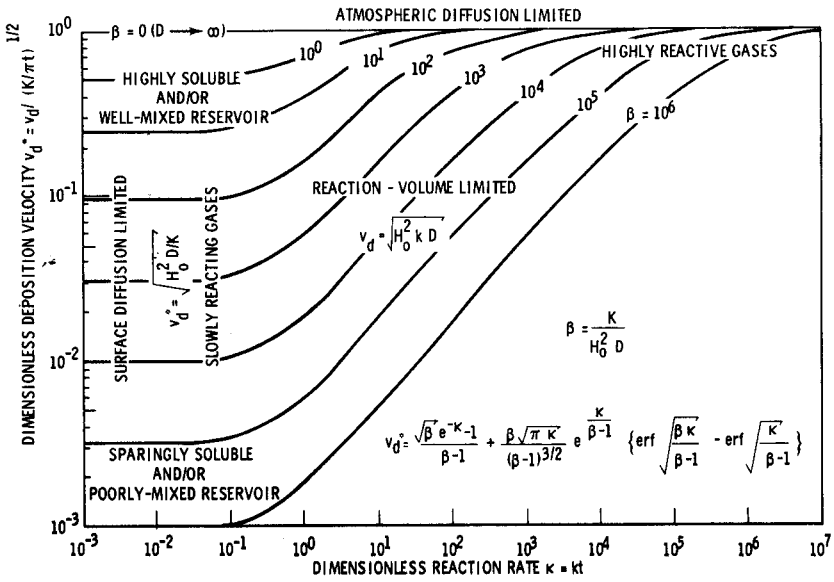


Figure 11. A plot of Eq. (32) which demonstrates that the dry deposition velocity for gases is frequently dictated by other than atmospheric phenomena.

demonstrates that dry deposition can be rate-limited by slow mixing in the ground water, low solubility, or slow reaction rate. The plot of (32) shown in Figure 12 suggests that the model may have some merit for the interpretation of dry deposition to vegetation.

In summary then, both for dry and wet deposition of gases, atmospheric considerations are usually of secondary importance. The atmosphere can deliver a flux of pollutant gas of about (5 cm sec^{-1}) ($\bar{u}$/1m sec^{-1}) χ_o, dry, and a flux of about $H_o \chi_o p$, wet, where p is the precipitation rate. If the sink will not accept this flux then the

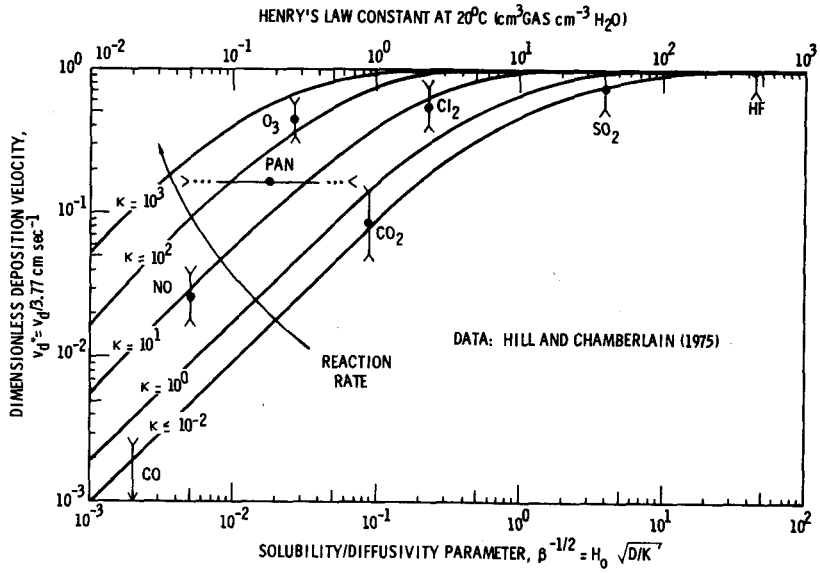


Figure 12. A second plot of Eq. (32), in this case with $\beta^{-1/2}$ on the lower abscissa and the reaction rate as a parameter. For a given diffusivity in the sink, D, and atmospheric diffusivity, K, then $\beta^{-1/2}$ is a constant multiplied by the overall partion coefficient, H_o, which in turn is proportional to the Henry's law constant. Consequently, by conveniently shifting the upper abscissa and normalizing the deposition velocities as measured by Hill and Chamberlain (1975) by their measured value for HF, it can be seen that the theory is capable of reflecting the measured data for the dry deposition of gases to alfalfa. The error bars on the data are subjectively estimated by the author.

process is rate-limited elsewhere than in the atmosphere, and it is therefore not an atmospheric problem. In this case the author must acknowledge his incompetence and leave the problem to soil scientists, biologists, etc., to unravel the complicated chemistry.

C. DRY DEPOSITION OF PARTICLES

Dry deposition of particles is somewhat simpler than gases because atmospheric transport is almost always rate-limiting. In addition, it is usually correct to assume that particles are not re-entrained into the atmosphere, unless the wind speeds are high as in a dust storm (Slinn, 1975c). Nevertheless the problem is complicated. Here results

will first be given for dry deposition of particles to a smooth surface, not because it is very significant to the practical problems of interest at this meeting, but because it is simpler and introduces fundamental concepts. Then a model for dry deposition to a canopy will be presented.

1. PARTICLE DEPOSITION ON A SMOOTH SURFACE

A new theory for dry deposition of particles from a turbulent fluid to a smooth surface was recently presented by the author (Slinn, 1975c); here it will only be outlined. This model rejects the "free-flight" model of Friedlander and Johnstone (1957) and its variations (e.g., Chamberlain, 1960; Davies, 1966) and instead develops Owens' (1969) suggestion that the particles finally reach the surface, convected by bursts of turbulence. Then the collection of particles by a surface depends on a collection efficiency similar to the collection efficiency for particles in a viscous jet impactor. From this picture and the definition of the deposition velocity as the flux to the surface divided by the (assumed constant) free-stream air concentration, one obtains the deposition velocity

$$v_d = v_s + 10^3 \frac{cm}{sec}\left(\frac{\dot{m}''}{1\ g\ cm^{-2}sec^{-1}}\right) + \frac{u_*^2}{\beta \bar{u}} E_j \qquad (33)$$

where v_s is the particle's settling velocity and the author suggests for the collection efficiency

$$E_j = 10^{-3/St} + \frac{\beta}{\gamma}(Sc)^{-0.6} \qquad (34)$$

in which $St = \tau u_*^2/\nu$ is the particle's Stokes number based on the characteristic velocity u_* and the viscous length scale ν/u_*. In (33), β and γ are empirical constants. The second term on the rhs of (33) accounts for a diffusiophoretic contribution to v_d (thermophoresis is usually negligible): $\dot{m}''$ (>o for condensation) is the water vapor mass flux.

Equation (33) is plotted in Figure 13, using $\beta = \gamma = 0.4$, and compared with some experimental data. For a polydisperse aerosol and contaminant distributed among the particles according to $ca^j n(a)$, then the contaminant flux is, of course, obtained by integrating (33), weighted by $a^j n(a)$, over all particle sizes. It would almost always be consistent with the accuracy of the model to approximate the resulting integral just by evaluating (33) at the particle size a_j given in (21). It might also be useful to mention that if u_* exceeds the threshold velocity shown in Figure 14, then even if the "sandblasting effect" of other particles is ignored (Slinn, 1975c), particles can be resuspended from the surface.

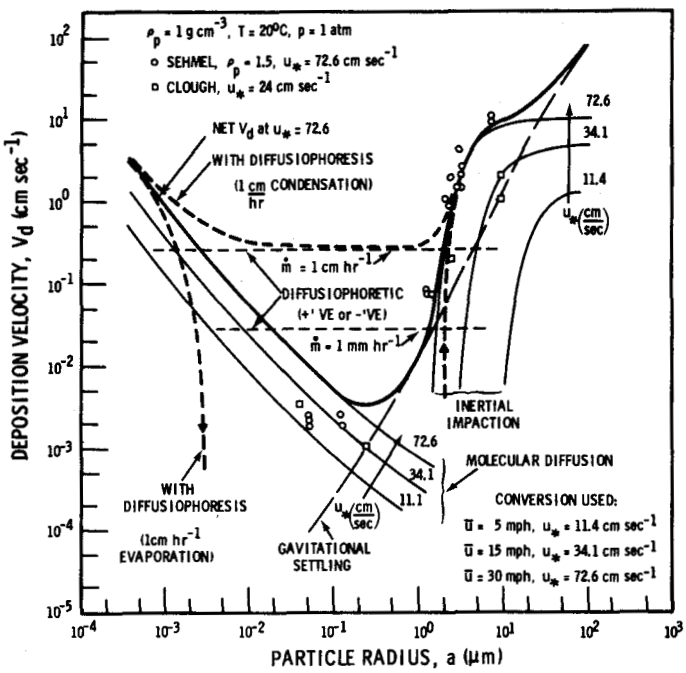


Figure 13. The deposition velocity as given by Eq. (33) with $\beta=\gamma= 0.4$ compared with experimental data. Notice that (33) is evaluated using a particle density, ρ_p = 1 g cm^{-3} whereas Sehmel's (1973) data is for particles with ρ_p = 1.5 g cm^{-3}. The water vapor mass flux $\dot{m}''$ has been divided by the density of water to give $\dot{m}$.

2. PARTICLE DEPOSITION IN A CANOPY

An outline of a new theory for dry deposition in a canopy, which emphasizes the canopy's filtration effect was given in Slinn (1975c). Here further details are developed. Figure 15 shows the assumed fluxes. From this picture there results the obvious steady-state continuity equation

$$\frac{\partial \chi_c}{\partial \chi} + \frac{(\alpha u_* + CH)}{\bar{u}_c H}\chi_c = (\alpha u_* - \frac{u_* E_j}{\bar{u}_g \beta})\chi_B \qquad (35)$$

where C is the fraction of the a-particles filtered out per second by the canopy. If χ_B is a constant then (35) predicts an x- independent solution in a distance $O[\bar{u}H/(\alpha u_*+CH)]$ which is typically about 10 canopy heights. Then for x- independent conditions, (35) can easily be

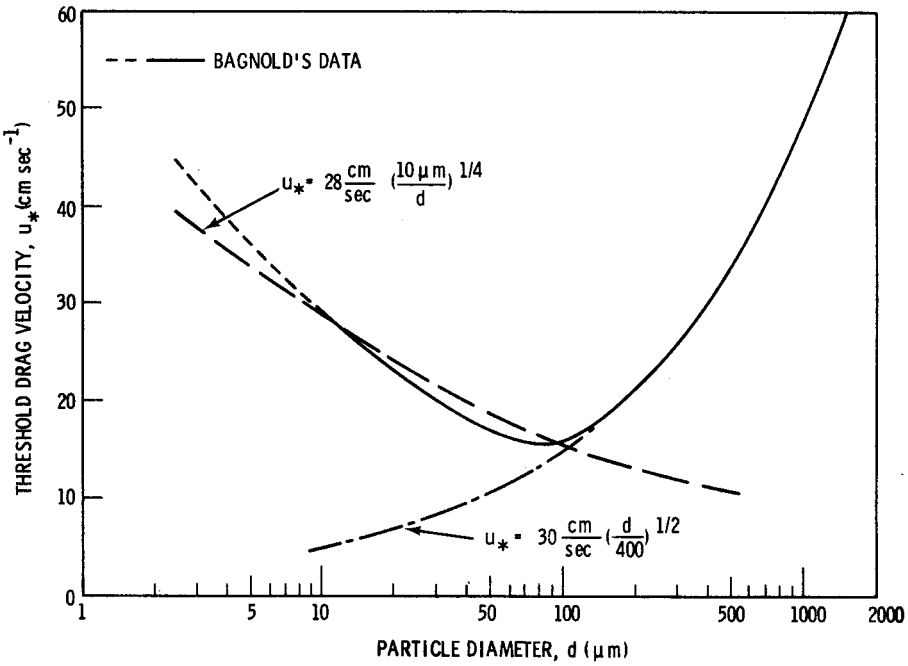
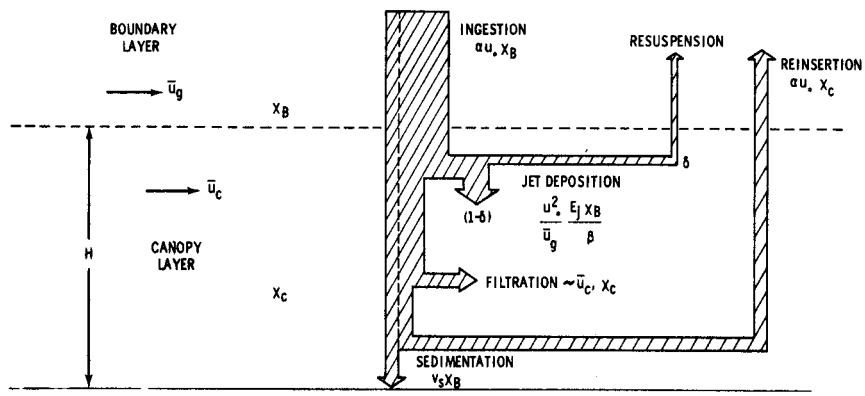


Figure 14. The critical friction velocity required to move monodisperse aerosol particles along a flat plate as measured by Bagnold (1960) and as fit with a semi-empirical theory (Slinn, 1975c). It should be noted that for a polydisperse aerosol, once some particles are set in motion then a sandblast effect occurs, moving many.



DRY FLUXES OF POLLUTION IN A CANOPY

Figure 15. Assumed pollutant fluxes in a canopy.

solved to give χ_c in terms of χ_B. From this result, the deposition velocity, the net flux to the canopy divided by χ_B, becomes

$$v_d = v_s - \frac{\delta u_*^2 E_j}{\bar{u}_g \beta} + \frac{\alpha u_*}{\alpha u_* + CH}\left[CH + \frac{u_*^2 E_j}{\bar{u}_g \beta}\right] \tag{36}$$

This is essentially the same result as given in the earlier report (Slinn, 1975c).

Here some new results will be presented concerned with the canopies filtration efficiency. The amount of contaminant removed during dt by a single collector of cross-sectional area normal to the wind equal to A is $\bar{u}_c$ dt $A\mathbb{E}\chi_c$ where $\mathbb{E}$ is the collection efficiency. If the number of collectors, per unit volume, of cross-sectional area A to A+dA is N(A)dA then the total removal per unit volume during dt is

$$C\chi_c dt = \chi_c \int_{\substack{\text{all} \\ \text{collectors}}} \mathbb{E}\,\bar{u}_c dt \;\; AN(A)\; dA. \tag{37}$$

This integral would obviously be extremely difficult to evaluate for real canopies. Here it will be approximated as were the similar integrals in the precipitation scavenging problem. For vegetative canopies it is noted that the total biomass per unit volume is essentially

$$B = \bar{\rho} \int_{\substack{\text{all} \\ \text{collectors}}} \lambda AN(A)\; dA \tag{38}$$

where $\bar{\rho}$ is an average mass density of the foliage and λ is a typical length scale (e.g., radius) of individual fibers. $B/\bar{\rho}$ might be called a packing density. Upon comparing (37) and (38) it is suggested that the removal rate be approximated by

$$C = \frac{\bar{u}_c B}{\lambda \bar{\rho}}\,\mathbb{E}(a,\lambda) \tag{39}$$

which is to be used in (36).

Equation (36) with (39) is plotted in Figure 16 for the case of the parameters shown. The canopies filtration effect is governed by the parameter $\gamma = HB/\lambda\bar{\rho}$. To evaluate (39) the collection efficiency $\mathbb{E}$ was taken to be the same as for snowflakes, with the characteristic length scale λ = 1mm (see Figure 4). The rationale for the choice to use this collection efficiency is governed by two considerations. One is that the physical processes governing the collection in both cases (viz., Brownian diffusion, interception, inertial capture, etc.) are

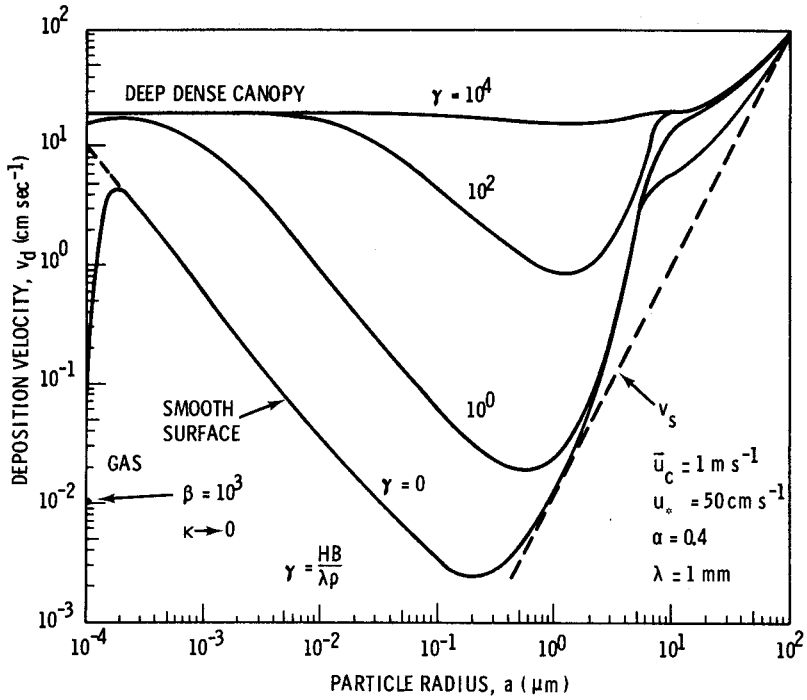


Figure 16. A plot of Eq. (36) with the removal rate given by (39), demonstrating a significant increase in deposition velocity for particles smaller than about 10 μm, with increases in canopy height, H or biomass, B. There is a similar increase of v_d with increasing wind speed within the canopy, $\bar{u}_c$. The increase in v_d with decreasing characteristic dimension of the collectors, λ, is even more dramatic because of the concomittant increase in the collection efficiency. At the left-hand side of the plot is qualitatively indicated the possible reduction in v_d for gases because of non-atmospheric effects. This reduction can be significantly less in a canopy (compare the dashed and solid portions of the $\gamma = 10^0$ curve) because of the increased collector area.

the same and therefore the collection efficiencies will be similar. The second consideration is that although the analogy almost certainly fails in detail, the general accuracy of the predictions are so crude as to tolerate inaccuracies in the specification of Ξ.

There is not yet available sufficient data to test (36) and to evaluate the parameters α, β, γ and δ. Nevertheless it can easily be

seen from (36) and (39) that the theory is consistent with the following experimental results:

- a linear increase and then saturation of v_d with $\bar{u}_c$ and H (Hill and Chamberlain, 1975).
- an increase of v_d with roughness height (Sehmel, 1975).
- an increase of v_d with biomass (Heinemann, et al., 1975).
- the reduction in v_d caused by resuspension (Chamberlain, 1967; Slinn, 1975c).

To account for the observed variations (Heinemann, et al., 1975) of v_d for gases as a function of humidity and biological activity (e.g., stomata openings), a reintroduction of the surface, rate-limiting arguments is needed. Such considerations lead to the reduction in v_d for gases, qualitatively as shown in Figure 16, using the results given in Figure 11 for the β of (32) equal to 10^3 and for $\kappa = 0$.

D. SOME APPLICATIONS

In this closing section use of the formulae given above for wet and dry deposition will be illustrated by applying them to two questions which are of current interest: What is the relative importance of wet and dry deposition? What sources contribute to pollutant deposition in a specific location? It might be noticed that these two questions generally deal with larger space and time scales then the "microphysical" scales with which this paper has so far been concerned; consequently a few remarks will be made about "macroscale" deposition processes. First, though, a few comments on philosophy of approach may be appropriate.

It is clear that the total problem of relating air pollution sources to resulting effects is extremely complex. Some links in the chain are: source characteristics, Q; pollutant transport and diffusion, P; chemical and physical transformations, T; wet and dry removal fluxes, F; resulting air concentrations, χ; fluxes to receptors, F; and details of various types of effects, E. It is noted that in this chain, Q-P-T-F-χ-F-E, wet and dry removal fluxes, F, enter in two places, and it might have been surmised from the previous sections where it was generally assumed that χ was known, that the focus here would be on the sub-chain χ-F-E. It will not be, although of course the formulae can be applied to this sub-chain. Of main concern here will be accounting for wet and dry removal processes so that sources, Q, can be related to resulting air concentrations, χ.

The reason for this emphasis follows from the practical viewpoint that the primary goal is to relate sources to effects (or damages). In most cases (the nuclear accident case may be an exception) evaluating the fluxes in the sub-chain χ-F-E is practically superfluous (although scientifically interesting) because effects can be correlated directly with air concentrations. On the other hand it at present appears to be extremely important to develop predictive formulae for the wet and dry removal link to predict the air concentration resulting from sources at large ($\gtrsim$ 100 km) distances. At shorter distances, evaluating the fluxes is of less significance because at this scale not only can effects be correlated with air concentrations, in many cases (e.g., in the neighborhood of the SO_2 sources at Sudbury) the effects can be correlated directly with the source strengths. Thus on the local scale ($\lesssim$ 100 km) it appears, from a practical viewpoint, that none of the links in the chain linking Q to E, viz. P-T-F-χ-F are of much significance. But, again, it appears to be imperative at the present time to devote substantial effort to evaluating the removal fluxes link in the long-range problem; otherwise we will not be able to respond to practical questions such as: what additional damages will be incurred, for example in New England forests, caused by the proposed 200 new coal-fired power plants to be constructed in the U. S. during the next decade?

1. SOME COMMENTS ON MACROSCALE ASPECTS OF REMOVAL PROCESSES

In the earlier sections of this report the emphasis was on microscale aspects of the removal processes. Above it was emphasized that large scale aspects appear to be more important from a practical viewpoint. Here some comments will be made about applying the formulae developed to larger space scales and it will be seen that some simplifications are possible.

Consider first precipitation scavenging. A qualitative indication of the deposition pattern for pollution from a specific source as a hypothetical stable warm front passes is shown in Figure 17. Similar sketches can be drawn for scavenging by other storm systems. Interestingly, a cold front will invert the lobes of deposition patterns, as can easily be checked from a simple sketch. From such sketches and the realization that the removal rates for most real pollutants by typical storms is $O(1\ hr^{-1})$, i.e., in a distance of less than 100 km, it can be concluded that even the scale of individual frontal storms is still too small if we are to relate sources to the effects occurring at great distances.

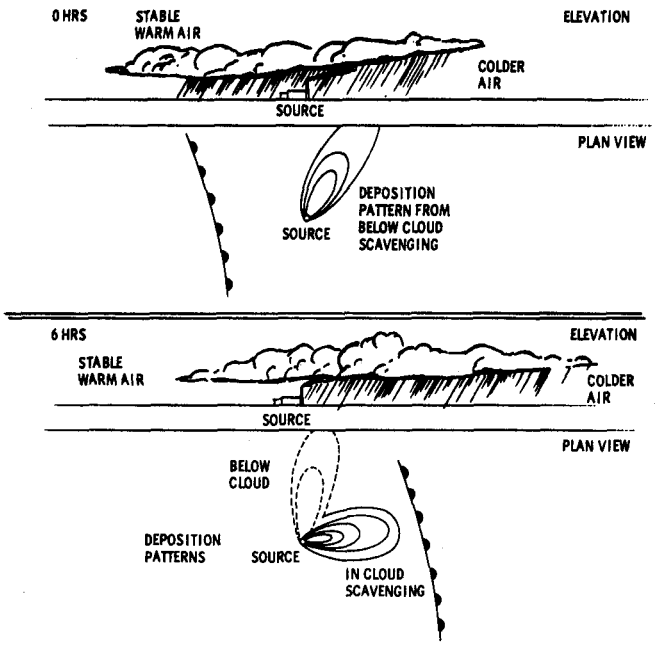


Figure 17. A qualitative plot of a pollutant's wet deposition pattern as a hypothetical, stable warm front passes a pollution source. Similar sketches can be easily made for other storm systems and lead to some interesting differences in deposition patterns. The main point to notice, however, is that the deposition pattern is typically local to the specific source (typically within ∿100 km).

The magnitudes of the time and space scales of interest in the long range wet deposition problem are derived here from the following considerations:

(a) For the large-scale problem, most wet removal of industrial pollutants occurs by in-cloud scavenging;

(b) In-cloud scavenging typically removes 10-90% of the pollutant ingested by the storm, depending on the efficiency with which the storm removes cloud water;

(c) The long range wet removal space scale is dictated by the distance over which the material is transported, between its encounters with storms which efficiently remove their precipitation.

Consequently, for the large (synoptic and greater) space scale and to a first approximation, precipitation scavenging can be viewed as a Poisson process in time: corresponding to the Poisson random selection of points in a time interval, there is the "random" occurrence of precipitation events, say with average frequency $\bar{\nu}$, each of which removes ingested pollution, say with average efficiency, $\bar{\varepsilon}$. In this way, the statistics of scavenging events reduces to a study of the statistics of rain events and the variability of ε. Some details will be given in a later subsection, but it is already clear from knowledge of the Poisson process that the average (e-fold) residence time of pollution removed with average efficiency $\bar{\varepsilon}$ is of the order of $(\overline{\varepsilon\nu})^{-1}$. The corresponding space scale is of the order of $\bar{u}(\overline{\varepsilon\nu})^{-1}$ where $\bar{u}$ is a representative wind speed between efficient storm events.

For the analysis of large space scale dry deposition, a major reorientation of concepts is not needed: The formulae developed earlier in this paper can be used although some consideration should be given to physical and chemical changes of the pollution as it is transported, and to estimating typical values for canopy heights, biomass, etc. Indeed, not only can the previous results be used with little change, but it is relatively easy to carry the analysis further and thereby estimate the ground level air concentration. This will be done later by assuming that for space scales larger than about 100 km, the pollution is well-mixed in the lowest layer of the atmosphere. We turn to some of these details now in our response to the two rhetorical questions asked earlier.

2. THE RELATIVE IMPORTANCE OF WET AND DRY DEPOSITION

Whether wet or dry deposition is more important depends sensitively on the distance from the source, the pollution type and its initial release height. For example, it is quite incorrect to generalize to all pollutants the results for stratospheric bomb debris that typically 90% is deposited wet, the remaining, dry because in this case the debris enters the troposphere from above, frequently during intense storm systems, and therefore in-cloud scavenging can be expected to be substantially more effective than dry deposition. In contrast, near a specific ground level source in an arid region it is relatively simple to demonstrate that dry deposition can predominate (Slinn, 1975b). Here some estimates are given for the relative magnitudes of pollutant wet and dry deposition from the atmosphere's mixed layer to a forest in the northeastern United States.

To make these estimates consider first the case of small (e.g., $SO_4^{=}$) particles. For such particles their gravitational settling speed can be ignored as, indeed, can the settling of most particles for the large scale problem. From previous sections and from data it can be assumed that a typical deposition velocity for such particles to a forest, and averaged over a long time period, is $0.3 \lesssim V_d \lesssim 3$ cm sec^{-1}.

The flux is approximated by $v_d\bar{\chi}$ where $\bar{\chi}$ is a representative value for the pollutant's air concentration. A similar crude estimate for the wet deposition flux can be found using the washout concentration ratios developed earlier. From the theory and data it can be estimated that the wet flux is 10^5 to 10^6 multiplied by $p\bar{\chi}$ where p is the precipitation rate. Using these values, multiplying by the time during which they operate, and recalling that the total rainfall in the area is about 100 cm yr^{-1}, then we have that the ratio of dry to wet deposition is

$$\frac{D}{W} \sim \frac{(0.3 - 3 \text{ cm sec}^{-1})(3 \times 10^7 \text{ sec yr}^{-1})}{(10^5 - 10^6)(100 \text{ cm yr}^{-1})} \sim O(1). \qquad (40)$$

That is, to within an order of magnitude, wet and dry deposition of $SO_4^=$ particles are of comparable importance. Similar estimates are valid for gases such as SO_2. Because of this it should be emphasized that in the title of this meeting the word "precipitation" is not restricted to what the weatherman talks about; here "precipitation" should mean "deposition", both wet and dry.

3. SOURCES CONTRIBUTING TO DEPOSITION

The other topic to be briefly addressed here is to estimate the spaces scales over which pollutants such as $SO_4^=$ are transported. For the case of dry deposition of a pollutant whose average concentration in the mixed layer (of height $\bar{h}$ and mean wind speed $\bar{u}$) is $\bar{\chi}$, the governing steady-state continuity equation (ignoring horizontal diffusion) is

$$\bar{u}\bar{h} \frac{\partial \bar{\chi}}{\partial x} = -v_d \bar{\chi} . \qquad (41)$$

Therefore the e-fold dry deposition length scale is $\lambda_d = \bar{u}\,\bar{h}/v_d$. This can predict substantially different numerical values. For example, over a forest in winter, if $\bar{u}$ = 5 m sec^{-1}, $\bar{h}$ = 200 m and v_d = 1 cm sec^{-1}, then $\lambda_d \sim 10^2$km. In contrast, say for 0.1 μm particles over water during a well-mixed summer day, with $\bar{u}$ = 5 m sec^{-1}, $\bar{h}$ = 2 km and v_d = 0.1 cm sec^{-1}, then $\lambda_d \simeq 10^4$ km. Consequently, depending on meteorological and other factors, $10^2 \lesssim \lambda_d \lesssim 10^4$ km and thus sources which are of the order of 10^4 km upwind can contribute to the dry deposition of pollution in a specific forest.

Now consider the wet removal space scale. As was indicated earlier, it is usually not profitable to pursue a washout model leading to an expression such as

$$\bar{u} \frac{\partial \chi}{\partial x} = - \langle \psi \rangle \chi \qquad (42)$$

which leads to an e-fold length of 10 to 100 km, because (42) is, at best, applicable only when there is precipitation. Instead, the appropriate large space scale for wet removal is related to the distances

over which the pollutant is transported between efficient storm events. From statistics presented by Huff (1971), it is noted that 67% of the storms in east central Illinois, during the period 1955-1964, lasted for less than 1 day, and for the 50-year period 1906 - 1955, 63% of the total precipitation occurred at a rate of 0.1 to 1 inch per day. Then roughly, if these two statistics are incorporated with a typical annual precipitation of 40 inches per year, we obtain that on the average, an efficient ($\sim$ 0.5" precipitation) storm occurs once in every 4.5 days, ignoring any seasonal variation. If this result is typical for the region, and if the average pollutant removal efficiency, $\bar{\varepsilon}$, is in the range $0.1 \lesssim \bar{\varepsilon} \lesssim 1$, then for $\bar{\nu} \gtrsim (5\ d)^{-1}$ and $\bar{u} \gtrsim 5\ m\ sec^{-1}$, the wet removal space scale, λ_w, is typically in the range $10^3 \lesssim \lambda_w = \bar{u}(\overline{\varepsilon\nu})^{-1} \lesssim 10^4$ km. Thus $\lambda_w \gtrsim \lambda_d$, which is consistent with (40); that is, wet and dry deposition are typically of comparable importance.

From these results, it is seen that both wet and dry removal length scales can be crudely estimated to be 10^2 - 10^4 km, and that more exact estimates can be made for specific pollutants and weather conditions. Incidentally, this range of length scales is suggested both for $SO_4^=$ particles and SO_2 gas. In the latter case there is the question of its rate of conversion to $SO_4^=$ but in this regard we note that few estimates of this rate would suggest the space scale is greater than 10^4 km and that the conversion can be accelerated within a storm or at the earth's surface. From these estimates arises a strong argument against the "tall-stack solution" to the pollution problem. It is a "solution" only if one lives in a small country or if, say, the 200 new coal-fired power plants to be constructed in the U.S. during the next decade are distributed, for example: 100 near Cape Cod and the other 100 near Cape Hatteras--and the load is shunted between the two centers, depending on which site has westerly winds!

CONCLUSIONS

In this report a number of semi-empirical expressions have been suggested which can be used to estimate wet and dry removal of particles and gases from the atmosphere. The formulae are semi-empirical in that their forms have theoretical bases but free parameters have been chosen to fit experimental data. By reviewing these formulae it can be seen that new data would be most helpful in the following areas:

- The collection efficiency for drops and 0.1-1.0 μm, monodisperse particles;

- The collection efficiency for snowflakes and particles of essentially all sizes;

- The rate of growth of real pollutant particles within plumes, caused by water vapor condensation;

• Rainout and snowout data unbiased by simultaneous dry deposition;

• In-cloud scavenging of particles ingested naturally into large-scale (frontal) storm systems;

• Solubility and reaction rates for gases at low concentrations in polluted rainwater and in soil water;

• The dependence of dry deposition in canopies on canopy height, biomass, wind speed, humidity and type of foliage.

The author expects that most of the formulae presented are capable of predictions to within an order of magnitude and in some instances, to within a factor of 2 or 3. It is noted for future studies, however, that pursuing accuracy to within a factor of 2 is of questionable value since rarely could the pollutant's air concentration be predicted to within this accuracy.

Many applications of the formulae presented could be described, especially for deposition in the neighborhood of specific sources. However, the author believes that the most important applications are to larger space scales and of those considered here it was concluded that wet and dry deposition of most industrial pollutants are of comparable importance and that the removal space scales for both processes are typically 10^2 - 10^4 km. At such distances it is of course true that diffusion dilutes the contribution from a specific source but as the distribution of sources becomes more diffuse and ubiquitous, diffusion becomes of no significance to the receptor.

ACKNOWLEDGMENTS

This work was supported financially in part by Battelle Institute's Physical Science Project and in part by US ERDA Contract E(45-1)-1830.

APPENDIX

The following is a list of frequently used symbols, their dimensions and, in case of multiple use of a single symbol, the equation number in which the symbol appears.

a = aerosol particle radius, L

B = biomass per unit volume, ML^{-3}

c = $(2/3-S_*)$, Eq. (10)

= concentration of gas in precipitation, units L^{-3}, Eq. (27)

C = canopy removal rate (fraction of a-particles filtered out per second), T^{-1}

D = molecular diffusion coefficient, L^2T^{-1}

$E(a,R)$ = particle/drop collision efficiency

$\mathcal{E}(a,\ell)$ = particle/snowflake collision efficiency

$\mathfrak{E}(a,\ell)$ = particle/canopy-fiber collision efficiency

$E_j(a)$ = jet collection efficiency

h = mixed layer height, L, Eq. (41) or $H_2 - H_1$, L, Eqs. (25) and (26)

H = canopy height, L, Eq. (35)

= Henry's law constant

H_0 = overall partition coefficient

k = reaction rate, T^{-1}

K = atmospheric diffusivity, L^2T^{-1}

$\mathbf{K}$ = second order tensor atmospheric diffusivity, L^2T^{-1}

$n(a)da$ = number of particles per unit volume of radii a to a + da, L^{-3}

$N(R)dR$ = similarly, for raindrops, L^{-3}

p = precipitation rate, LT^{-1}

Pe = RV_t/D = Péclét number

R = raindrop radius, L

R_m = volume-mean drop radius, L

Re = RV_t/ν = Reynolds number

s = $\tau V_t/R$ = Stokes number

s_* = critical Stokes number = $\dfrac{(12/10) + (1/12)\ \ln(1 + Re)}{1 + \ln(1 + Re)}$

Sc = ν/D = Schmidt number

St = $\tau u_*^2/\nu$ = Stokes number in turbulent flow

$\bar{u}$ = mean wind speed, LT^{-1}

$\bar{u}_c$ = mean wind speed in canopy, LT^{-1}

$\bar{u}_g$ = mean wind (geostrophic wind) above canopy, LT^{-1}

u_* = friction velocity, LT^{-1}

v_s = particle settling velocity, LT^{-1}

v_t = drop terminal velocity, LT^{-1}

$\langle v_t \rangle$ = average snowflake terminal velocity, LT^{-1}

V = μ_w / μ_a = ratio of dynamic viscosities, water to air

α = attachment rate, T^{-1}, Eq. (17)

= empirical constant, Eq. (35)

β = $K/(H_0^2 D)$, Eq. (32)

= empirical constant, Eq. (33)

κ = kt, nondimensional reaction rate, Eq. (32)

= concentration of contaminant in precipitation, units L^{-3}, Eq. (25)

= a/R, interception parameter, Eq. (10)

λ = radius of plume- or cloud-drops, L, Eq. (20)

= characteristic length (e.g., radius) of fibers in a canopy, L, Eq. (38)

ν = kinematic viscosity of air, L^2T^{-1}

ψ = removal rate, T^{-1}

$\langle \psi \rangle$ = space-average removal rate, T^{-1}

$\bar{\psi}$ = particle-average removal rate, T^{-1}

ψ_r, ψ_s = rain, snow removal rates, T^{-1}

$\bar{\rho}$ = average mass density of foliage, ML^{-3}

τ = particle relaxation time, T

SUBSCRIPTS

f,g,h = free, growing, hosted

2m = two meter

0 = ground level

t = total

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INVESTIGATION ON EFFECTS OF THE FOREST CANOPY ON ACID AND SULFUR PRECIPITATION IN THE RUHR DISTRICT, GERMANY

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ABSTRACT

Ecosystem analysis as part of the International Biological Program, has shown that a considerable amount of nutrient input comes from the air through the filter action of vegetation. As investigations were carried out in remote areas, it appeared highly desirable to explore the conditions in the Ruhr district, one of the major industrial areas of the world.

Samples were taken every fortnight from rain collected by means of a .5 m^2 gutter. Amount of rainfall and concentration of sulfur and hydrogen ions were determined in the laboratory.

Results show a very clear increase in the concentration of sulfur (S) and hydrogen (H^+) ions under the canopy of stands of beech (Fagus sylavatica L.), oak (Quercus sp.), Scots pine (Pinus sylvestris L.), and Norway spruce (Picea abis Karst), in this order, when compared with rain collected outside the forests above vegetation. This increase cannot be explained by the loss of water through interception in the crown because precipitation of S and H^+ per square meter shows the same trend.

The results are discussed under the aspects of air pollution control and acidification of soils. The improvement of air quality which would be the effect of any filtering action of the vegetation appears positive for industrial regions, whereas the additional input of acids into forest ecosystems may have negative effects on productivity and water quality even at a great distance from the source of emission.

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AEROSOL DEPOSITION ON PLANT LEAVES

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ABSTRACT

An aerosol generator and wind tunnel system designed for use in aerosol deposition is described. Gross deposition on rough pubescent leaves was nearly 7 times greater than on smooth, waxy leaves. Results suggest that aerosol deposition, on a per unit area basis, for single horizontal streamlining leaves is similar to that for arrays of leaves under similar flow conditions. Wind reentrainment of $PbCl_2$ particles was negligible while 2.54 cm of simulated rainfall was sufficient to remove 85 percent of recently applied aerosol.

INTRODUCTION

The primary source of lead in most communities is from the particulate emissions from automobiles. This lead is transported by the atmosphere from the highway and deposited on soil and plant surfaces. In this study we examine the deposition of aerosol particulate on plant leaves as well as its removal via wind reentrainment and rain water washing.

The deposition of aerosol particulate on plant leaves is controlled by characteristics of the aerosol (size, chemical composition, cloud density), the leaf surface (roughness, pubescence, moisture, stickiness), and the environment in which the plant lives (relative humidity, wind speed). Once a toxic aerosol is deposited on a leaf surface it may gain entrance into the interior of the plant and be translocated throughout the plant to cause adverse effects on physiological processes within the plant. It is the possibility of physiological plant damage from lead particulate that formed the

impetus for this study. By being able to accurately predict the extent of particle deposition on plant leaves under various conditions and its subsequent removal by the action of wind or rainfall, an estimation of plant dosage can be ascertained for aerosol particulate.

Since the primary objective in the first part of this investigation was to study the gross deposition of an aerosol on plant leaves in a well-defined flow field and not the resulting physiological response, it was proposed that a uranine aerosol (sodium salt of 3, 4-dehydroxyl-fluoran) be used in place of lead aerosol. The primary reason for this was the ease with which uranine can be quantitatively analyzed as opposed to lead. An initial series of experiments was conducted to demonstrate the validity of this approach. We then compared (1) particle deposition on smooth, waxy leaves with that of rough, pubescent leaves and (2) deposition on single leaves with that on groups or assemblages of leaves. Additional experiments with lead-fumigated plants included (3) wind reentrainment and (4) rain water washing of deposited lead.

EXPERIMENTAL SYSTEM

A 0.929 m^2 steel wind tunnel ≈7.3 m in length was constructed as a transport system for the deposition studies (Wedding and Stukel, In press). Air entering the tunnel is passed through an absolute particle filter (99.99% capture efficiency for particles greater than 0.3 μm diameter) before entering the test section. Monodisperse aerosol particles, produced by a vibrating orifice aerosol generator (Berglund and Liu, 1973; Wedding and Stukel, 1974) are carried into the wind tunnel by a stream of dry, filtered air that is passed through a static eliminator (Po 210 source) to remove excess residual particle charge. Air flow within the wind tunnel is then passed through a stairmand disk (Green and Lane, 1957) to increase mixing and homogeneity of particles in the airstream. Consequently the turbulent scale of the air stream is greatly increased. To reduce the large-scale turbulence, the air is first passed through a flow straightening element (grid of 2.54 cm diameter holes) and then through a series of 0.158 cm mesh (0.045 cm diameter wire) grids spaced 2.54 cm apart (Baines and Peterson, 1951). The turbulence scale is thus reduced to nearly isotropic conditions. This is conducive to obtaining a uniform cloud profile during aerosol experiments. Also, the effects of surface characteristics in aerosol deposition can be best determined in a flow regime of this nature where deposition induced by random large-scale fluid perturbations is held to a minimum. The air stream then enters a 1.22 m long Plexiglass test section equipped with access ports at the top and bottom.

Air flow is induced by a blower on the exit end of the wind tunnel, controlled by a damper on the blower, measured by the pressure drop across a calibrated American Society of Mechanical Engineers-standard

nozzle, and exhausted through a ventilating hood. The contamination of exhaust air is prevented by two absolute particle filters placed in the exit section of the wind tunnel.

Measurements of particle cloud concentration were taken with an isokinetic sampling probe at different locations in the test section. The cloud concentration of 3.02 $\mu g\ m^{-3}$ was uniform throughout the test section (Wedding and Stukel 1974). All leaf deposition experiments were conducted at a wind speed of 268 cm sec^{-1} and an aerosol cloud density of 44.9 $\mu g\ min^{-1}$ for the 0.929 m^2 cross-sectional area of the test section. Fumigation periods varied in length from 10-35 min. Relative humidity and air temperature varied between 55-60% and 24-28°C, respectively.

For the wind reentrainment and rain water washing experiments a fumigation chamber was constructed in which the aerial portions of 10 plants could be uniformly fumigated simultaneously. This chamber was lighted from above with fluorescent lamps to maintain normal plant physiological activity and correct daylength during fumigation periods. Fumigation periods of 15 to 20 hr were necessary to obtain the desired leaf concentration of 500 to 1000 μg lead g^{-1} dry weight. $PbCl_2$ aerosol particulate with a diameter of 1.5 to 3.0 μm was used in these experiments. The wind reentrainment experiments were done in the previously described wind tunnel with horizontal trailing leaves at wind velocities of 2.3, 4.8, and 7.0 m sec^{-1} for 1 hr and the rain water washing with a rain producing module (Chow and Yen, 1974) located at a height of ≃ 3 m above the plants. Rainstorm size was kept constant at 2.54 cm with intensity varying from 2.54 cm hr^{-1} to 10.2 cm hr^{-1}. Runoff was collected at regular intervals throughout each rain treatment and analyzed for lead content.

Uranine was analyzed fluorometrically by washing fumigated leaves (or filter paper from the isokinetic sampling probe) with a known amount of deionized water and measuring the concentration of uranine in the wash water with a calibrated Turner fluorometer. Similar preparations of unfumigated leaves were used as blanks in these determinations. Lead was analyzed by the Heavy Metals Analytical Laboratory at the University of Illinois, Urbana, using standard atomic absorption techniques for the analysis of plant material.

Leaves of sunflower *(Helianthus annuus* L.) and tulip poplar *Liriodendron tulipifera* L.) were used in the gross deposition studies. These species were chosen to be representative of plants with large differences in leaf surface characteristics so as to bound the correlation between surface roughness and deposition. Leaves were either fumigated individually or in groups (leaf assemblages). Single leaves were supported at the petiole in a trailing position, parallel to the air flow in the wind tunnel. Leaf assemblages were constructed by placing the petioles of the leaves into small openings of a "stem" such that the base of the petioles were immersed in water. In this manner, leaf number and leaf area could be varied over a wide range. Leaf area

was determined by planimetering outline tracings of individual leaves with a Lasico Polar Planimeter and expressed as the area of one side for each leaf. By rotating the "stem" during fumigation a reasonable approximation to a tree can be modeled with wind striking the assemblage from all sides. This is not unlike the situation that an isolated tree might experience over time in an urban environment.

For the wind reentrainment and rain water washing experiments, soybean plants (*Glycine max* L.) were used. These were grown from seed for ≈5 weeks to a height of ≈30 cm in a controlled environment room at which time they were used in the experiments.

RESULTS AND DISCUSSION

The first experiment examined the similarity of gross depostion on leaves between particles of Pb and those of uranine dye. While it is known that uranine particles with a diameter of 6.77 μm are aerodynamically equivalent to $PbCl_2$ particles with a diameter of 3.36 μm, it was not clear that the deposition of these two aerosols would be the same under identical conditions. To compare the two aerosols, sunflower leaves were used as the deposition surface. The sunflower leaves were placed horizontally within the test section, such that during fumigation they assumed a stable position in the air stream with very little movement. The results of these experiments (Figure 1) show that the aerosol collected by leaves fumigated with uranine was essentially identical to that of leaves fumigated with $PbCl_2$ particles. This confirmed that fumigation with 6.77 μm diameter particles could be successfully substituted for 3.36 μm diameter $PbCl_2$ particles in at least some aerosol deposition experiments. It should be noted, however, that no conclusions on adverse physiological effects should be drawn from the use of particles with aerodynamically equivalent diameters because the ease of entrance of particles into the leaf is dependent on particle size.

The second experiment was designed to test the hypothesis that differences in leaf surface characteristics play a major role in influencing aerosol deposition. Rough pubescent leaves of sunflower were compared to the glaborous leaves of tulip poplar. Single leaves were positioned horizontally in the test chamber and fumigated with uranine articles. It was believed that this orientation would best discriminate between differences in surface characteristics by the following reason. The particles are transported to the deposition surface primarily by turbulent diffusion and under these flow conditions, if a particle attaches to the surface, it has a high probability of remaining (Wedding and Stukel, In press). Thus, any greater degree of capturing ability exhibited by one species over another would be due essentially to an increased deposition area caused by greater roughness or hairiness. This roughness profile appears most prominently to the particles when the leaf is parallel to the direction of particle trajectory. The

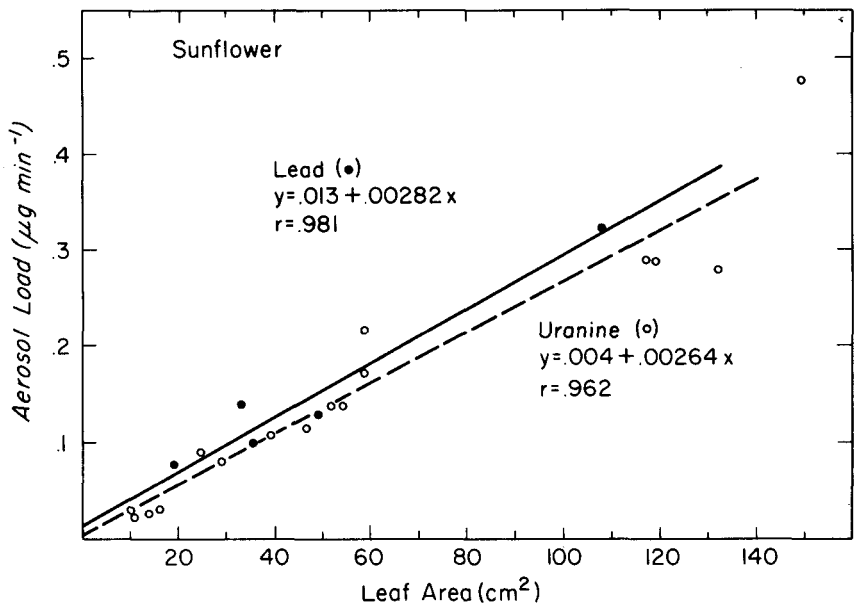

Figure 1. Comparison in aerosol deposition between $PbCl_2$ particles of 3.36 μm and uranine dye particles of 6.77 μm diameter on single streamlining leaves of sunflower. Aerosol load is the amount of particulate on the leaf after 10-35 min of deposition expressed on a per minute basis. Leaf area, determined from outline leaf tracings, is equal to the surface area of one side per leaf.

deposition rate on the pubescent leaves of sunflower was nearly 7 times that of the nonpubescent leaves of tulip poplar. As all other conditions during the fumigation of these two species were the same, it is concluded that the difference in aerosol deposition is due only to differences in leaf surface characteristics. The data appear to conform to a linear relationship as indicated by the regression coefficients.

In the next experiment, the rate of deposition for a group or assemblage of leaves was studied. The results indicate that the deposition rate per unit leaf area for the assemblages was essentially identical to the single trailing leaves--i.e., the rate was linearly related to the total leaf area as shown in Figure 2. The increase in leaf area was achieved by making the "tree" more and more dense or decreasing the effective flow area between the leaves. As deposition by impaction is negligible for this particle size and flow rate, one might expect the rate of deposition to decrease or level off somewhat as the porosity of the tree approached that of a solid object. This was not the case. Also, the random motion of the leaves flapping violently would cause considerably different flow conditions to prevail

than that of the single trailing leaf with little motion. Even though the fluid dynamics are different, the functional form and value of the results are the same.

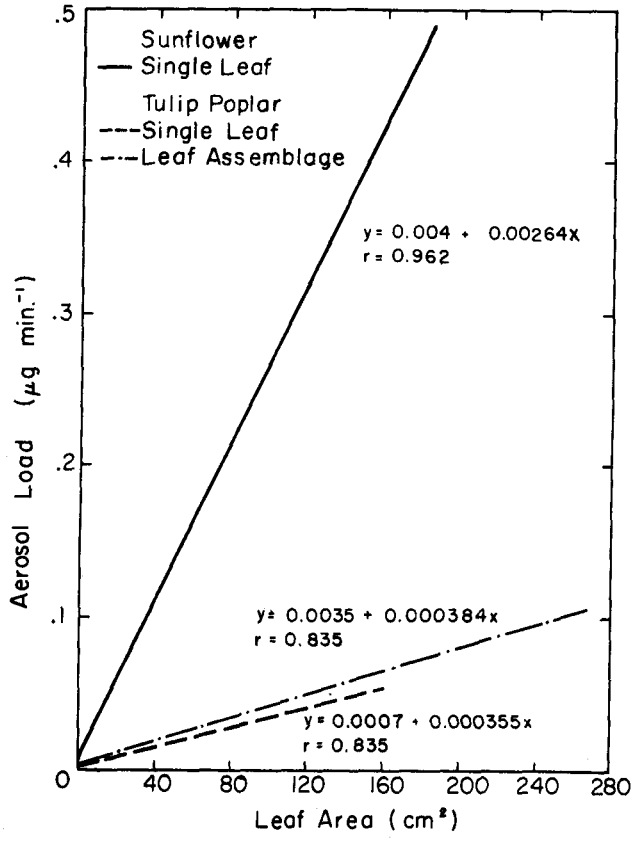

Figure 2. Deposition of uranine dye particles on single leaves and leaf assemblages of tulip poplar compared with single leaves of sunflower. Aerosol load and leaf area are expressed as in Figure 1.

In our experiments there was no wind reentrainment of deposited $PbCl_2$ aerosol particulate. This was true even at a windspeed of 7 m sec^{-1} during which the leaf assumed a fairly violent fluttering action throughout the 1 hr reentrainment treatment. The lack of particulate reentrainment was not unexpected from previous theoretical considerations (Wedding and Stukel, In press).

In the final experiment we examined the effects of simulated rain water washing on removal of deposited $PbCl_2$. We found that (1) 2.54 cm of rain was sufficient to remove 85% of the deposited $PbCl_2$, (2) the

amount washed off was independent of intensity over the range of 2.54 cm hr^{-1} to 10.2 cm hr^{-1}, and (3) no additional $PbCl_2$ could be removed dr during an additional 2.54 cm of rain. These results were obtained for a recently deposited, relatively insoluble aerosol particulate. The washoff of a more soluble particulate such as sulfate may be more complete with less rainfall. However, it is difficult to predict what the rate of washoff might be in the case of a longer particulate residence on leaf surfaces. Surface chemical reactions might take place over time that would make deposited particulate less vulnerable to wash off through greater insolubility, greater adsorption, or absorption into the leaf.

These results suggest that a dose-response curve can be quantitatively determined for plants growing in an environment where the ambient aerosol cloud concentration is known. The apparent simplicity of the relationship between surface area and deposition suggests that mathematical models for aerosol deposition on plant surfaces via the diffusion process are possible. This is a step toward formulation of a quantitative model to assess the potential damage of toxic aerosol particulate on crop yield.

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A portion of this research has been published in ENVIRON. SCI. TECHNOL., 9, 151 (1975). Work supported in part by Grant NSF GI 31605 from the RANN program of the National Science Foundation.

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ACIDITY OF TREE BARK AS A BIOINDICATOR OF FOREST POLLUTION IN SOUTHERN POLAND

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ABSTRACT

pH values and buffering capacity were determined for bark samples of 5 deciduous trees (oak, alder, hornbeam, ash, linden), one shrub (hazel) and one coniferous tree (scots pine) in the Cracow Industrial Region (Southern Poland) and for comparison in the Białowieża Forest (North-Eastern Poland). The correlation was found between acidification of tree bark and air pollution by SO_2 in these areas. All trees showed the least acidic reaction in the control area (Białowieża Forest), more acidic in Niepołomice Forest and the most acidic in the centre of Cracow city. The buffering capacity of the bark against alkali increased with increasing air pollution. The seasonal fluctuations of pH values and buffering capacity were found. Tree bark is recommended as a sensitive and simple indicator of air pollution.

1. INTRODUCTION

Industrial gas emissions, predominantly those of sulphur dioxide, cause acidification of rainfalls with sulphuric acid (Odén 1968). SO_2 is given off into the atmosphere where it is oxidized and hydrated and as a result returns to earth with precipitation in form of sulphurous or sulphuric acid. This in turn causes acidification and sulphuration of the environment including various components of the forest ecosystem. Sensitive bioindicators of chemical changes in the forest environment include many biological materials e.g. pH of tree bark (Skye 1968, Staxäng 1969, Grodzińska 1971). The tree bark represents a material which persists in the ecosystem for exceptionally long periods. Deciduous trees usually have lower bark acidity than coniferous trees (Barkman 1958). Bark acidify is readily affected by air pollution (Skye 1968, Staxäng 1969, Grodzińska 1971, msc.a,b). Tree bark acidity was used as a bioindicator in the Cracow Industrial Region in Southern Poland. Three zones were selected in this area: (1) the centre of Cracow city (700,000 inhibitants); (2) the neighbourhood of the steel

mill and (3) Niepołomice Forest situated 20-40 km to the east from Cracow and the steel mill. Since north western winds prevail in this region (Anioła, Małecki 1967, Hess 1967, 1969) Niepołomice Forest is strongly affected by pollutants from the steel mill and from the city. Niepołomice Forest is a large forest complex (11,000 ha), It consists mainly of scots pine and to a smaller extent of deciduous trees (e.g. oak and hornbeam). The Białowieża Forest, a relatively unpolluted region in north eastern Poland, was used as a reference standard.

2. MATERIALS AND METHODS

Five species of deciduous trees: linden *(Tilia cordata Mill.)*, ash (*Fraxinus excelsior* L.), oak (*Quercus robur* L.), hornbeam (*Carpinus betalus* L.) and alder (*Alnus incana* (L.) Mnch), one deciduous shrub - hazel (*Coryllus avellana* L.), as well as one coniferous species - pine (*Pinus sylvestris* L.) were selected for the investigations. These species are common both in the natural forests and in the city parks.

Bark samples were collected from 170 trees on the average from 5 specimens of a given species in each locality. All the samples were collected in the early spring (March - April 1970 and 1971). The modified Swedish method was used in preparing the samples for analysis and in determining their pH and buffer capacity (Skye 1968, Staxäng 1969, Grodzińska 1971). pH was determined with a pH-meter, type LBS-66, with a glass electrode.

3. RESULTS

The bark of all tree species showed acid reaction (Fig. 1). The lowest values were found for pine bark and the highest ones for ash bark. In all cases, differences in bark acidity between samples could be related to particular localities. The localities form a logical series starting from the less acidic in the unpolluted area of the Białowieża Forest, then through the slightly polluted Niepołomice Forest up to more acidic areas in the neighbourhood of the steel mill and the most acidic one in the centre of Cracow. Bark samples from individual stations differed not only in the pH value per se, but also in buffer capacity (Fig. 2, 3). This capacity increased with concentration of SO_2 in the air. During titration of the oak bark, 2 ml of alkali were required for neutralization of the samples from clean forests of Białowieża, while samples from the centre of Cracow required 5 ml 1 n NaOH. A similar phenomenon was observed during analysis of the barks of linden, ash, hazel and pine. All samples showed greater capacity to buffer against alkali than against acid. Very large

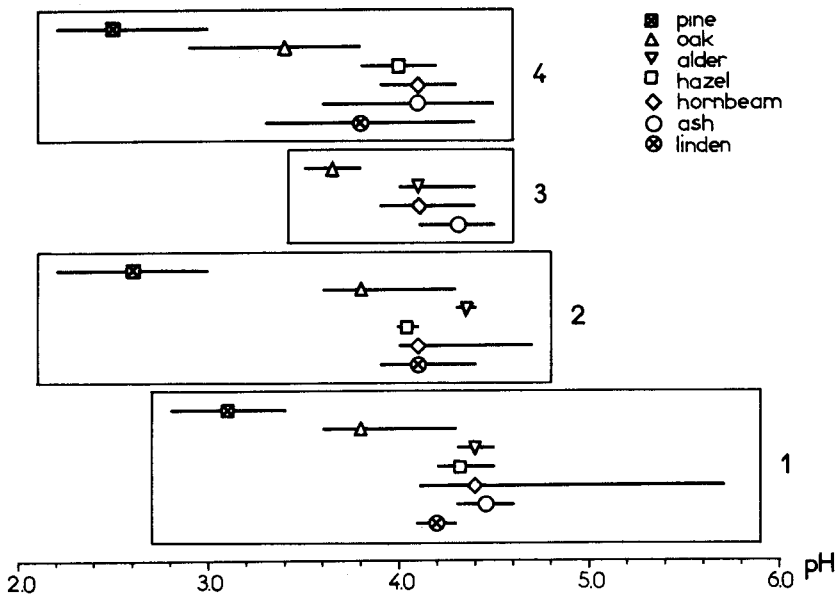

Figure 1. Total range and mean of pH of tree bark sampled from different localities. 1- Białowieża Forest; 2- Niepołomice Forest; 3- neighbourhood of the steel mill; 4- Cracow City.

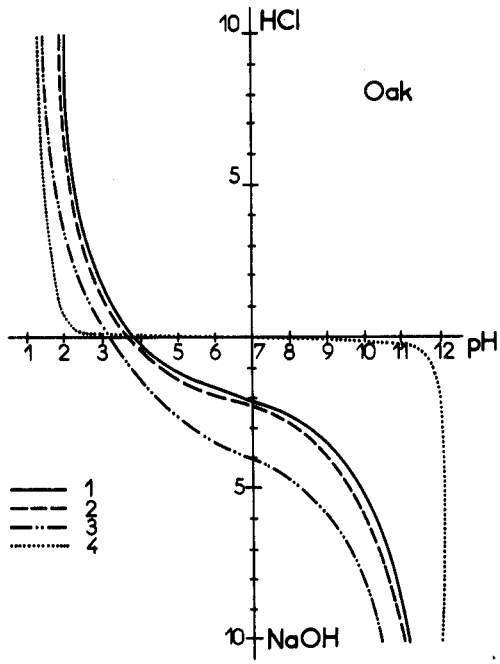

Figure 2. Buffer curves for oak from different localities. 1- Białowieża Forest; 2- Niepołomice Forest; 3- Cracow City; 4- distilled water.

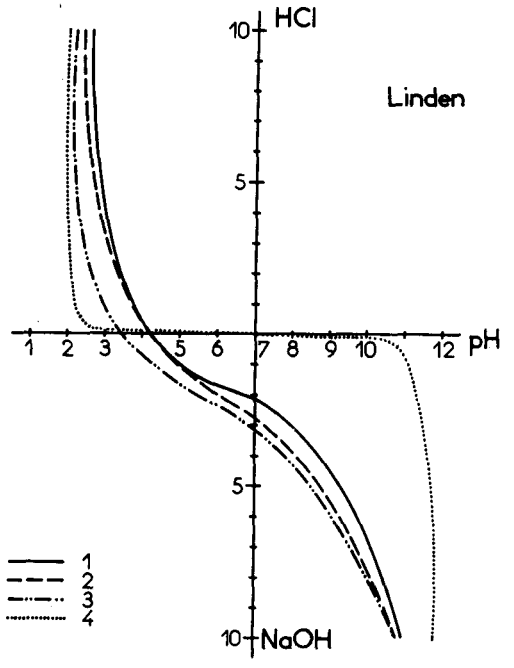

Figure 3. Buffer curves for linden from different localities. 1-4 as in Figure 2.

buffering capacity was found for the oak and linden (Fig. 2, 3).

The pH values of tree bark changed during the year. The most acidic reaction was shown by the bark in early spring, while the least acidic reaction was found in the summer. Maximum differences were found in linden bark (0.61 pH units), slightly less in oak bark (0.35 pH units) and the least in pine bark (0.26 pH units). Buffering capacity also fluctuated during the year. In all tree species, the greatest buffer capacity against alkali was found at early spring. For example, the neutralization of pine bark required 6 ml 1 n NaOH in April but only 4 ml during the summer season. This trend is also clearly evident in the linden and oak bark. The buffering capacity against acid was small in all trees and did not show clear fluctuations during the year. The acidification of tree bark in particular months was correlated with the concentration of SO_2 in the air and rainfall.

4. DISCUSSION

Sulphur dioxide is produced during the burning of fuels containing sulphur. Coal is the chief energy source used for heating homes in the city of Cracow and for steel production. This coal contains 1-3% sulphur. Cracow city emits five times more SO_2 than the processing plant (Anioła, Małecki 1967). For this reason the highest concentrations of SO_2 were recorded in the centre of Cracow, slightly lower in the outer zone of the city and in the neighbourhood of steel mill and the

lowest in the Niepołomice Forest (Kasina 1971, Morawska-Horawska 1971). A good correlation was found between the SO_2 concentration in these areas and the acidity of the tree bark (Grodzińska 1971, msc. a,b).

The SO_2 emissions are subject to seasonal change (Kasina 1970), the largest occuring in wintertime, the smallest in the summer months. Similar changes were observed in tree bark acidity (Grodzińska msc.c). For this reason all samples for the study were collected in early spring i.e. after the winter season during which SO_2 concentration is the highest.

Bark acidity changed with the depth of bark (Härtel, Grill 1972) the external parts of the bark (< 3 mm) being the most acidic. The difference in pH between external and internal layers of bark was especially significant in the strongly polluted areas. For this reason, the external layers of bark should be taken for bioindication studies.

Acidity of oak and scots pine bark was determined in some other regions in Poland (Grodzińska msc. b, Zdanowska msc.). Bark of both species showed less acidic raaction in Copper Centre in south western Poland (Grodzińska msc. b) and in the neighbourhood of the steel mill near Warsow (Zdanowska msc.) than in the Cracow Industrial Region. The observed acidity was correlated with the magnitude of SO_2 emissions in these areas. In all these industrial centres, however, the bark was more acidic than in Białowieża Forest, the control region.

The pH values and buffering capacity of the bark of linden, ash, oak and pine in the Cracow Region are similar to those found in the polluted area of Southern Sweden (Skye 1968, Staxäng 1969), but they are still less acidic than in Stockholm (Skye 1968). On the other hand, tree bark in the Białowieża Forest is more polluted than the bark in some areas of Sweden (Skye 1968, Staxäng 1969). Thus larger differences in the pH values of tree bark are observed in Sweden than in Poland, where bark samples from all localities are relatively acidic. This fact may be explained by the higher acidification of rain and snowfalls in all of Central and Western Europe.(pH 4.5-5.0) in comparison with the Scandinavian countries (pH 4.5-6.0) (Odén 1968).

Both from these and from earlier studies (Skye 1968, Staxäng 1969, Grodzińska 1971) it follows that pH of the bark is a sensitive indicator of air pollution by SO_2. The bark of linden and ash trees being the least acidic and most rough in surface texture is particularly suitable for determination of the degree of air pollution.

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THE EFFECTS OF A HIGH-STACK COAL-BURNING POWER PLANT ON THE RELATIVE pH OF THE SUPERFICIAL BARK OF HARDWOOD TREES

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ABSTRACT

The Allen S. King Generating Plant near Bayport, Minnesota delivers 420 tons of sulfur dioxide to the atmosphere daily from a 789 foot (240 m) stack. Dispersal from this height theoretically minimizes harmful effects of the gases on vegetation. Six years of post-operational pH tests on hardwoods, in the area, show fluctuations in, but no significant increase of the bark acidity. Recorded pH values around the power plant were not significantly different from values obtained in several other localities in Minnesota. None of the pH values in Minnesota were within the ranges shown to be damaging to lichens in Swedish studies. Values for pH ranged from 4 to 9.

INTRODUCTION

In 1968 Northern States Power Company opened the Allen S. King coal-powered generating plant near Bayport, Minnesota on the St. Croix River. At full production about 420 tons of sulfur dioxide are emitted to the atmosphere daily from a 789 foot (240 m) high stack. Dispersal from that height theoretically minimizes harmful effects on vegetation. To check these effects several vegetation studies were implemented using known SO_2-sensitive species such as white pine, *Pinus strobus*, various lichen species and various agricultural crops. Since lichens are sensitive to the ultimate effects of sulfur dioxide, several lichen plots were marked on various trees in the vicinity of the King Plant and in control areas 150 km from the plant. Incidental to the study was the monitoring of bark pH of various hardwood trees to determine if the acidity was in the range damaging to lichens. It is these pH values and others taken for comparison purposes which will be reported in this paper.

DATA COMPARISON

The critical pH for prevention of corticolous lichen growth was determined by Skye (1968). Some of his pH data are given in Table I for seven species of trees in a lichen free zone, a transition zone, and in a control area near Stockholm, Sweden.

	Control Area pH	Transition Zone pH	Lichen Free Zone pH
Acer platanoides	6.2 - 5.1	4.5 - 3.2	3.7 - 2.9
Tilia vulgaris	4.7 - 4.1	3.3 - 2.8	2.9 - 2.4
Ulmus spp	7.1 - 4.7	3.9 - 3.1	2.9 - 2.4
Quercus robur	4.5 - 3.8	3.2 - 2.6	2.8 - 2.4
Fraxinus excelsior	5.9 - 5.4	4.9 - 3.5	3.5 - 2.9
Pinus silvestris	3.4 - 3.1	3.0 - 2.7	2.9 - 2.5
Betula spp	4.5 - 3.3	3.6 - 2.8	4.1 - 2.7

Table I. The lichen free zone is within Stockholm, Sweden, the control area is in the agricultural landscape and the transition zone is in between.

To determine whether damaging ph ranges existed in the King Plant area, bark samples were tested beginning in 1970 and during each year through the early part of 1975. The resulting pH values are given in Table II. Fourteen trees in the vicinity and three control trees between 80 and 150 km from the King Plant are included. Six of the trees increased in bark acidity after the original 1970 sample but two of the six were control-area trees. Ten of the trees from the King Plant vicinity decreased in the acidity when the 1975 samples were compared to the 1970 samples. Acidity in all cases was less than those shown by Skye (1968), Table I, to be critical for prevention of lichen growth.

Several other tests were made to show the range of variation in bark acidity: (1) among different size trees of the same species; (2) among several samples from a single tree; (3) among several species from the same forest stand; (4) among trees in the vicinity of another power plant before operation; (5) among trees of the same species along a transect at intervals of 30 km from Grand Rapids to St. Cloud, Minnesota; (6) on different sides of trees in the vicinity of a power plant

Location	Host Tree	1970	1971	1972	1973	1974	1975
1. Point Road	Ulmus americana	5.65	5.87	6.23	6.68	6.55	6.09
2. Monitor 4	Quercus alba	5.78	6.07	6.35	6.50	6.80	5.93
3. Monitor 4	Quercus velutina	5.30	5.60	6.00	5.77	5.70	5.25
4. Monitor 5	Quercus macrocarpa	5.91	5.85	6.70	6.07	6.40	5.82
5. Monitor 7	Ulmus americana	7.07	5.94	6.70	6.43	6.80	6.20
6. Monitor 2	Ulmus americana	5.43	6.27	6.40	6.14	6.60	6.34
7. Monitor 3	Quercus macrocarpa	5.60	5.87	6.22	6.25	6.80	6.29
8. Square Lake	Quercus macrocarpa	5.50	5.67	6.11	6.03	6.22	5.70
9. Monitor 6	Quercus velutina	5.80	5.57	6.06	5.81	5.69	5.53
10. Monitor 1	Quercus macrocarpa	5.50	5.91	6.05	5.43	5.86	5.87
11. Monitor 1	Quercus velutina	----	5.35	5.85	5.56	5.52	5.54
12. Carlson M 1	Ulmus americana	----	5.48	6.32	6.16	6.20	6.17
13. Monitor 8	Populus grandidentata	5.20	5.83	6.22	6.20	6.60	5.99
14. KDWB Tower	Quercus macrocarpa	5.55	5.62	6.90	5.79	5.43	5.67
15. Monticello	Quercus macrocarpa	5.68	6.27	6.90	6.70	6.40	5.95
16. Fair Haven	Quercus macrocarpa	6.65	6.85	7.08	6.40	6.90	6.06
17. Fair haven	Tilia americana	----	6.32	6.25	6.72	6.90	6.00

Table II. Trees are arranged in order of distance from the A.S. King Generating Plant. Trees 1 through 14 are in the near environs, tree 15 is about 80 km west and trees 16 and 17 are about 150 km west.

with known acid-rain fallout from a faulty stack scrubber. The results of each of these tests will be discussed below.

(1) Bur oak trees were tested at two locations north of St. Cloud, Minnesota, near Heim's Mill Dam and at Little Rock Bayou. The following pH values were recorded on 13 May 1973 for nine trees, the first figure is the circumference in centimeters, the second is the pH of the bark: 79 cm, 6.05; 81 cm, 6.02; 91 cm, 6.11; 104 cm, 6.51; 117 cm, 6.90; 132 cm, 6.85; 160 cm, 6.20; 173 cm, 6.52. The difference between the lowest and highest pH was 0.88 but tree size does not appear to be a significant factor in bark pH. A similar comparison was made in Partch's Woods north of St. Joseph, Minnesota using ten sugar maples on 5 April 1975: 68 cm, 5.64; 114 cm, 6.66; 127 cm, 6.40; 155 cm, 6.45; 160 cm, 6.22; 165 cm, 5.74; 165 cm, 7.06; 173 cm, 6.66; 177 cm, 6.31; 190 cm, 6.00. The pH difference is 1.42 with no apparent size correlation.

(2) On 13 March 1975 twelve bark samples, from four sides and three different levels between the base and up to 3 meters, of a white oak in Partch's Woods were tested to determine pH variation of a single tree. The pH ranged from 5.90 to 6.38 with no correlation of direction or distance above ground.

(3) Several other trees were also tested in Partch's Woods with the following results, circumference in centimeters, species and pH listed in that order: 38 cm ironwood, *Ostraya virginiana*, 6.21; 41 cm ironwood, 6.57; 46 cm ironwood, 6.09; 26 cm paper birch, *Betula papyrifera*, 5.13; 58 cm paper birch, 5.03; 239 cm red oak, *Quercus rubra*, 5.79; 91 cm basswood, *Tilia americana*, 6.02; 53 cm basswood, 5.79; 89 cm sugar maple, *Acer saccharum*, 5.66; 61 cm american elm, *Ulmus americana*, 6.25.

(4) Similar tests were made on 18 trees in connection with pre-operational studies at a new power plant in Sherburne County, Minnesota. Most of the pH values were between 5 and 9 with the exception of a Russian olive, *Elaeagnus angustifolia*, with a pH of 4.91. An american elm near Bertram Lake west of Monticello, Minnesota had a pH of 9.10 in 1974 and a year later two different readings on the same day of 7.15 and 5.19.

(5) Bur oak pH values were obtained at 30 km intervals between Grand Rapids and St. Cloud, Minnesota. The location, circumference and pH are listed as follows: Cohasset, 216 cm, 6.11; Remer, 79cm, 5.95; Emily, 79 cm, 5.63; Ironton, 41 cm, 5.47; Brainerd, 107 cm, 6.06; Little Falls, 94 cm, 6.03; Little Rock Lake, 175 cm, 5.86.

(6) In response to a reported malfunction of a power plant stack-scrubber in northern Minnesota, several pH values were obtained to determine if any abnormal acidification resulted: (a) Ten bark samples were collected from a single 94-cm basswood tree 400 meters northwest of the power plant. Five of the samples were taken from the northwest side of the tree away from the power plant and five were taken from the southeast side facing the plant. The samples were collected at 30 cm, 90 cm, 150 cm, 210 cm and 270 cm above the ground in both directions. The pH values from the side facing the plant ranged between 5.09 and 5.19, while the values from the other side of the tree ranged between 5.57 and 5.73. Height above the ground was not significant in either direction. (b) Five other trees were sampled at the same time and place. Two samples from each tree were taken from the southeast and northwest sides. The circumference, species, direction and pH are listed in that order as follows: 94 cm green ash, *Fraxinus pennsylvanica*, NW 5.84, SE 5.05; 68 cm ironwood, *Ostraya virginiana*, NW 5.85, SE 4.38; [illegible] cm bur oak, *Quercus macrocarpa*, NW 6.04, SE 5.49; 140 cm basswood, *Tilia americana*, NW 5.48, SE 5.17; 91 cm sugar maple, *Acer saccharum*, NW 4.35, SE 4.45. (c) A 94 cm bur oak at a distance of 3.2 km had a pH of 5.67 on the side facing away from the power plant and 5.52 facing toward the plant. At a distance of 6.4 km east of the plant, the east side of a bur oak had a pH of 6.17 and the west side facing the plant had a pH of 6.26. Apparently only very near the plant was there a directional effect with higher acidity on the side facing the plant.

GENERAL CONSIDERATIONS

Several explanations for variation in the acidity of bark have been suggested by various researchers. Sjögren (1961) discusses differences in pH for samples of small and large pieces of bark. He says that pieces smaller than 1 cm^2 show lower pH values than samples consisting of larger pieces of bark. He also considers that these larger samples show better agreement with pH in bark under natural conditions. Hale (1955) states that by pulverizing the samples one would obtain slightly incorrect pH values. Skye (1968) pulverized his samples while in this study the samples were not pulverized. This could account for some of the less acidic values. The pieces of bark were also of variable size, consisting of both small and larger pieces, resulting in an average value for pH. The nature of soil, prevailing winds and general air mass movements can also influence pH. In Minnesota the western part of the state has soil of limestone origin and air mass movements are west to east which could bring in dust to act as a buffer giving more basic pH values. Lichens are sensitive to strong acidity but in no case has any evidence of injury by acid rain to lichens or of any pH which would be in the range necessary to cause injury to lichens.

In considering the effectiveness of the high stack in dispersing sulfur dioxide and other gases in the King Plant area, there has been no increase of bark pH of any significance. Only a few trees have shown an increase in acidity in the critical zone around the plant while the rest have decreased. It can be assumed that there is little or no fallout of damaging acid rain in the area. The changes which have occurred are insignificant compared to the variations in a single tree or among those of one species. In the case of the other power plant where known acid rain fallout occurred, the acidity became greater on the side of the trees facing the power plant but the effect became insignificant only a short distance away. In that case the stack was also shorter and had developed a faulty scrubber.

The sampling technique has been the same throughout this study and no significant increase of acidity has developed. The primary objective of this study was to determine changes in pH which might be detrimental to the growth of lichens. The pH values are generally less acidic than in the Swedish studies possibly due in part to differences in technique but more likely because of greater amounts of atmospheric pollutants in Sweden. Major changes in acidity should eventually become evident if methods of evaluation remain the same. Another reason for more acidic values is the difference in buffering action of bark of different species.

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EFFECTS OF SIMULATED RAIN ACIDIFIED WITH SULFURIC ACID ON HOST-PARASITE INTERACTIONS[1,2]

D. S. SHRINER[3].

ABSTRACT

Wind-blown rain, rain splash, and films of free moisture play important roles in the epidemiology of many plant diseases. The effects of simulated rain acidified with sulfuric acid were studied on several host-parasite systems. Plants were exposed, in greenhouse or field, to simulated rain of pH 3.2 ± 0.1 or pH 6.0 ± 0.2. Simulated "rain" of pH 3.2 resulted in: 1) an 86% inhibition in telia production of *Cronartium fusiforme* on *Quercus phellos*; 2) a 66% inhibition of reproduction of *Meloidogyne hapla* on field-grown *Phaseolus vulgaris*; 3) a 10% decrease in the severity of *Uromyces phaseoli* on field-grown *Phaseolus vulgaris*; and 4) an inhibition of *Rhizobium* nodulation of *Phaseolus vulgaris* and *Glycine max* by an average of 73%. Effects on halo blight of kidney bean (caused by *Pseudomonas phaseolicola*) depended upon the segment of the disease cycle in which the "rain" occured: a) simulated rain of pH 3.2 applied to plants before inoculation stimulated disease development; b) suspension of inoculum in "rain" of pH 3.2 decreased inoculum potential; and c) "rain" of pH 3.2 applied to plants after infection inhibited disease development. Scanning electron microscopy of epicuticular waxes on leaves of *Quercus phellos* and *Phaseolus vulgaris* showed marked erosion of those surfaces by "rain" of pH 3.2, indicating possible influences on the structure and function of plant cuticles.

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[1]Portion of Ph. D. thesis submitted by the author under the direction of Drs. E. B. Cowling and A. S. Heagle, North Carolina State University.

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[3]Publication No. 876, Environmental Sciences Division.

These results suggest that the acidity of rain is a new parameter of environmental concern, and underline the need for study of the consequences of prolonged exposure of both agronomic and natural ecosystems to this stress factor.

INTRODUCTION

Preliminary studies of effects of acidic precipitation on vegetation have suggested that significant direct effects on plant productivity, as measured by growth and yield, are unlikely to be of major short-term importance under conditions of precipitation acidity currently occurring over widespread areas of N.A. and Europe (Wood and Bormann, 1974). Of equal interest, however, are the possible indirect effects, chronic and subtle in nature, which may result in long-term effects on ecosystems as a result of man's increased burdening of such systems with acidic precipitation. Typical of such indirect effects are the interactions of plants as hosts with the large variety of organisms capable of parasitizing those plants.

Many plant-parasitic microorganisms require wind-blown rain, rain splash, or films of free moisture for dispersal, movement on leaf surfaces, and establishment, growth and reproduction of these organisms once dispersed (Walker, 1957).

For these reasons, the effects of a simulated rain solution acidified with sulfuric acid were studied with a range of host-parasite systems.

MATERIALS AND METHODS

Seeds of Red Kidney beans *(Phaseolus vulgaris* 'Red Kidney') were either planted in field plots or germinated in vermiculite, and transplanted after one week to 10 cm clay pots in a greenhouse. Plants were inoculated with commercial *Rhizobium* inoculum (Nitragin Co., Milwaukee, Wisc.) at planting or transplanting. Detailed methodology has been discussed (Shriner, 1974). Plants were subsequently exposed to sulfuric acid solutions as simulated rain. Chemical constituents of the base water solution were chosen to approximate concentrations of major ions known to be present in natural precipitation. Concentrations of sodium, calcium, magnesium, potassium, ammonium, nitrate, chloride, and sulfate in the simulant are given in Table I, as compared to average concentrations occuring at four research watersheds in the United States. Two conditions of acidity were compared, pH 6.0 ± 0.2 and pH 3.2 ± 0.1, with sulfuric acid being the primary source of added

Table I. Comparison of chemical composition of the rainfall simulant with natural rainfall collected at four watersheds in the U.S.

	Na^+	Ca^{++}	Mg^{++}	K^+	NH_4^+	NO_3^-	Cl^-	$SO_4^=$
	Concentration, mg/ℓ							
pH 6.0 ± 0.2 Simulant	0.09	0.14	0.04	0.06	0.22	0.12	0.19	< 0.20
pH 3.2 ± 0.1 Simulant	0.09	0.14	0.04	0.06	0.22	0.03	0.19	50-70
Walker Branch-[1] Watershed, TN	0.26	0.93	0.14	0.22	0.13	0.26	--	--
H. J. Andrews-[1] Watershed, OR	0.08	0.21	0.04	0.01	0.02	0.01	--	--
Coweeta-[1] Watershed, NC	0.22	0.25	0.05	0.11	0.02	0.14	0.35	--
Hubbard Brook-[2] Watershed, NH	0.12	0.21	0.06	0.09	0.22	1.31	0.42	3.1

[1]Henderson, 1975.

[2]Likens and Bormann, 1972.

acidity. The two acidity conditions were chosen because pH 6.0 reasonably approximates the equilibrium pH of CO_2 dissolved in water, and thus, a theoretical "unpolluted" rain; pH 3.2 represents an acidity of rainfall at the lower end of the range of so-called "acid" rainfall as determined from measurements in both the eastern United States and northern Europe (Likens and Bormann, 1974). Likens and Bormann (1974) found sulfate to account for 62% of the anions (milliequivalent basis) in precipitation at their New Hampshire sampling point.

The simulated rainfall was applied to the plants by means of a simulation apparatus capable of delivering droplet sizes in the range of 0.6 - 1.2 mm diameter. Droplets of mean drop size (0.9 mm) achieved approximately 80% of terminal velocity (Shriner, 1974). The simulant was applied daily for six days per week in greenhouse studies, and three days per week in field studies, where applications of the simulant were superimposed on natural rainfall incident at the site. Amounts and frequencies of simulant to be applied were based on five-year averages of precipitation data from a weather station at the field site. Simulant was applied at rates of 2.5 to 3.8 cm/hr for weekly totals between 1.9 and 5.7 cm.

RESULTS

Five host-parasite systems were investigated. In three of these five cases, significant inhibition of some parameter of disease development occurred (Table II). Production of telia of the fusiform

Table II. Effects of simulated rain acidified with sulfuric acid on host-parasite interactions.

Host-Pathogen System	Acidity of Simulated Rain: Pre-inoculation (pH)	Inoculation (pH)	Post-inoculation (pH)	Disease Measure	
Greenhouse Studies				Infected leaves/plant[1]	Telia/Infected Leaf[1]
Quercus phellos-*Cronartium fusiforme* Oak-Pine Rust of Oak	3.2	3.2	3.2	3.8*	15*
	6.0	6.0	6.0	6.5	115
				Dead leaflets/plant[2,3] (no.)	
Phaseolus vulgaris-*Pseudomonas phaseolicola* Holo Blight of Bean	3.2	3.2	3.2	0.0a[4]	
	3.2	3.2	6.0	0.0a	
	3.2	6.0	3.2	4.2d	
	3.2	6.0	3.2	4.8d	
	6.0	3.2	3.2	0.0a	
	6.0	3.2	6.0	0.0a	
	6.0	6.0	3.2	2.0b	
	6.0	6.0	6.0	3.2c	
			LSD .05	0.77	
Field Studies				Eggs/plant[5]	%root galled[5,6]
Phaseolus vulgaris-*Meloidogyne hapla* Root Knot Nematode on Beans	3.2	3.2	3.2	74*	26
	6.0	6.0	6.0	217	50
				% leaf area affected at: 7 weeks	9 weeks
Phaseolus vulgaris-*Uromyces phaseoli* Rust of Beans	3.2	3.2	3.2	22*	48
	6.0	6.0	6.0	31	45

*ANOVA significant, p=0.05

[1]Each value is the mean of 6 plants/treatment.

[2]Number of inoculated leaflets (max. 6/plant) which were dead on plants which developed symptoms characteristic of halo blight.

[3]Each value is the mean of 5 plants.

[4]Values in a column followed by the same letter were not significantly different, $LSD_{.05}$.

[5]Each value is the mean of 18 plants/treatment.

[6]Percent of root area galled by *Meloidogyne hapla*.

rust organism *(Cronartium fusiforme)* on the host willow oak *(Quercus phellos)* was inhibited by 86%. Natural epidemics of two pathogens were inhibited by "rain" of pH 3.2: reproduction of *Meloidogyne hapla*, a root-knot nematode was inhibited by 66% on field-grown kidney beans; there was a delay in the development of a bean rust *(Uromyces phaseoli)* epidemic on field-grown kidney beans -- this was evident after seven weeks, but not after nine weeks.

Effects on halo blight of kidney beans (caused by *Pseudomonas phaseolicola)* depended upon the segment of the disease cycle in which the acidic treatment occurred: a) simulated rain of pH 3.2 applied to plants before inoculation stimulated disease development; b) suspension of inoculum in "rain" of pH 3.2 decreased its capacity to induce disease; and c) "rain" of pH 3.2 applied to plants after infection inhibited disease development (Table II).

During routine observation of kidney beans for these host-pathogen studies, an apparent difference was observed in nodulation of the bean plants by the symbiotic nitrogen-fixing bacteria of the genus *Rhizobium*. Experiments were subsequently established to study this effect.

Greenhouse and field studies with kidney bean and greenhouse studies with soybean *(Glycine max* 'Lee'), all resulted in significant (>65%) inhibition of nodule formation on root systems of plants treated with "rain" of pH 3.2 (Table III). Assay of the plants by the acetylene-reduction technique showed a decrease in nitrogenase activity proportionate to the degree of inhibition of nodule formation. Inhibition of nodulation was accompanied by growth reductions most frequently when the plants were cultured in soils of low cation exchange capacity (< 3 me/100g whole soil). No consistant decreases in plant growth or yield were correlated with the observed effect on nodulation when the plants were grown in soils of higher cation exchange capacity (>3 me/100g whole soil), however. Studies of the relationship of time and duration of exposure suggested that the greatest inhibition occurred when the "rain" was applied during the period of greatest increase in nodule activity (Stewart, 1966). Since nodule activity requires host substrates, the removal of such materials by leaching may be important to the mechanism of nodule inhibition (Stewart, 1966). This aspect of the problem is currently being investigated by the author.

Examination of leaf surfaces of kidney beans with the scanning electron microscope following treatment with the "rain" revealed extensive erosion of the cuticular waxes of leaves exposed to solutions of pH 3.2 when compared to controls. Shriner (1974) has recently reviewed the functional role of plant cuticles in relation to these observations. Of greatest importance to the observed effects on host-parasite interactions are the role of cuticular waxes as a physical barrier to fungi and bacteria, and the efficiency of the cuticle as a barrier to loss of water from leaves. Alterations of either of these functions could help to explain the observed predisposition of host plants to greater disease development.

Table III. Effect of "rain" acidified with sulfuric acid on Rhizobium nodulation and growth of leguminous plants.

Species and Experiment No.	Simulated Rain (pH)	Nodules/ Plant (No.)	Dry Wt.[3] /nodule (mg)	Fresh Weight/Plant Shoots (g)	Roots (g)	Pods (g)
FIELD						
Kidney bean-1[4]	6.0	29	0.62	43.70	4.10	15.10
	3.2	7*	0.76	42.30	3.80	13.60
GREENHOUSE						
Kidney bean-1[5]	6.0	15	0.67	6.05	7.88	1.86
	3.2	1***	0.40	5.96	5.74	1.81
Kidney bean-2[5]	6.0	49	0.60	9.63	9.34	5.26
	3.2	11*	0.60	5.63*	8.14*	3.05*
Soybean-3[2],[6]	6.0	65**	0.52	3.55	4.62	--
	3.2	24	0.51	3.02	3.53	--

[1]*Phaseolus vulgaris* 'Red Kidney'

[2]*Glycine max* 'Lee'

[3]Dried at 85 C for 24 hours

[4]Each value is the mean of 6 replications, each with 15 plants

[5]Each value is the mean of 5 replications, each with a single seedling

[6]Each value is the mean of 8 replications, each with a single seedling

*Difference significant at p=0.05; **p=0.01; ***p=0.001

SUMMARY AND CONCLUSIONS

Many environmental stress factors play important roles in the disease cycles of plant parasites. These factors may be active on the parasitic organism, on its host, or on the host-parasite complex. Results of this study demonstrate that solutions of an acidity similar to that known to occur in natural acidic rains can affect processes involved in host-parasite interactions. These results are presented with recognition and emphasis of the limitations that must be considered when interpreting their significance and implications to natural biological systems: a) the pH values selected for investigation - pH 3.2 and pH 6.0 - represent only the approximate extremes of acidity observed in natural rainfall; b) sulfuric acid was assumed to be a major component of the acidity in ambient precipitation; and c) the relative effects of cations and anions in the simulated "rain" can not be distinguished.

With those limitations in mind, however, the results underline the need for study of the consequences of prolonged exposure of both agro-

nomic and natural ecosystems to the subtle, indirect influences of acidic precipitation on ecosystem structure and function, even in the absence of obvious direct injury to these systems.

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CUTICULAR FEATURES AS INDICATORS OF ENVIRONMENTAL POLLUTION

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ABSTRACT

Several leaf cuticular features such as stomatal frequency, stomatal size, trichome length, type, and frequency, and subsidiary cell complex respond to environmental pollution in different ways and hence can be used as indicators of environmental pollution in an area. Several modifications in cuticular features under polluted environments seem to indicate ecotypic or survival significance for the plant species under investigation.

INTRODUCTION

Numerous studies have revealed the detrimental effects of environmental pollution on plants under natural and controlled conditions. Hill and Thomas (1933) reported that sulfur dioxide decreased the yield of alfalfa. Chamberlain (1934) observed that dirt, smoke, and the gases of a large city were fatal to conifers, especially *Pinus banksiana*. The plants showed chlorosis and necrosis. Solberg and Adams (1956), reported that fluoride and sulfur dioxide destroyed the spongy mesophyll and the lower leaf epidermis of plants. Scheffer and Hedgcock's (1955) study of the forests of the Northwestern United States revealed the characteristic effects of sulfur dioxide injury on leaves. Pyatt (1970) investigated lichens as possible biological indicators of air pollution in a steel-producing town in Wales and found that generally the lichen flora decreased in number of species present with increasing proximity of the source of pollution. Feder (1970) recorded a decrease in floral productivity and branching in geranium subjected to oxidant-type pollutants. It was quite evident from a survey of literature that the possibility of utilizing leaf cuticular and morphological features as indicators of environmental pollution needed investigation, although their significance in taxonomic and ecological studies is well documented (Au, 1969; Sharma and Dunn, 1969; Sharma, 1972). Therefore, the purpose of this report

is to indicate the progress achieved in establishing the concept of using leaf cuticular patterns in studying environmental pollution.

MATERIALS AND METHODS

White clover *(Trifolium repens L.)*, red clover *(Trifolium pratense L.)*, and sweetgum *(Liquidambar styraciflua L.)* plant populations were studied in the rural and metropolitan areas of Kentucky and Tennessee, USA. Mature leaf samples were collected in summer to make slides of the upper and lower epidermis using Duco cement (Williams, 1973). These slides were used to study cuticular features such as stomatal frequency, stomatal size, trichome length, type, and frequency, and subsidiary cell complex. Floral productivity and leaf size were also studied in the plant populations of relatively unpolluted and polluted habitats. The type and major sources of pollution in four study areas in Tennessee are indicated in Table 1.

TABLE 1: DISTRIBUTION AND ENVIRONMENT OF RED CLOVER POPULATIONS

Population	Number of samples	Location*	Type of pollution	Source of pollution
A	3	Reelfoot Lake	Sulfur dioxide, ozone	Vehicular traffic
B	3	Memphis	Sulfur dioxide, particulate matter, carbon monoxide, other oxidants	Vehicular traffic, jet airport power plant, manufacturing plant, other industrial units
C	3	Nashville	Particulate matter, sulfur dioxide, carbon monoxide other oxidants	Vehicular traffic, power plant, jet airport, fertilizer plant, textile plant, other industrial units
D	3	Knoxville	Sulfur dioxide, particulate matter, carbon monoxide, other oxidants	Vehicular traffic, power plant, air port, manufacturing plant, other industrial units

* in Tennessee, U.S.A.

RESULTS AND DISCUSSION

The morphological and cuticular findings in the selected populations of red clover and white clover are summarized in Tables 2 and 3 (Sharma and Butler, 1973, 1975). It was found that in the large, metropolitan, industrial cities of Memphis, Nashville, and Knoxville the stomatal frequency values were lower than the measurements made in the rural, relatively unpolluted or less polluted area near Reelfoot Lake in northwest Tennessee. This adaptation could decrease the amount of poisonous gases getting into leaf tissues and thus protect the plant against pollution. The populations in polluted areas had

TABLE 2: SUMMARY AND COMPARISON OF LEAF CUTICULAR PATTERNS AND FLORAL PRODUCTIVITY IN RED CLOVER POPULATIONS

Trait		Population A	Population B	Population C	Population D
Stomatal frequency ($\bar{x}\pm\hat{0}$)	upper	25.9±6.0	14.4±3.4	13.9±4.1	17.1±3.4
	lower	59.3±9.5	44.6±2.5	43.3±7.9	47.2±9.7
Stomatal size range (μ)	upper	8-10	8-15	8-15	8-16
	lower	8-16	8-14	8-16	8-15
Trichome density/cm^2	lower	80	220	196	175
Trichome length, μ ($\bar{x}$)		283	366	379	336
Subsidiary cell complex (cells)		3-4	3-4	3-4	3-4
Avg. number of flowers/ inflorescence		87	61	56	67

$\bar{x}$=mean
$\hat{0}$=standard deviation

TABLE 3: LEAF CUTICULAR FEATURES AND FLORAL PRODUCTIVITY IN WHITE CLOVER POPULATIONS

Trait		Population A	Population B
Stomatal frequency ($\bar{x}\pm\delta$)	upper	153.4±14.1	96.8±10.3
	lower	44.3± 9.6	37.2± 7.8
Stomatal size range (μ)	upper	10-15	7-17
	lower	17-25	15-25
Trichome density/cm^2	lower	*U=25	U=60
		**M=60	M=123
Trichome length,μ ($\bar{x}$)		82	95
Subsidiary cell complex (cells)		3-4	3-4
Avg. number of flowers/ inflorescence		69	47

$\bar{x}$= mean
δ= standard deviation
U= unicellular trichome
M**= multicellular trichome

barbed, longer, and more trichomes on their leaf surfaces. This adaptation would have the effect of lowering the average leaf temperature and hence decreasing the rate of metabolic reactions associated with various harmful gases in and around leaves (Fig. 1A). The long, barbed trichomes also might act as filters and insulators and keep the dust particles away from stomatal openings (Fig. 1B). The trichomes in red clover leaves were unicellular and had a ring of elongated cells around their base (Fig. 1C). White clover had both unicellular and multicellular trichomes on their lower leaf surfaces (Table 3).

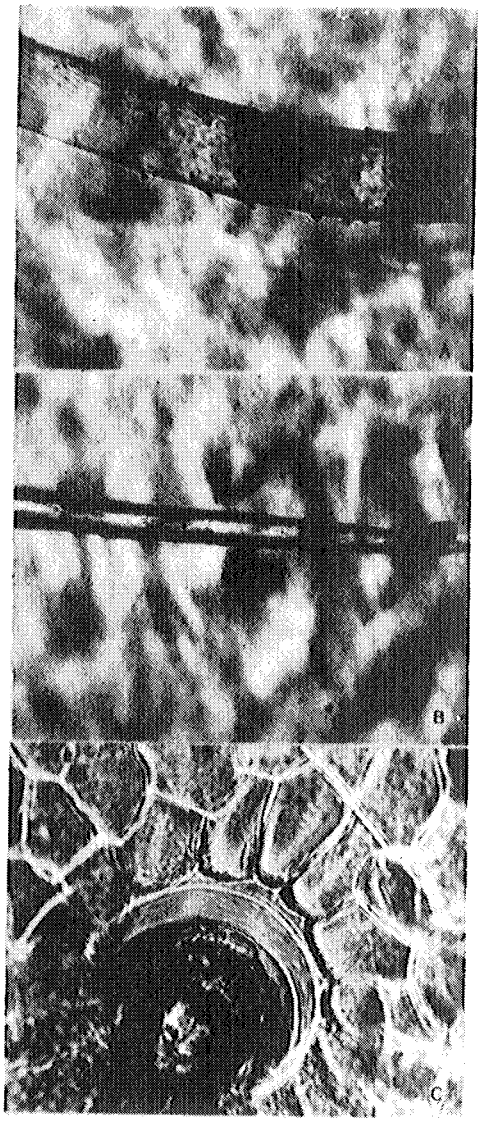

Figure 1. Trichomes in *Trifolium pratense L.*
A. Showing 'barbed' surface, 200X.
B. A simple, pointed trichome with a trapped dust particle, 100X.
C. A ring of elongated cells around trichome base, 200X.

Production of flowers was low in polluted-area populations. Subsidiary cell complex and stomatal size range remained unaffected by pollution within a plant species. Similar results were obtained in sweetgum and sugar maple populations (Sharma and Tyree, 1973; Sharma, 1975).

CONCLUSIONS

It is evident that environmental pollution retarded production of flowers in the plant species investigated. Stomatal frequency decreased in polluted area populations while trichome density and trichome length increased. Subsidiary cell complex and the stomatal size range were not affected by environmental pollution. It is, therefore, concluded that these features can be used as indicators of environmental pollution in an area. It is further suggested that such patterns in the plants of polluted areas may be of significance in determining the degree and perhaps the type of pollution.

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THE EFFECTS OF ACID RAIN ON NITROGEN FIXATION IN WESTERN WASHINGTON CONIFEROUS FORESTS[1]

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ABSTRACT

We investigated both the current status of nitrogen fixation in western Washington forests, and the potential effects of acid rain on this vital process.

Even the low concentrations of sulfur dioxide presently found in the Northwest are thought to have an adverse effect on nitrogen fixation by limiting the distribution of the epiphytic nitrogen-fixing lichen, *Lobaria pulmonaria*, which is found mainly in deciduous forests. A close relative, *L. oregana*, was found to be the major nitrogen fixer in old-growth coniferous forests. It fixes less nitrogen following exposure to sulfuric acid of pH 4 or less.

A more serious threat to nitrogen fixation than acid rain is the practice of deliberately suppressing red alder to keep it from competing with Douglas fir. Also, *L. oregana* is a late successional species and does not develop in forests where short cutting cycles are practiced.

INTRODUCTION

One possible effect of acid precipitation mentioned in the Report of the Swedish Preparatory Committee for the U.N. Conference on the Human Environment (Engstrom, 1971) was a depressing effect on nitrogen fixation. We set out to determine whether that was likely to be the case in western Washington coniferous forests.

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[1]This study was supported by a grant for Student Originated Studies from the National Science Foundation.

Since nitrogen is a major limiting factor in northwest coniferous forests (Gessel et al., 1951), a decrease in N_2-fixation could seriously affect the forest ecosystem.

The effects of acid rain on nitrogen transformations other than fixation should also be considered in evaluating the effects of acid rain on the nitrogen economy of an ecosystem. Nitrification is inhibited by low pH (Alexander, 1967), which might result in conservation of nitrogen since nitrate is relatively soluble and more readily lost to streams or groundwater in some ecosystems (Likens, et al., 1970). Also, if oxides of nitrogen, rather than sulfur, are the source of the acid, then there will be an increased input of nitrate in rainwater. This is often the case in the northeastern U.S. (Likens, 1975). However, the nitrate ion is rare in rain in our area (Cole and Johnson, 1974). Our study was limited to nitrogen fixation by free-living microorganisms and by lichens.

SITE DESCRIPTIONS

QUINAULT

The Quinault site lies on the west side of the Olympic Penninsula at an elevation of about 100 m, in an old-growth spruce/hemlock forest with some remaining old-growth Douglas fir. The annual precipitation of about 4.5 m falls mostly in the form of rain and is largely free of man-made pollutants.

The litter and humus layers are well developed and extend to a depth of 20 cm. The soil is fine, dark, and free of rocks.

The mixed overstory includes *Picea sitchensis, Tsuga heterophylla, Thuja plicata, Pseudotsuga menziesii, Alnus rubra, Rhamnus purshiana,* and *Acer circinatum.* The understory consists of *Polystichum munitum, Blechnum spicant, Rubus spectabilis, Vaccinum parvifolium, Gaultheria shallon, Oxalis oregana, Trillium ovatum,* and mosses.

CENTRALIA

The Centralia site lies about 10 km northeast of the new coal-fired power plant near the town of Centralia, in a second-growth Douglas fir forest. The elevation is about 500 m and the topography is steep and dissected. The annual precipitation is considerably less than at Quinault and is presumably acidified by sulfur emissions from the power plant. This site was chosen to provide baseline data for evaluating the effects of the power plant, as it is unlikely that there have been major effects on the ecosystem to date.

The litter layer in this area is less than one centimeter deep. The soil is dark and rich in humus.

The overstory vegetation consists of *T. heterophylla, P. menziesii, Acer macrophyllum,* and *A. rubra.* The understory includes *T. ovatum, Montia sp., Smilacina racemosa, V. parvifolium, Disporum hookeri, R. spectabilis, Galium triflorum, Berberis aquifloium, Asarum caudatum, Dicentra formosa,* and saxifrage.

CEDAR RIVER

The Cedar River site lies in the foothills of the Cascade Mountains east of the metropolitan area of Seattle-Tacoma. The site is in an even-age Douglas fir forest on a level site within the University of Washington's Thompson Experimental Forest, at an elevation of 200 m.

The ground is extremely rocky and there is no definite litter layer. The soil is light in color and contains little organic matter.

The overstory contains *P. menziesii* and *A. circinatum.* The understory consists of *Holidiscus discolor, P. munitum, Pterdium aquilinum, Rubus ursinus, G. shallon, R. spectabilis, Linnea borealis,* and mosses.

RAIN, THROUGHFALL, AND SOIL PH

METHODS

Rain pH was monitored in Lacey (adjacent to Olympia) from November 5 to December 11, 1974. Samples were collected daily and frozen until shortly before the pH was measured. All pH measurement was by the glass electrode method.

Although it seldom rains in Washington during the summer, we put out polyethylene bottles with funnels at each of our study sites to collect rainfall and throughfall. Rainfall and throughfall, if any, were brought back to the laboratory for pH determination.

Measurement of soil and litter pH followed the method of C.B. Davey (1974). Twenty milliliters of soil are stirred for thirty minutes with enough distilled water to give "the consistency of heavy cream." pH is then measured using the glass electrode method.

RESULTS AND DISCUSSION

The frequency distribution of rain pH in Lacey, Washington weighted according to volume, is shown in Figure 1. While the rain during the

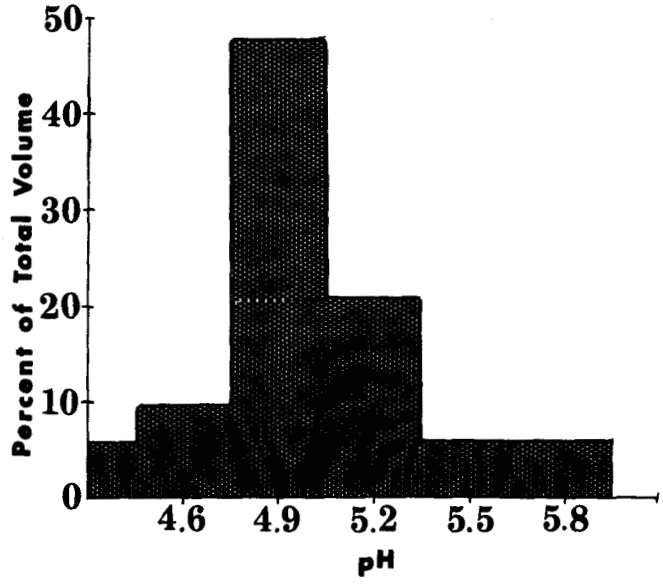

Figure 1. Frequency distribution of rain pH for Lacey, Washington, from November 5 to December 11, 1974.

sampling period was not startingly acid, it appears that rain pH in this area is no longer under carbonic acid control.

Table I summarizes the pH values we found for rain, throughfall, litter, and soil at our three study sites.

TABLE I

pH values for rain, throughfall, litter, and soil.

SITE	SAMPLE	MEDIAN	MAX	MIN	N
Quinault	rain	5.76	5.47	6.30	4
	throughfall	5.10	4.20	6.24	11
	litter	4.24	3.93	4.34	4
	soil	4.70	4.13	5.76	6
Centralia	throughfall	4.66	4.58	5.62	5
	litter	4.64	4.22	5.15	3
	soil	6.02	5.84	6.04	3
Cedar River	rain	4.24	4.24	4.24	1
	throughfall	4.62	4.09	6.95	5
	soil	5.17	4.28	5.94	5

Although limited, our data are consistent with the hypothesis that the coniferous forest canopy buffers normal rain to a lower pH value, and acid rain to a higher pH value. Both rain and throughfall were less acid at Quinault than at the two second-growth sites, yet the litter and soil were more acid at Quinault.

PH BUFFERING STUDY

Acid rain does not ensure that soil microorganisms will be exposed to lowered pH, at least not immediately. pH buffering by the forest canopy has been reported by Eaton et al. (1973) and Cole and Johnson (1974). Additional buffering takes place in the litter and soil.

METHODS

We attempted to simulate the effects of acid rain on soil water in the laboratory, using apparatus patterned after that described by Tim Wood elsewhere in these Proceedings. Soil samples were placed in Buchner funnels on a turntable and rotated under a stream of "rain" adjusted with sulfuric acid to pH 3. Water passing through the soil or litter in the funnels was collected in beakers and pH measured by the glass electrode method. Rain was applied at the rate of about 0.5 cm/hr. The major difference between our methods and those of Wood is that we measured leachate pH at about ten minute intervals over the course of a several hour rain application, but only repeated the application once or twice for each soil sample.

RESULTS AND DISCUSSION

The results of this experiment were highly variable, but those of a typical application of simulated acid rain are shown in Figure 2. Over a period of four to eight hours the pH of water passing through our soil or litter samples dropped appreciably, in some cases nearly to the pH of the acid being applied.

However, the initial leachate pH of a second simulated acid rain application a day or two later was generally nearly as high as that for the first application. This is consistent with the findings of Wood and others that a great deal of acid can be applied to soil without permanently acidifying it. However, even the temporary acidification of soil water which we observed could be highly significant for soil microorganisms.

In an attempt to determine whether the pH recovery mechanism in soil and litter is biological in nature, we autoclaved some soil samples and repeated the acid treatment. Buffering was greatly

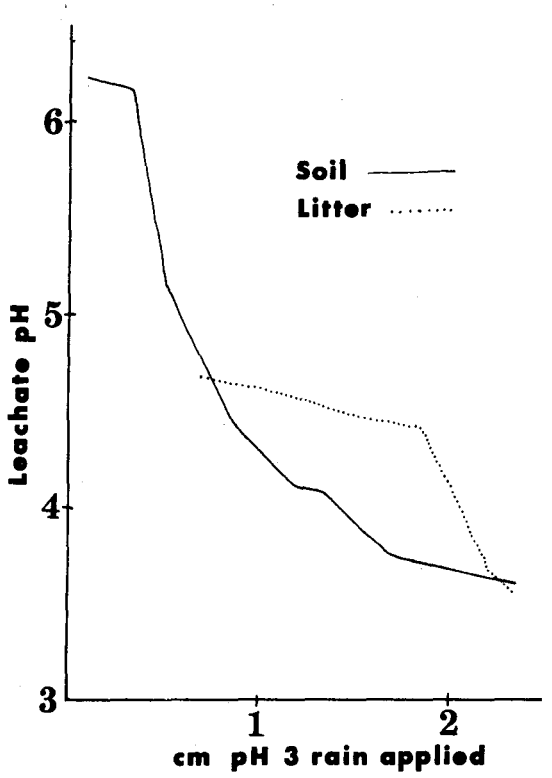

Figure 2. Leachate pH trends for soil and litter from the Centralia site. About 2.5 cm of simulated pH 3 "rain" was applied over a four hour period.

increased, to the extent that there was little decrease in leachate pH over several hours. Possibly lysis of cells occurred, releasing organic buffers.

C. O. Tamm (1975) suggests that rapid but temporary acidification of soil water can be explained by purely physical and chemcial properties of the soil. If the soil is composed of large aggregates of particles, only a small fraction of the cation exchange sites are exposed to the acid applied in a given application. These sites are quickly leached, but a large number of unleached sites remain, which may in turn be exposed to cation exchange leaching if the soil is disturbed in any way between acid applications.

MEASUREMENTS OF NITROGEN FIXATION

GENERAL METHODS

Nitrogen fixation was measured by the acetylene reduction method (Hardy et al., 1968). This method is based on the fact that the nitrogenase enzyme is a powerful reducing catalyst. It will act on acetylene as a substrate and reduce it to ethylene. The rate of nitrogen fixation can be calculated from ethylene production.

Samples for which N_2-fixation was to be determined were placed in 20 ml culture tubes stoppered with gas-tight rubber septums. The tubes were then evacuated by hand using a 50 cc syringe, and flushed with a

gas mixture of 10% acetylene, 20% oxygen, and 70% argon. Acetylene was generated by reacting calcium carbide with water and scrubbing the resulting gas with concentrated sulfuric acid. Oxygen and argon were industrial welding grade.

At the end of the incubation period, which varied from 30 minutes to 24 hours, ethylene production was measured by gas chromatography. A Gowmac model 750 gas chromatograph with flame ionization detector was used. A 2 m column packed with Poropak R was run at 50-60° C using helium as the carrier gas at a flow rate of 30 ml/minute. Typical retention times were 130 seconds for ethylene and 170 seconds for acetylene. Ethylene concentration was determined using acetylene as an internal standard, and ethylene production was calculated by subtracting the concentration of ethylene impurity in the acetylene. Calculated rate of nitrogen fixation was based on the theoretical ratio of 3 moles C_2H_4 produced per 1 mole N_2 fixed (Hardy et al., 1968).

Two modifications of our usual methods were used for some samples. First, for some of the epiphyte samples we added 0.05% CO_2 to the gas mixture. Second, for some of our later work, we simply injected 2 cc of acetylene into the stoppered tubes, rather than replacing the air in the tubes with gas mixture as above. The first modification gave slightly higher rates of ethylene production; the second gave slightly lower rates. Neither difference was statistically significant.

SOIL AND LITTER

Although buffering by the canopy may protect litter and soil from abnormally acid throughfall, we carried out a program of experimental acididication of soil and litter to see what effect it would have on N_2-fixation.

Soil plots were isolated for experimental treatment by sinking plastic cylinders of about 30 cm diameter into the soil to a depth of 10-15 cm. One plot at each site was untreated and used as a control. The other four received 5.12 liters of either pH 6.0, pH 5.0, pH 4.0, or ph 3.0 water, applied with a sprinkling can, to simulate 5 cm of rain. The water was prepared with tap water adjusted to the correct pH with H_2SO_4. Samples of litter and soil were collected for acetylene reduction analysis both immediately before and 30 minutes after the acid application. The above procedures were followed at each field site. Thus the acid treatment plots each received three applications of "acid throughfall" or a total of 15 cm. After rate of fixation was measured, samples were oven-dried and weighed.

There was no detectable N_2-fixation in most of the soil samples. The rate of ethylene production prior to acid application, in moles C_2H_4/g soil/hr, was 1.6×10^{-11} to 7.7×10^{-11} for Quinault, zero for Centralia, and zero to 1.4×10^{-11} for Cedar River. Fixation in

untreated litter was somewhat higher: 1.3×10^{-10} for Quinault, zero to 3.9×10^{-11} for Centralia, and zero to 1.9×10^{-10} for Cedar River.

Application of acid had little effect on the small amount of fixation taking place in the soil. Both soil and litter were very dry at Centralia and Cedar River, as is usual in western Washington in summertime, and most of the water or acid applied was absorbed by the litter layer, leaving the soil dry. The effect on fixation in litter was more pronounced, and is shown in Figure 3. At the two second-growth sites,

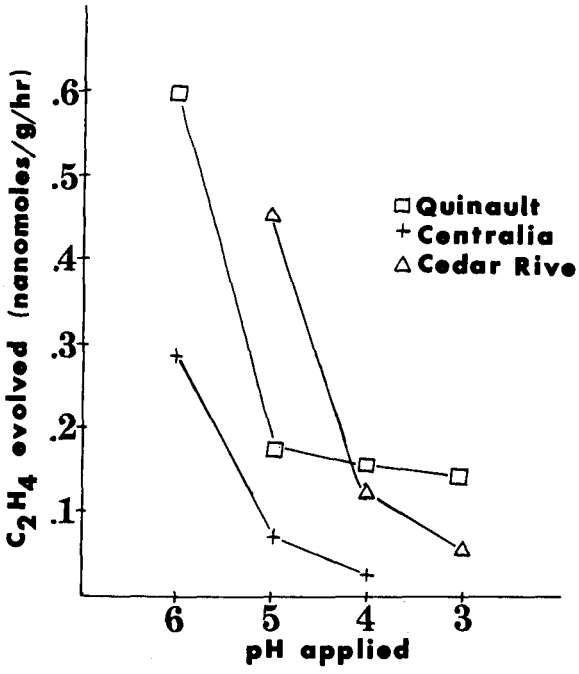

Figure 3. Rates of nitrogen fixation, expressed as ethylene production, for litter following application of 5 cm of water of the pH shown.

N_2-fixation was actually stimulated by application of acid, but was stimulated more by dilute acid than by concentrated acid. At Quinault, where litter was more moist and initial rate of fixation greater than at the other two sites, there was a decrease in fixation after application of acid of pH 4 or lower. An extremely high rate of 3.7×10^{-9} moles C_2H_4/g/hr, from the Centralia pH 3 plot, was omitted from the graph. This high rate does not indicate stimulation of fixation by acidity, since we found that the pH of the soil in that plot was actually higher than in the others, despite three applications of pH 3 "throughfall." Rather, this illustrates the heterogeneity of litter with respect to buffering and/or N_2-fixing capacity.

Rates of nitrogen fixation were low in litter and even lower in soil. Moisture appears to be the major limiting factor, at least in summer, although pH is also important, fixation being inhibited by low pH. Application of large quantities of acid was not sufficient either to saturate the soil with water, or to effect a major change in pH.

NEEDLE SURFACE MICROORGANISMS

The surfaces of some conifer needles support a community of algae, fungi, bacteria, and micro-lichens. This community, collectively known as "scuzz" (Sherwood, 1971), is often present in quantities large enough to be plainly visible without magnification. We examined Douglas fir, *Pseudotsuga menziesii* needles by both light and scanning electron microscopy. Large bacteria were seen by light microscopy on slides prepared from scuzz. Under scanning electron microscopy the complex tangle of fungal hyphae and masses of algal cells could be seen. Sherwood and Carrol (1974) studied the fungal flora of needle surfaces. Jones (1970) found N_2-fixing bacteria on Douglas fir needles in Great Britain.

We found rates of acetylene reduction by scuzz of 2.1×10^{-9} moles/g needles/hr using our normal gas mixture, but only 1.7×10^{-10} moles/g/hr when oxygen was omitted. Rates of ethylene production by scuzz scraped from needles were from .87 to 1.3×10^{-8} moles/g scuz/hr. These rates are substantially higher than those for litter.

EPIPHYTIC LICHENS

The epiphytic lichen *Lobaria pulmonaria* was reported by Millbank and Kershaw (1970) to fix nitrogen despite its lack of a blue-green phycobiont. They found that internal cephalodia in the lichen contain the N_2-fixing blue-green alga *Nostoc*. William Denison (1973) reported that the closely related species, *Lobaria oregana*, is abundant in the canopy of old-growth coniferous forests in Oregon, and makes a significant contribution to the nitrogen economy of these forests by fixing atmospheric nitrogen. He also describes a method of climbing old-growth trees with comparative ease and safety.

We climbed an old-growth *Picea sitchensis*, Sitka spruce, at the Quinault site and collected a supply of *L. oregana* for study purposes. The lichen is easy to maintain since it can be dried and kept indefinitely until ready to use. Fragments of lichen are simply moistened to restore metabolic activity, and were incubated in an environmental chamber under controlled conditions of temperature and photoperiod. The intensity of illumination used was 800 ft-candles.

To estimate the rate of fixation under winter conditions, we programmed the chamber for 9 hours of light at 10°C and 15 hours of dark at 5°C. For a 24 hour period, the weighted mean rate of ethylene production was 8.3×10^{-7} moles/g/hr. This is equivalent to 2.8×10^{-7}. moles N_2/g/hr, which is slightly more than the maximum rate reported by William Denison (1973), 2×10^{-7}. Thus, *L. oregana* fixes nitrogen at a a rate roughly 1,000 times that of litter and 10,000 times that of soil.

We studied the effects of pH on N_2-fixation by *L. oregana* and *L. pulmonaria*. Fourteen samples of each species were soaked in distilled water for one hour. The rate of fixation for each lichen fragment was then determined for a four hour incubation period at 20°C and 800 ft-candles. The lichens were then air dried overnight.

The next day, the same procedure was followed except that the lichens were soaked in water adjusted to pH 8, 6, 4, or 2 with NaOH or H_2SO_4. The mean rate of fixation following this treatment, divided by the rate for distilled water soak, is shown in Figures 4 and 5. The graphs also show standard deviations. Rate of fixation appears to be lower at low pH. However, there is a great deal of unexplained

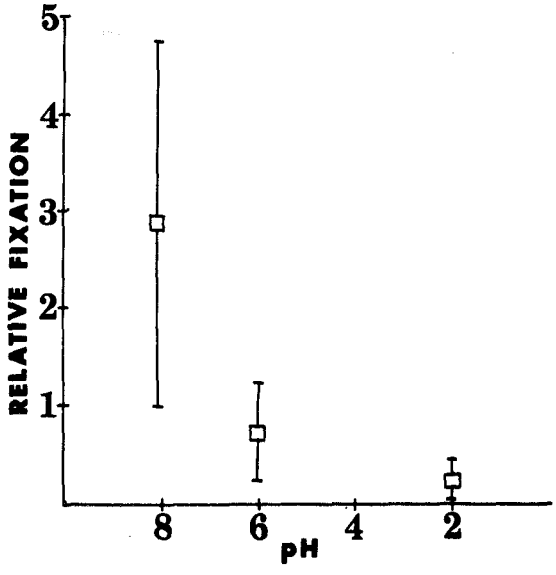

Figure 4. Short-term effects of pH on nitrogen fixation by *Lobaria oregana*.

variance.

After air drying the samples again, we repeated the distilled water soak to see whether the adverse effect of low pH lasted beyond the treatment itself. The results are shown in Figures 6 and 7. The rate of fixation after the second distilled water soak, divided by that for the first distilled water soak, is graphed as a function of the pH of the intermediate soak. The pH 2 treatment, at least, appears to have a severe and possibly permanent adverse effect on fixation.

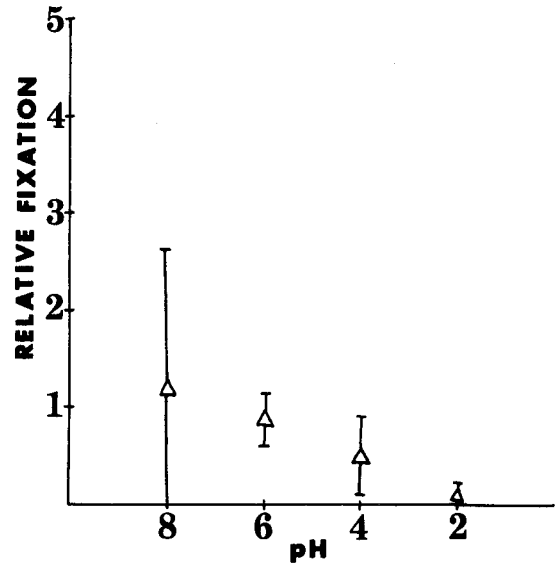

Figure 5. Short-term effects of pH on nitrogen fixation by *Lobaria pulmonaria*.

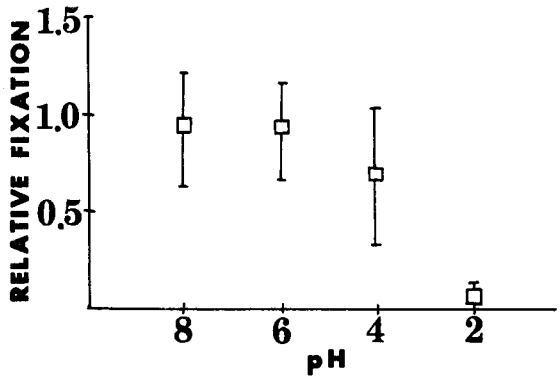

Figure 6. Lasting effects of pH on nitrogen fixation by *Lobaria oregana*.

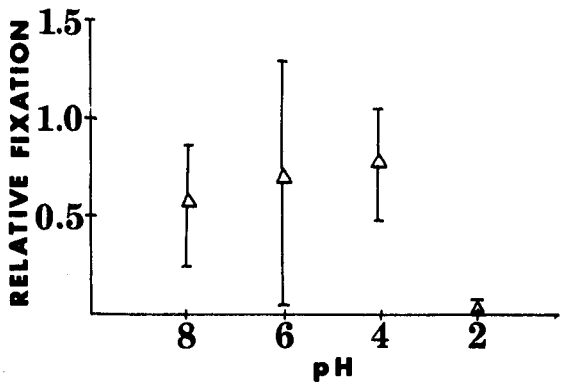

Figure 7. Lasting effects of pH on nitrogen fixation by *Lobaria pulmonaria*.

Other factors which might affect N_2-fixation were also investigated. The optimum temperature for fixation seems to be between 20 and 30° C for both *Lobaria* species. The fixation rate is lower at low light intensities and zero when the lichens are dry. We believe that N_2-fixation by these lichens is presently limited by temperature and possibly light in the winter, and by moisture in the summer. Acid rain could be important if it became more prevalent.

CULTURING OF NITROGEN-FIXING MICROORGANISMS

Despite low rates of nitrogen fixation in soil and litter, we attempted to culture the microorganisms involved, in order to identify them, study pH tolerance in pure culture, etc. Jurgensen and Davey (1971) found from zero to 3000 nitrogen-fixing bacteria per gram of soil in western Washington. We know of no reports of nitrogen-fixing blue-green algae from forest soils in this area.

BACTERIA

Soil samples were selected from the soil, humus, and litter layers at each site. 1.0 g of each sample was dissolved in 10 ml of distilled water. This solution was then further diluted 1:100, 1:1000, and 1:10000, with four plates being inoculated from each dilution. The following culture medium was used for bacteria:

900 ml	Basal salts medium (Aaronson, 1970)
1 ml	Micronutrient stock (Jurgensen and Davey, 1971)
100 ml	10% (w/v) dextrose (d-glucose) solution
10 ml	0.1% (w/v) $FeCl_3$ solution.

In addition, 1 ml of 1% (w/v) yeast extract was added to one-half of the plates. Some additional plates had biotin and thiamine added.

We incubated half the plates from each dilution aerobically and half anaerobically. We used a steel wool technique (Parker, 1955) to achieve anaerobiosis, which we confirmed using a methylene blue indicator. Both aerobic and anaerobic plates were incubated at 25 to 27°C.

After three days, small round mucoid colonies were observed on all of the plates. These were gram and spore stained and transferred to fresh plates and tubes.

When these cultures were tested by the acetylene reduction method for nitrogen fixation, no fixation was detected. Consequently, we did not attempt to identify the bacteria in the cultures. Davey (1974) points out that many bacteria will grow in "nitrogen-free" media, without the ability to fix nitrogen.

We did get measurable fixation by cultures of scuzz bacteria. From the appearance and rapid growth of the colonies, as well as the high rate of fixation, the decreased fixation when incubated in the absence of oxygen, and the large size of the bacteria, we speculate that a species of *Azotobacter* may be present in scuzz. The pH of throughfall and presumably of water flowing over the surfaces of conifer needles probably exceeds *Azotobacter's* tolerance for acid. However, perhaps among the masses of algae on the surfaces of some needles are sites where the micro-environment is more hospitable.

BLUE-GREEN ALGAE

Samples of soil, litter, and decaying wood were collected at each site and 0.5 g of each sample was swirled vigorously in a 50 ml sterile dilution blank for five minutes to distribute the organic matter. This solution was then used to inoculate 125 ml flasks with 0.75 ml aliquots and 50 ml serum jars with 0.25 ml aliquots.

A revised Chu #10 medium (Gerloff, *et.al.*, 1950) was modified to exclude all sources of combined nitrogen by substituting $CaCl_2$ for the original $Ca(NO_3)_2$. The pH of one third of the media was left unadjusted at pH 7.5 to 9.0, while one third was adjusted with 0.1 N HCl to pH 7, and the final third was adjusted to pH 4.5, which was the approximate pH of the litter. One third of all the flasks contained a small amount of glass wool to serve as a physical substrate for algal growth (Bold, 1942).

All flasks were incubated at 23 to 25°C. The serum bottles were incubated in air-tight disiccators under a 1% CO_2 atmosphere, at 25°C.

Microscopic examination of the cultures revealed no algal growth after eight weeks. This supports the findings of M. A. Line (1971), who similarly failed to find nitrogen-fixing members of the phylum Cyanophyceae (blue-green algae) in acidic soils. The Cyanophyceae have been found to be viable in the limited pH range of 5.7 to 9.0 (Allison *et. al.*, 1937). The pH values shown by the litter and soil layer in all three sites examined were considerably lower than that suggested for minimal growth. It is possible that some micro-habitats not examined could have pH values suitable for free-living blue-green algae, but it seems doubtful that significant amounts of nitrogen could be contributed thereby.

CONCLUSIONS

Rain in western Washington is slightly more acidic than one would expect under natural conditions. Increased urbanization and industrialization or relaxation of air quality standards could lead to increased precipitation acidity. Low pH can have an adverse effect on nitrogen fixation, but the severity of this effect depends on other factors as well, some of which are under man's control.

Let us consider in turn the various N_2-fixers and the factors affecting each. It is important to keep in mind the relative quantities of nitrogen fixed by various ecosystem components. The amount of nitrogen contributed by an organism is the product of its rate of fixation and its abundance. Table II gives fixed nitrogen contributed to the

TABLE II

Nitrogen contributed by selected ecosystem components.

	Fixation rate (moles C_2H_4/g/hr)	Amount (kg/ha)	N_2 fixed (kg/ha/yr)
Centralia litter	3×10^{-11}	1×10^{4}	0.03
Cedar River soil	5×10^{-12}	1×10^{6}	0.4
Quinault litter	1×10^{-10}	1×10^{5}	0.8
Quinault soil	5×10^{-11}	1×10^{6}	4.1
Lobaria oregana	4×10^{-7}	4×10^{2}	12.0

three ecosystems studied, based on our estimates of mean annual fixation rate and quantity of soil, litter, and *Lobaria oregana*. The estimated amount of *L. oregana* is based on data published by William Denison (1973). For comparison, Zavitkovski and Newton (1968) estimated that *Alnus rubra*, red alder, contributes 100 kg N/ha/yr. We were unable to calculate a contribution for scuzz without knowing more about its abundance.

The low rate of N_2-fixation in soil and litter is probably largely due to naturally acid conditions. *Azotobacter* and the blue-green algae are excluded by low pH. Moisture is also limiting in summer. Buffering by the canopy, litter, and soil may protect soil and litter microrganisms from the effects of acid rain, particularly if it is an infrequent occurence.

Nitrogen fixation by *Lobaria oregana* would probably be decreased by acidic rain. In addition this species is highly sensitive to atmospheric sulfur dioxide. William Denison (1974) found that the closely related species *L. pulmonaria* was severly damaged by a five week exposire to 50 $\mu g/m_3$ of SO_2. The main impact of man on this species, however, is destruction of its habitat, the old-growth forest. The cutting cycles currently practiced by the forest industry are not long enough to allow this species to develop. It might be possible to inoculate younger forests with the lichen to get some N_2-fixation even with shorter cutting cycles.

Red alder also contributes large amounts of fixed nitrogen. It is frequently suppressed deliberately, because it competes with Douglas fir. Newton *et al.* (1968) discuss the coexistence of alder and Douglas fir. They also suggest longer cutting cycles. In this regard, the greater fixation in soil and litter at the old-growth site deserves mention. It is possible, however, that this is entirely due to higher rainfall in summer there than at the other two sites.

The significance of N_2-fixation by needle surface microorganisms needs further investigation. We suspect that the amount of nitrogen fixed by these scuzz microorganisms is rather small. However, its ecological significance is increased by the possibility of direct foliar absorption. We have observed more scuzz near cities than in presumably less polluted areas. It is possible that some scuzz microorganisms use hydrocarbons from air pollution as an energy source. However, there is no evidence that N_2-fixing microorganisms are so stimulated. Also, air pollution or acidic rain may damage cuticular wax which would otherwise limit the growth of scuzz.

Another interesting area for research is N_2-fixation in recently logged areas. We found no detectable N_2-fixation in a single investigation of soils in clearcut areas. However, some clearcuts have large numbers of N_2-fixing members of the genera *Peltigera* and *Leptogium*. The ecology of these lichens is worthy of further study.

Lobaria pulmonaria is native to the deciduous forests of the Pacific Northwest. It is very abundant in the few remaining areas where it can tolerate the air pollution. Robert Denison (1975) reported that it appears to be limited to areas where the mean annual SO_2 concentration is less than 5 $\mu g/m^3$. Since its rate of fixation is about three times that of *L. oregana,* it could be an important input of fixed nitrogen if air quality were to improve dramatically.

It is clear that short cutting cycles, suppression of alder, and air pollution have resulted in a decrease in natural nitrogen fixation, with acid rain a possible threat in the future. It remains to be seen whether the practice of applying artificially fixed nitrogen to forests will be an adequate substitute. In any case, the high energy cost and pollution associated with artificial fixation should make preservation of natural nitrogen fixation a consideration in forest management and air

quality criteria.

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THE INFLUENCE OF AN ENDOMYCORRHIZAL SYMBIOSIS ON NITROGEN MOVEMENT THROUGH SOIL COLUMNS UNDER REGIMES OF ARTIFICIAL THROUGHFALL AND ARTIFICIAL ACID RAIN

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ABSTRACT

The effect of artificial acid rain on nitrogen uptake by a fungus [*Glomus mosseae* (Nicol. & Gerd.) Gerd. & Trappe] endomycorrhizal with roots of sweetgum tree seedlings (*Liquidambar styraciflua* L.) was investigated by applying 3 kinds of test solutions to the surfaces of soil profiles planted with five combinations of sweetgum seedlings and fungus. Soil profiles were taken from a deciduous forest and were reconstituted in plastic pipes. Test solutions applied in different months were 1) artificial throughfall, 2) high ionic strength solutions first of pH 5.9 and later of pH 3.0, and 3) artificial eastern U.S. acid rain. The five combinations of soil and plants used were: 1) sterilized soil, 2) sterilized soil + sweetgum seedlings, 3)sterilized soil + mycorrhizal fungus on pruned sweetgum seedlings, 4) sterilized soil + sweetgum seedlings + mycorrhizal fungus, and 5) sterilized soil + sweetgum seedlings + mycorrhizal fungus + indigenous microorganisms. Nitrogen concentrations in soil solution samples collected by filter candles from 5 and 25 cm depths within the soil columns were determined colorimetrically.

Differences in the soil solution nutrient concentrations among the five soil-tree-fungus treatments are interpreted as nutrient uptake or loss by plants. Following application of artificial throughfall solutions, mycorrhizal roots significantly decreased the NO_3-N and NH_4-N concentrations of soil solutions. The application of high ionic strength solutions of pH 5.9 and 3.0 produced greater NO_3-N and NH_4-N concentrations in the soil solution in columns containing the mycorrhizae than in columns containing either soil alone or in columns containing soil + sweetgum seedlings. Mycorrhizal roots appeared to loose nitrogen. When artificial eastern U. S. acid rainfall was used to acidify the top 5 cm of soil to a soil solution

pH of 2.0, NO_3-N concentrations were unaffected by soil-tree-fungus treatments while ammonia appeared to be excluded from soil exchange sites, apparently by H^+ ions. Ammonia uptake by mycorrhizal roots was not detectable and may have been masked by high NH_4-N concentrations in the soil solution or inhibited by competition with H^+ ions for the cation carrier sites at the nutrient "uptake surfaces" of the plants. Because soil solution nutrients not taken up by plants or by exchange sites in soil can be lost by leaching, it appears that acid rain will promote the leaching of NH_4-N from soil profiles but will have little influence on NO_3-N loss.

INTRODUCTION

Mycorrhizae often increase the uptake of nutrients by host plants. This study was designed to determine the effect of solutions having pH values of 3.0 and 2.0 on the nitrogen uptake capacity of mycorrhizal roots. The pattern of soil solution nitrogen concentrations in soil columns having five combinations of soil, tree seedlings, and endo-mycorrhizal fungus are reported here for three regimes in which test solutions were applied. The test solutions were: 1) artificial throughfall, 2) high ionic strength solutions of pH 5.9 and pH 3.0, and 3) artificial eastern U. S. acid rainfall. These solutions were applied to the surfaces of soil columns in plastic pipes. The effect of the type of solution applied and of the seedling and fungus treatment combinations on nutrient concentration were determined by monitoring changes in soil solution chemistry. Decreased concentration of nitrogen in the soil solutions in columns containing seedlings and seedlings + fungus compared to concentrations in columns containing soil alone is assumed to reflect nitrogen uptake by plants.

METHODS

The soil profiles were reconstituted in 15 cm diameter polyvinyl chloride pipes from A, B, and C horizon soil material taken from the Coweeta Experimental Watershed in Franklin, North Carolina. Soil filled pipes were steam heated to 90°C for three 8-hour periods to kill indigenous mycorrhizae. Ceramic water collecting candles were inserted through pipe walls into the soil at 5, 25 and 45 cm depths below the soil surface. Each water collecting candle was attached to a sample collecting bottle which could be evacuated to between -.1 and -.2 bars by use of a cartesian diver vacuum regulator and water pump aspirator system. Bottles at 5 and 25 cm were evacuated when water samples were needed while bottles at the 45 cm depth were evacuated continuously in order to prevent accumulation of water and development of anaerobic

conditions at the bottoms of the soil columns. The soil columns were therefore flow through systems in which depletion of soil solution nutrients by plants could be interpreted as a reduction in the loss of nutrients by leaching.

Soils were planted with seeds of sweetgum, (*Liquidambar styraciflua*), a deciduous forest tree, which had been sterilized for 30 seconds in 30% H_2O_2. Seedlings were thinned to three per pipe. Spores of the endomycorrhizal fungus, *Glomus mosseae*, were placed in certain soils as shown in Figure 1. At three months the tree seedlings were pruned back in some treatments.

The resulting five soil-fungus-tree treatments, each replicated 8 times were: 1) sterile soil with tree seedlings pruned back, leaving only roots, 2) sterile soil + tree seedlings, 3) sterile soil + fungus supported by pruned back seedlings, 4) sterile soil + tree seedlings + fungus, and 5) sterile soil + tree seedlings + fungus + indigenous microorganisms. Indigenous microorganisms were reinoculated by preparing a slurry of distilled water and forest soil, then filtering the slurry and applying the filtrate to the tops of the appropriate soil columns. Application of test solutions was begun when seedlings were 6 months old. Concentrations of NO_3-N and NH_4-N in samples of soil solution were determined colorimetrically (Strickland and Parsons, 1960, Solorzano, 1969). When solution pH was less than 5, samples were titrated with NaOH to pH 7 before nitrogen determinations were made. Reported values were adjusted for volume change.

RESPONSE TO ARTIFICIAL THROUGHFALL SOLUTIONS

Artificial throughfall solutions containing major cations at concentrations mimicking those in the hardwood forest throughfall (Best and Monk, 1975) and either NH_4-N or NO_3-N at concentrations of 8.7 mg nitrogen per liter were applied, 500 ml to each pipe. Different solutions were applied on different days. All soil columns simultaneously received the same solution. The sequence of solution additions was distilled water, NH_4-N containing artificial throughfall, distilled water, NO_3-N containing artificial throughfall, and distilled water. One day after each solution addition, the soil solution samples were collected from 5 and 25 cm depths for analysis. Overall average soil solution nitrogen concentrations for the 5 solution additions for each of the 5 and 25 cm depths are shown in Figures 1A and 1B.

Concentrations of NO_3-N in soil solutions at the 5 cm depth were significantly depleted in soil columns containing mycorrhizae compared to soil columns containing either soil alone or containing soil + tree seedlings. The concentrations of NO_3-N in soil solutions of the latter two treatments ranged from 3 to 15 times greater than concentrations of NO_3-N applied, showing that considerable NO_3-N was present in the soil before artificial throughfall and distilled water solutions were added.

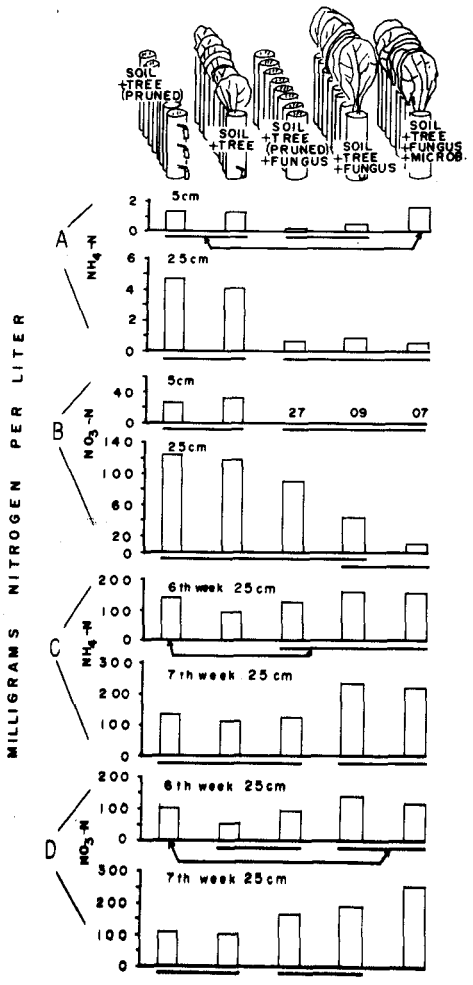


Figure 1. Mean NH_4-N and NO_3-N concentrations in soil solutions collected from 5 soil-tree-fungus treatments each replicated 8 times and subject to artificial throughfall (A and B) and to high ionic strength (C and D) nutrient additions. Horizontal bars connect means not significantly different ($p < .05$ level) as determined by Student-Newman-Keuls multiple range test (Sokal and Rohlf, 1969).

Concentrations of NH_4-N in soil solutions from the 5 and 25 cm depths were significantly depleted by mycorrhizae.

These results show that mycorrhizal roots significantly decreased the nitrogen concentrations in the soil solution. Nutrient flow past a particular depth can be estimated as the soil solution nutrient concentration multiplied by the water flow rate. Leaks at the bottoms of some columns prevented accurate water flow estimation. However, because the water flow rates through columns of soil alone are greater than through columns containing transpiring plants, we can infer that in columns where plants reduced the soil solution nutrient concentrations they also reduced the nutrient loss from that depth in the column by leaching. Mycorrhizal roots therefore decreased nitrogen movement in solution through the soil columns. These data provide a baseline for interpretation of the next experiments.

RESPONSE TO HIGH ION LOAD TREATMENTS

Solutions containing 1.2 g HCl, 6.8 g H_2SO_4, and 2.4 g HNO_3 per

liter were adjusted with NH_4OH to produce solutions of pH 5.9 for the first 500 ml application and pH 3.0 for the second application. This was done to evaluate the effect of the added ions on K, Mg, Ca, and Na movement at pH values corresponding to the Coweeta soil solution pH values and to acid rain pH values. Because these solutions contained high concentrations of nitrogen, they were not particularly helpful in evaluating the effect of the mycorrhizae on nitrogen movement. However, during the 6th and 7th weeks after solution applications, soil solution NO_3-N and NH_4-N concentrations at the 25 cm depth were greatest in columns containing mycorrhizal roots. In these columns, soil solution NO_3-N and NH_4-N concentrations increased from the 6th to the 7th week. Increased exudation by mycorrhizal roots and oxidation of the exudates may explain increased soil solution nitrogen concentrations.

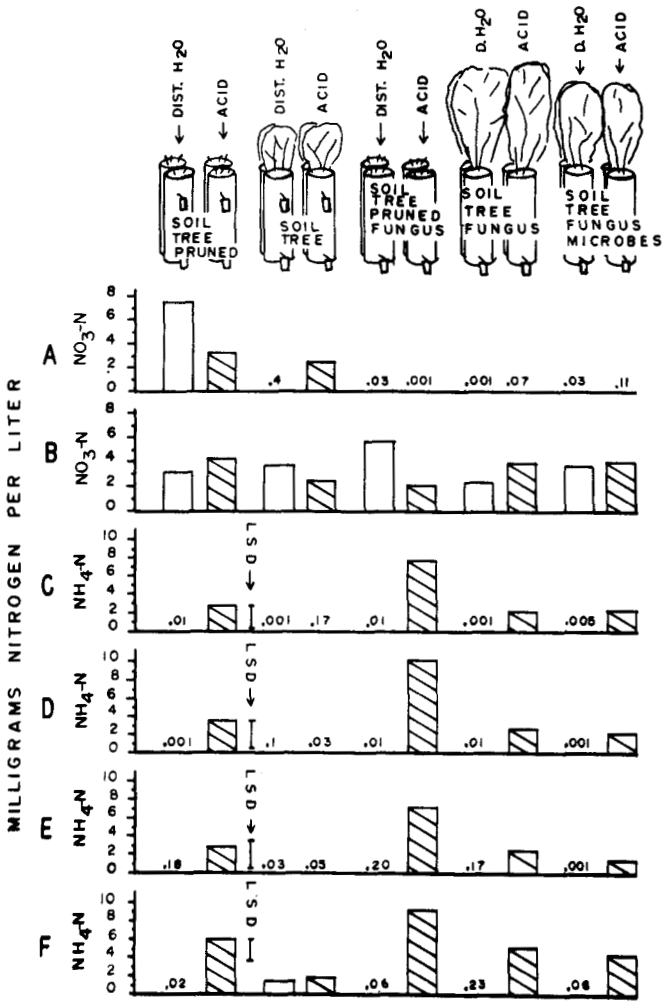
At this point four of the eight replicate soil columns in each of the five soil-tree-fungus treatments were taken apart to assess the extent of mycorrhizal infestation in the tree roots and to determine the plant weights. According to D. Marx (personal communication), U.S.D.A. Plant Pathologist, there was no evidence of damage to either the roots or to the mycorrhizal hyphae by any of the high ionic strength solution treatments.

RESPONSE TO EASTERN UNITED STATES ARTIFICIAL RAINFALL

Artificial acid rain was made from laboratory reagents and deionized water following the SO_4:NO_3:Cl ratio of about 14:7:1 reported by Cogbill and Likens (1974) for precipitation over the eastern United States. These solutions were used in a modified experimental design. The null hypothesis was that soil + tree + fungus treatments had no effect on the amounts of nitrogen in the soil solution of the top 5 cm of soil following acidification of the soil solution to pH 2.0.

The four remaining replicate pipes of each of the five soil + tree + fungus treatments, Figure 2, were used for the experiments. For each of the five soil + tree + fungus treatment types, the first two pipes received distilled water, 500 ml per application, as a control. The second pair of pipes received 500 ml of artificial acid rain. The pH of the soil solution samples from the 5 cm depth was determined 24 hours after solution applications. Because the soil solution pH changed very slowly, solutions of 0.001, 0.01, and finally of 0.1 molar H^+ were applied in efforts to reduce the soil solution pH to 2.0. A total of 0.33 moles of H^+ per pipe was required. After acidification to pH 3.0, HNO_3 was deleted; thus, subsequently applied acid solutions contained H_2SO and HCl only.

When the soil solutions reached pH 2.0, samples were retained for nitrogen analysis. This established the background concentrations. The abilities of the plants and of the soils to take up nitrogen were then tested by application of nitrogen in distilled water and in acid solutions of pH 2.0 to appropriate soil columns. Based on the few published values for nitrogen concentrations at which maximum nitrate uptake occurs in maize (Becking 1956 ; Epstein 1972), a concentration of 10 mg



Figures 2A-2F. Mean concentrations of NO_3-N and NH_4-N in soil solutions at a depth of 5 cm from 5 soil-tree-fungus treatment combinations (S-T-F). Within each S-T-F treatment, the first pair of soil columns received solutions of distilled water (Blank Bars) while the second pair received artificial acid rain (Hatched Bars) until a pH of 2 was attained at the 5 cm depth. Background concentrations of NO_3-N and NH_4-N were then determined. Abilities of plants to take up nitrogen were evaluated by adding nitrogen at concentrations of 10 mg N/liter in solutions of distilled water or in acid, applied 500 ml at a time to the surfaces of appropriate soil columns. Soil solution samples were collected after 24 hours. Least significant difference (LSD) values for ($P<.05$) relate only to columns which received acid. Fig. 2A. NO_3-N background concentrations on 18 June before nitrogen addition. Fig. 2B. NO_3-N concentrations following NO3-N additions averaged for the samples from 26 June and 7 December. Fig. 2C. NH_4-N concentrations on 18 June before NH_4-N additions. NH_4-N concentrations following NH_4-N additions are shown for 25 June in Fig. 2D, for 7 July in Fig. 2E, and for 11 July in Fig. 2F.

nitrogen per liter was chosen for application. Carrier solutions of acid or of distilled water containing nitrogen were applied to appropriate soil columns. Soil solution samples were collected 24 hours later for analysis. Additions of NO_3-N were made first as $NaNO_3$ on 25 June and with KNO_3 in December. The NH_4-N applications were made with NH_4Cl on 24 June and on 6 and 10 July. Data on nitrogen concentrations in the soil solutions were subjected to the SAS REGR analysis of variance procedures (Service, 1972) with a computer. When significant interaction effects were found in the resulting 3-way and 2-way analysis of variance tables they were broken down into 1-way tables with the SAS ANOVA program. In this way, the possible significance of differences among soil-tree-fungus treatment combinations receiving distilled water could be tested separately from those receiving acid. Results from the analysis of variance procedures are summarized in Table 1. Least significant difference (LSD) values generated by the SAS ANOVA program are given in Table 1 for each the distilled water and the acid receiving soil columns, but to avoid confusion, they are shown graphically in Figure 2 ONLY for columns which received acid.

Before NO_3-N addition to soil columns, background NO_3-N concentrations in the soil solutions were lowest (Figure 2A) in columns containing mycorrhizae. This is similar to the pattern observed in the experiments with artificial throughfall reported above and shown in Figure 1. However, with the diminished numbers of replicate soil columns, analysis of variance showed that NO_3-N concentrations were not significantly (Table 1, Trial 2A) affected by the soil-tree-fungus treatments or by the type of carrier solution. After NO_3-N addition,

Table 1. Summary of probabilities that differences among soil solution concentrations of NO_3-N and of NH_4-N occurred by chance alone as determined by 3-way, 2-way, and 1-way analysis of variance. Experimental conditions consisted of five soil-tree-fungus (S-T-F) combinations and of solution additions (SOL). Solutions were either distilled water or artificial acid rain. Solutions were applied first without, then with either NO_3-N or NH_4-N added on different dates. The effect of sampling date in trial 2B was not significant thus it is not tabulated. Least significant difference (LSD) values are indicated. Mean NO_3-N and NH_4-N concentrations from trials A through F are shown in Figures 2A through 2F.

TRIAL	ION	ION SOURCE	SAMPLE DATE	ANOVA	SOURCES OF EFFECTS			LSD ($p < .05$)
					S-T-F	SOL	S-T-F by SOL	
2A	NO_3-N	background	18 June	2-way	.2	.7	.7	-
2B	NO_3-N	added	26 June 7 Dec	3-way	.6	.4	.009	-
2C	NH_4-N	background	18 June	2-way	.0004	.0001	.0004	-
				1-way, water	.6			-
				1-way, acid	.0051			2.5
2D	NH_4-N	added	25 June	2-way	.0003	.0001	.0003	-
				1-way, water	.04			.06
				1-way, acid	.0045			3.19
2E	NH_4-N	added	7 July	2-way	.03	.001	.04	-
				1-way, water	.7			-
				1-way, acid	.08			4.9
2F	NH_4-N	added	11 July	2-way	.0026	.0001	.0003	-
				1-way, water	.052			1.06
				1-way, acid	.006			2.4

concentrations of NO_3-N in the soil solution increased (Figure 2B) but they were not significantly (Table 1, Trial 2B) affected by application date, by soil-tree-fungus treatments or by the type of carrier solution. The movement of NO_3-N through soil columns was affected by the amount of NO_3-N added, but not by the other experimental conditions.

Before NH_4-N addition, concentrations of soil solution NH_4-N (Figure 2C) were significantly greater (Table 1, Trial 2C) in the acidified soil columns than in those receiving distilled water. Concentrations also differed significantly among the soil-tree-fungus treatments which received acid. Soil solution NH_4-N concentrations following the application of NH_4-Cl either in distilled water or in artificial acid rain are shown in Figures 2D, 2E and 2F. The NH_4-N concentrations in the soil solutions were significantly greater (Table 1, Trials 2D, 2E, 2F; Figures 2D, 2E, 2F) in columns which had received NH_4-N in artificial acid rain. Soil solution NH_4-N concentrations also differed significantly among soil-tree-fungus treatments. According to 1-way analysis of variance, NH_4-N concentrations differed significantly among soil-tree-fungus treatments receiving NH_4Cl in distilled water during only one of three trials while they always differed significantly among soil-tree-fungus treatments which received artificial acid rain (Table 1). Among soil columns receiving acid rain, taking the NH_4-N concentrations in the pipe containing soil as the reference level, several features can be seen. First, concentrations of NH_4-N were consistently highest in columns in which the fungus had been supported by pruned down seedlings. At the time of NH_4-N additions in acid rain the seedlings were dead, thus the high concentrations may result from their decay. Second, compared to the reference level, concentrations were slightly lower in columns containing soil + tree + fungus and in columns containing soil + tree + fungus + microbes. These mycorrhizal roots did not significantly deplete the soil solution NH_4-N. Third, NH_4-N concentrations in soil solutions from columns containing non-mycorrhizal seedlings were between 3 and 119 times lower than in columns containing soil alone. While this difference varies greatly among trials, according to LSD interval statistics, the non-mycorrhizal seedlings significantly depleted the soil solution NH_4-N. Concentrations were decreased to about the same levels found in columns containing the non-mycorrhizal seedlings which received NH_4-N in distilled water.

DISCUSSION

Under regimes of artificial throughfall, the fungus-tree-root symbiosis clearly decreased the NH_4-N and NO_3-N concentrations in the soil solutions. When solutions having high concentrations of NH_4^+, NO_3^- Cl^- and SO_4^{-2} and lower concentrations of Na^+, K^+, Mg^{+2}, and Ca^{+2} were added in solutions of pH 3.0, nitrogen losses appeared to increase in treatments where mycorrhizae were present. Increased rates of root

exudation and subsequent oxidation of exudates might explain this observation.

In experiments where nitrogen was applied in either artificial eastern U.S. acid rain or in distilled water to pairs of soil columns in each of the five soil-tree-fungus treatment combinations, there was no evidence of NO_3-N uptake by plants. The addition of NO_3-N increased concentrations of NO_3-N in the soil solutions of all columns about equally. The NH_4-N concentrations were significantly greater in columns which has received acid than in columns which had received distilled water. This was true of NH_4-N concentrations before and after NH_4-N additions. In soil columns to which NH_4-N was added in distilled water, most of the NH_4-N apparently went onto cation exchange sites since the average NH_4-N concentrations in solution sampled at the 5 cm depth did not attain even 1 mg N per liter although solutions of 10 mg N per liter had been applied to the soil surfaces. The purpose of applying NH_4-N in distilled water was to determine if, in fact, plants not receiving acid were actually capable of taking up nitrogen at the time NH_4-N was being applied to the corresponding acid-receiving soil columns. Uptake was to be estimated as the depletion of the NH_4-N concentration of the soil solution below concentrations observed in columns containing soil alone. The problem of nutrient uptake by soils such that possible uptake by plants can be measured might be solved in future studies by use of solid support materials having a lower exchange capacity than forest soils used in this study.

Among soil columns receiving NH_4-N in acid, concentrations of NH_4-N in soil solutions were not significantly depleted by mycorrhizal roots but were significantly depleted by non-mycorrhizal roots when compared to the NH_4-N concentrations in columns containing soil alone. Differences in the behaviors of mycorrhizal and non-mycorrhizal roots might have several causes. Cation carriers of mycorrhizal roots might be more subject to inhibition by hydrogen ions than are carriers in non-mycorrhizal roots. Negative relations between cation uptake and hydrogen ion concentrations have been reported. The uptake rates of the monovalent cations K, Cs, Rb, and Na (Jacobson et al 1960) and of the divalent cations Mn, Mg, and Ca (Maas et al 1969) by barley roots were found to decrease with decreasing pH. Further, the uptake of Rb by barley roots (Rains et al 1964) and of Ca, Zn, and Mn by sugarcane leaf tissue (Bowen 1969) were shown to have been inhibited by hydrogen which competed with these ions for binding sites on the cation carriers. Alternatively, instead of possible differences in their susceptibility to the inhibition of cation transport by hydrogen ions, the mycorrhizal and non-mycorrhizal root may have been exploiting different nitrogen sources in the experimental soil columns. It is possible that the non-mycorrhizal seedlings were exploiting nitrogen supplies mostly in the upper parts of the soil columns while the mycorrhizal seedlings were exploiting nitrogen supplies in regions beneath those which had been acidified and sampled for analysis. This needs to be tested by acidifying entire soil columns.

If mycorrhizal roots are more subject to the competitive inhibition of cation uptake by hydrogen ions than are non-mycorrhizal roots, then acidification of soil solutions, as might occur under long term acid rain conditions, would result in decreased cation uptake by mycorrhizal roots. In ecosystems where mycorrhizal roots are prevalent, decreased ion uptake could lead to decreased plant productivity. Decreased uptake of cations by plants and the displacement of cations off of exchange sites into soil solution could result in losses of nutrient capital from ecosystems by leaching.

ACKNOWLEDGEMENT

Research supported by the Eastern Deciduous Forest Biome, US-IBP, funded by the National Science Foundation under Interagency Agreement AG-199, BMS 69-01147 A09 with the Energy Research and Development Administration - Oak Ridge National Laboratory. Contribution no. 244.

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SNOW AS AN ACCUMULATOR OF AIR POLLUTANTS

ROBERT T. BROWN, Michigan Technological University, Houghton, Michigan.

ABSTRACT

Using simple analytical techniques, the amounts of air pollutants accumulated in winter snow were determined and the results correlated with lichen survival on trees. Pollutants measured were particulate matter, sulfate, and chloride. An inverse relationship was found between amounts of each of these pollutants and the abundance of various lichens.

INTRODUCTION

Michigan Technological University is located on the south side of a long narrow waterway which bisects the Keweenaw Peninsula, a basaltic and sedimentary rock projection extending about 120 km northeast into Lake Superior. The steep sides of this valley rise abruptly to an elevation of about 120 meters above lake level (183.4m) (Figure 1).

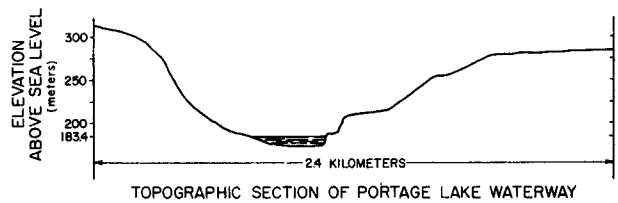

Figure 1. Location of study area. The slope on the right is Houghton where the study was conducted--a north facing slope.

The confined nature of this valley often gives rise to an atmospheric inversion, and the resulting concentration of air pollutants, especially on calm cold winter nights.

The annual snowfall over the past 25 years has averaged approximately 480 cm. This normally comes as gently falling flakes accumulating between one and six centimeters almost every day. As they fall, these flakes acquire air pollutants. In addition, the pollutants settle out and become a portion of the winter snow pack.

METHODS

By sampling the snow in March with a Mount Rose Snow Sampler, I was able to measure the pollution accumulation for the entire winter since the snow does not melt until later in spring. I sampled snow along a line from lake level to 280 m. taking samples at more or less equidistant points close to sugar maple trees. The tree lichen cover was estimated at breast height using a 25 cm × 25 cm flexible square divided into 100 equal sized sub-squares.

In the laboratory, we melted the snow samples and recorded water equivalent depth. After all twigs, leaves, seeds, and other debris were removed we filtered the water to remove particulate matter which consisted primarily of soot and fly ash. The dry weight of this particulate matter was then determined and recorded while the filtrate was evaporated to 20 ml. This was divided into two ten ml fractions; to one, I added a few drops of 1N Ba Cl_2 and to the other a few drops of 1N $AgNO_3$. By filtration, drying and weighing, I determined the weight of precipitates and thus a representation of the amount of sulfate ($BaSO_4$) and chloride (AgCl) which had been present in the atmosphere before falling out in the snow. Evaporation was carried out so that the formation of precipitates during titration would be visible.

RESULTS AND DISCUSSION

Figure 2 shows a comparison of lichen species present on a terrace 30 meters above lake level and at the top of the slope about 100 meters above lake level. Those few found on the terrace were, without exception, tiny and rare while those at the top of the slope were large and abundant as illustrated by Figure 3. The single large source of air pollution was the university heating plant at lake level. (condition now corrected)

Figures 4, 5, and 6 illustrate the inverse relationship between growth of lichens and the presence of air pollutants. Figure 7 shows the relationship between air pollution and remoteness from the primary pollution source. Brown (1974) discusses other aspects of this study.

FIGURE 2
OCCURRENCE OF LICHENS IN AREAS OF LITTLE AIR POLLUTION (TOP OF SLOPE) AND MORE AIR POLLUTION (VALLEY), SPRING, 1974

Lichen	Present on Top of Slope	Valley
Amphiloma lanugionosum (Hoffm.) Nyl.	X	
Cladonia coniocraea (Flk.) Spreng.	X	
Cladonia sp.	X	
Evernia mesomorpha Nyl.	X	
Hypogymnia sp.		X
Lecidia sp.	X	
Lobaria quercizons Michx.	X	
Mycoblastus sanguinarius Norm.	X	
Parmelia caperata (L.) Arch.	X	
Parmelia exasperatula Nyl.	X	X
Parmelia saxatilis (L.) Ach.		X
Parmelia subaurifera Nyl.	X	
Parmelia sulcata Tayl.	X	X
Physcia millegrana Degel.	X	
Usnea comosa (Ach.) Ach.	X	

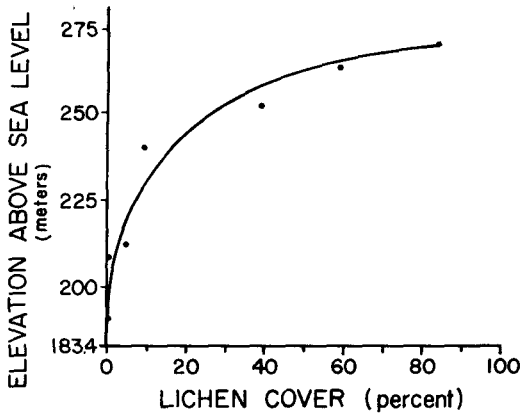

Figure 3. Relationship of lichen cover at breast height on sugar maple trees and site elevation above sea level.

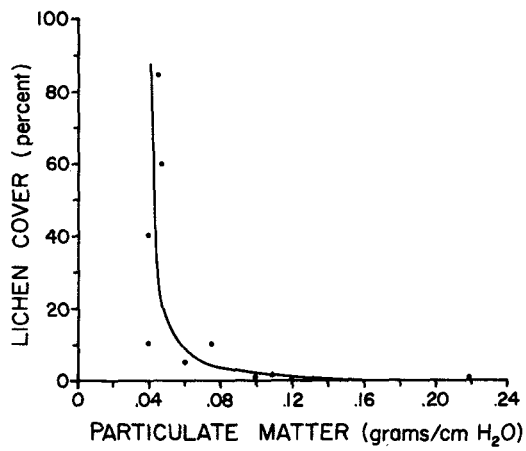

Figure 4. Relationship between particulate matter found in snow and lichen cover on tree bark.

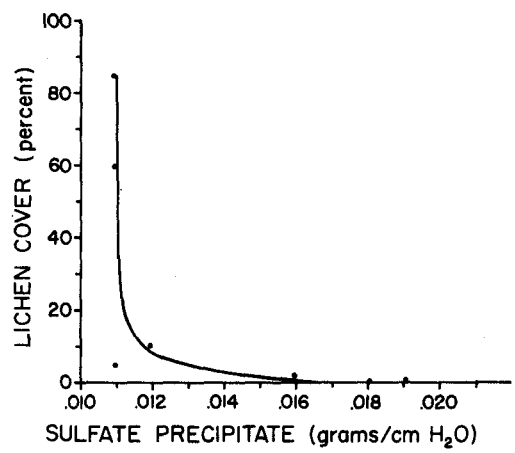

Figure 5. Relationship between sulfate precipitate found in snow and lichen cover on tree bark.

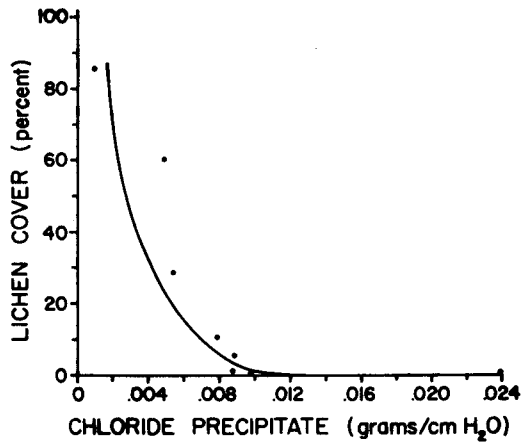

Figure 6. Relationship between chloride precipitate found in snow and lichen cover on tree bark.

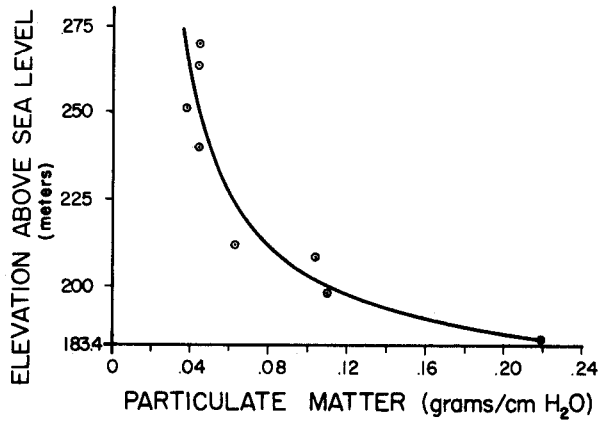

Figure 7. Comparison of amount of particulate matter in air pollutants found in snow and elevation above sea level.

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AIR POLLUTION INDICATIONS AND GROWTH OF SPRUCE AND PINE NEAR A SULFITE PLANT

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ABSTRACT

A preliminary study has been made around a sulfite plant in the north of Sweden. The emission of sulfur dioxide increased considerably in 1950 as a consequence of the introduction of lye-burning. Using the pH in pine bark and two common lichen epiphytes as indicators, the resistant Parmelia physodes and the very sensitive Alectoria implexa, the area studied was divided into regions with different degrees of air pollution, mainly sulfur dioxide:

1. Very high level of pollution
2. High level of pollution
3. Low level of pollution
4. Reference

In the first two regions the measured contents of sulfur dioxide in the air during autumn and winter 1970-71 were 1.5-5.1 pphm/month, 0.5-8 pphm/day and max 70 pphm/hour.

By employing growth quotients it was proved that the growth of annual rings of spruce and pine of these regions differed over late decades. Growth diminished with the degree of pollution. Regarding the growth of spruce all the regions differed significantly, as to the pine the regions 1, 2+3 and 4 differed substantially. By multiple regression analysis it was confirmed that the test plots most exposed to the smoke from the lye-pans had the most acid pine bark and the greatest growth reduction, but simultaneously a slight stimulation of growth has occurred near the factory. The pines were affected as early as 1950.

Later lichen investigations showed that region 2 and 3 cover 3-4000 ha and more than 10,000 ha of forest respectively.

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EFFECTS OF ACIDS ON FOREST TREES AS MEASURED BY TITRATION IN VITRO, INHERITANCE OF BUFFER CAPACITY IN PICEA ABIES

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ABSTRACT

The effect of acidic precipitation on vegetation is the result of an interaction between the acid and the plant. The metabolism of plants is dependent on optimal pH-values, which are maintained by regulation. There are differences in the effectiveness of regulation under such exogenous influences as acidic precipitation. These differences can be related to the resistance of plants to acidic precipitation or to certain pathogenic fungi. Such differences were measured as buffering capacity of homogenized leaves during titration with acid. There are significant differences in buffering capacity between clones in *Pinus* spp. and *Picea abies*. A highly significant variance in buffering capacity also was found among families of *P. abies*. Calculations of genetical parameters show that the phenotypical variance of buffering capacity is governed mainly by genetical factors.

Metabolic processes in plant cells are very sensitive to pH-changes. An optimal hydrogen ion concentration is maintained by regulation (Rypáček 1939, 1940), which acts against internal and external disturbances. The regulation processes involved can be explained by a cybernetic model (fig. 1) which shows regulation activity of a plant cell, disturbed by acid precipitation after having entered the cytoplasm.

Effects of pH-regulation can be tested by titration with H^+ or OH^-. As measurements in the plant cell are difficult, homogenized needles were titrated by which the actual buffering capacity can be measured. Buffering capacity, which is regarded as an indicator of vitality in plants (Rypáček 1939), should cause resistance of the plant to acidic precipitation. In addition to buffering capacity the regulating activity of the intact plant cell has to be taken in account.

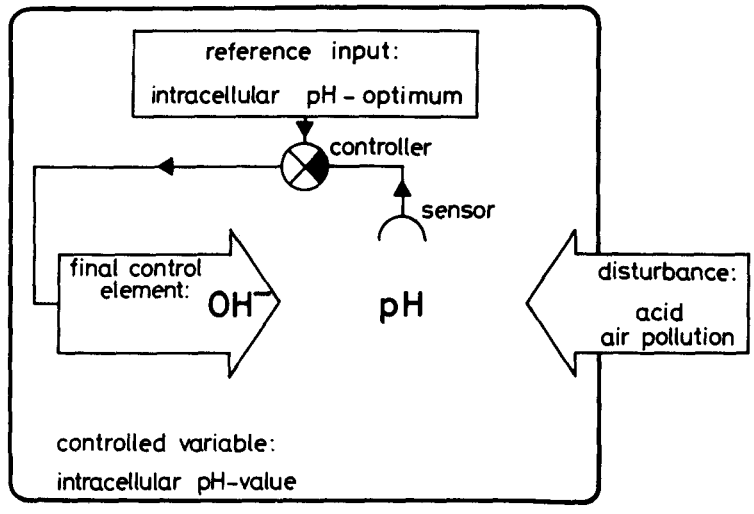

FIGURE 1. Cybernetic model of pH-regulation by a plant cell under influence of acid air pollution.

Relations between buffering capacity of needle homogenate and resistance to SO_2 were found by Grill and Härtel (1972), between buffering capacity and resistance to pH-changing fungi by Scholz and Stephan (1974).

First investigations with an automatic micro-titration method (Scholz 1975) showed significant differences in buffer capacity between *Pinus sylvestris* L., *P. strobus* L. and *P. nigra* Arn.. In this case titration was carried out with NaOH and the consumption of titrand in ml for a pH-change of one unit was taken as an index of the buffering capacity (fig. 2). *P. nigra*, which is known to be more resistant to air pollution than *P. sylvestris*, showed greater buffering capacity (the curves show averages for several clones). *P. strobus* was intermediate in both traits.

As buffering capacity could be an interesting trait for selecting trees resistant to air pollution, investigations on the genetic background of buffering capacity were carried on with *Picea abies* L. In Germany, this is an interesting species for both wood production and mechanical filtration of polluted air in industrial regions.

First the variation of buffering capacity between clones was tested. Tab I shows that almost 70% of the variation can be attributed to differences between clones and only about 8% to variation among isogenetical individuals. This points to genetic differences in buffering capacity.

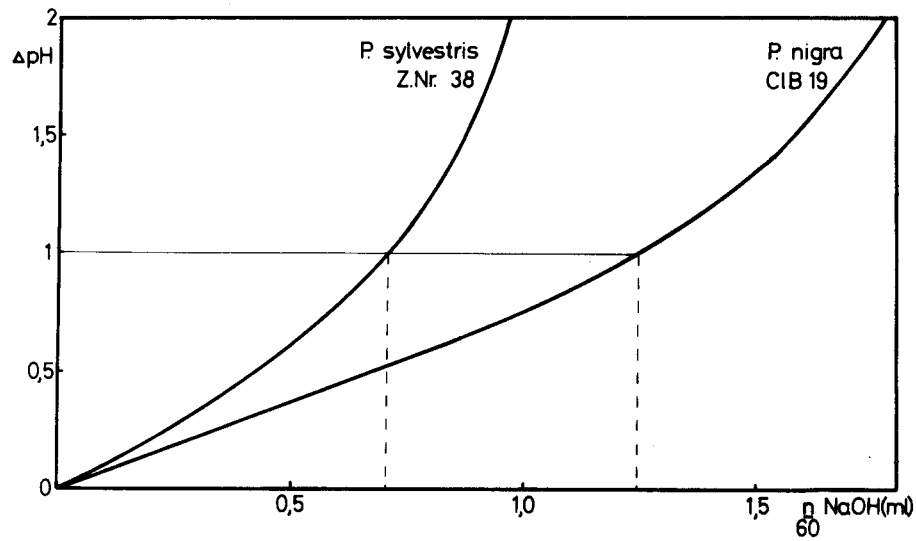

Figure 2. Titration curves of P. sylvestris and P. nigra, clones Z. Nr. 38 and Clb 19 represent the average of all investigated clones (from Scholz 1975).

TABLE I

Analysis of Variance of Buffer Capacity in Clones of Picea abies

Source of variance	d f	F-value	variance component	relative variance component
between clones	3	14.45894^{+++}	0.00697	68.81%
between ramets	12	2.62025^{+}	0.00079	7.80%
between samples	32	-	0.00237	23.40%

$^{+++}$significant at $p<0.001$

$^{+}$significant at $p<0.05$

To estimate genetic parameters for buffering capacity, controlled crossings of *P. abies* were investigated. Buffering capacity was measured as consumption of HCl in µl for a pH-change of one unit. Needle homogenates from 23 families of 7 parent trees, each family consisting of 24 trees, planted in a trial with 3 replications were titrated. An analysis of variance of buffer capacity shows that variance is mostly caused by differences between familes (Tab II). Variation between replications was relatively low. This means that genetical effects appear to be the main factors controlling variation in buffering capacity,

TABLE II

Analysis of Variance of Buffer Capacity in Families of Picea abies

Source of variance	d f	F-value	variance component	relative variance component
between families	18	32^{+++}	3.97	33%
between replications	2	<1	0	0
between families x replications	36	1.63^{+}	0.89	7.5%
between trees	171	3.69^{+++}	4.13	34%
between samples	228	-	3.05	25.5%

$^{+++}$significant at $p<0.001$

$^{+}$significant at $p<0.05$

whereas environmental effects which are estimated by the term "replications" appear to be of no practical importance.

To obtain information about the inheritance of buffering capacity a parent-offspring regression was calculated (fig. 3) which shows that there is a correlation between buffering capacity of parents and offsprings ($r = 0.39$; $0.28 < \rho < 0.48$; $p < 0.05$).

From the theoretical considerations (for further explanations see Kempthorne 1957), the additive genotypic variance σ_A^2 which is the decisive measure for any breeding program, can be estimated by using the covariance between parent and offspring (P and O)

$$\mathrm{cov}(P,O) = 1/2\ \sigma_A^2$$

The equation for calculating the coefficients of regression of offspring on parent and correlation between them is:

$$b_{OP} = \frac{\mathrm{cov}(P,O)}{\sigma_P^2}$$

and

$$r_{OP} = \frac{\mathrm{cov}(P,O)}{\sigma_P \cdot \sigma_O}\ ,\quad \text{respectively.}$$

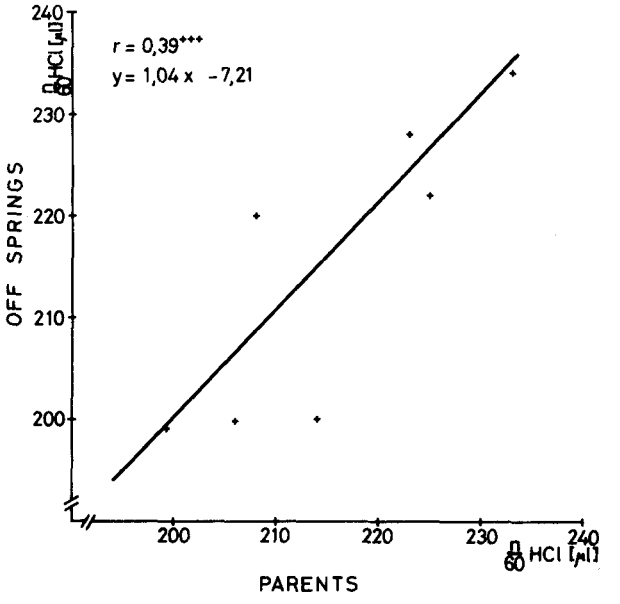

Figure 3. Regression of buffer capacity of offsprings on buffer capacity of parents of Picea abies (only means are plotted). ***p < 0.001

For we shall have $$r_{OP} = b_{OP} \cdot \frac{\sigma_P}{\sigma_O} = \frac{h^2_{n.s.}}{2} \cdot \frac{\sigma_P}{\sigma_O}$$

in which $h^2_{n.s.}$ denotes the heritability in the narrow sense ($h^2_{n.s.} = \sigma^2_A / \sigma^2_G$); the heritability can be estimated according to

$$h^2_{n.s.} = 2 \cdot r_{OP} \cdot \frac{\sigma_O}{\sigma_P}$$

The standard deviation for the parents should be not smaller than the standard deviation for the offsprings belonging to the same family

$$\sigma_P \geq \sigma_O \quad \text{and} \quad \frac{\sigma_O}{\sigma_P} \leq 1$$

Further investigations are required to calculate exactly the ratio σ_O / σ_P. On the basis of results obtained in this study, we shall assume $\sigma_O / \sigma_P \approx 1$, so that heritability can be estimated roughly by

$$h^2_{n.s.} = 2 \cdot r_{OP} = 2 \cdot 0.39 = 0.78$$

This value, which is definitely an over-estimate, indicates that about 78% of the phenotypical variance in buffering capacity is governed by genetical factors.

These investigations will be continued.

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ACKNOWLEDGEMENTS

We want to thank Mrs. R. Schmidt for her accurate technical assistance and Mr. D. Krusche for writing and performing computer programs.

ETIOLOGICAL STUDY OF THE SHORT NEEDLE DISEASE OF PINE

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ABSTRACT

The short needle disease of pines consists of dwarfing, crooking, twisting, and excessive elongation of random needles, failure of buds to develop, reduced lateral branch development and the premature casting of needles. The disease was initially associated with a power plant source of air pollution in the eastern United States during 1969; at that time the cause of the disease was unknown.

An examination of the literature revealed the short needle disease of pines had not been associated with air pollution prior to 1969. Information obtained from a series of field surveys and studies conducted to ascertain the nature and cause of the disease suggests the cause is biological. Conversely, information obtained during the same period of time does not support the thesis that the causal agent is "acid rain."

Treatment of developing candles and buds of Scotch and eastern white pines with "fly ash" and sulfuric and hydrofluoric acids did not implicate "acid rain" as the cause of the short needle disease. This conclusion is substantiated by the following: i) Sulfuric acid solutions of pH 1.7 to 2.7 induced either candle necrosis or needle necrosis and chlorosis but not short needles in field grown Scotch pines. ii) Sulfuric acid solutions of pH 3.7 and higher had no apparent effects. iii) In addition to symptoms similar to those induced by sulfuric acid, hydrofluoric acid solutions resulted in the development of some short needles. iv) Solutions of hydrofluoric acid resulted in more severe effects than had sulfuric acid of the same concentration; hydrofluoric acid is a "weak" acid compared to sulfuric acid. v) Buffered solutions of the two acids resulted in effects similar to those obtained with non-buffered acid solutions of the same concentration. vi) Treatment effects were observed at lower pH values than those of rain samples collected from the area of the pollution source.

vii) Symptoms at the bases of short needles induced by hydrofluoric acid were different from symptoms observed at the bases of short needles of diseased plants in the field.

The hypothesis that the cause of the short needle disease is biological is supported by the following: i) Symptom patterns on twigs and individual trees were not uniform. ii) Disease development in some plantations was typical of infection center patterns of disease distribution. iii) There were discontinuities in the distribution of affected plantations with respect to distance and direction from the pollution source. iv) The disease was not observed in plantations of young trees adjacent to plantations of severely affected older trees and in some situations it was not observed in plantations of older trees adjacent to affected plantations of older trees. v) Similar symptoms were observed in plantations in remote areas of Pennsylvania, Minnesota and Wisconsin. vi) Symptoms were not observed in the second flush of Virginia pines that had possessed symptoms in the initial spring flush. vii) The short needle disease was controlled by applications of insecticides and miticides applied at or during bud break. viii) Calcium oxide, a compound that one would expect to eliminate the problem if "acid rain" was the cause, had no apparent effect in controlling the disease. ix) Symptoms were induced in seedlings of Scots and eastern white pines placed in charcoal-filtered atmospheres and exposed to diseased branches from affected trees. x) Lesions, similar to those observed on the bases of short needles from diseased trees in the field, were observed on the bases of short needles in seedlings exposed to diseased branches in charcoal-filtered atmospheres.

DIVERSITY IN TREE SPECIES IN SOUTHEASTERN OHIO *BETULA NIGRA* L. COMMUNITIES

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ABSTRACT

Quantitative data were obtained for arboreal species within 50 lowland forests in southeastern Ohio., Thirty-seven communities were dominated by *Betula nigra* L. and 13 were dominated by *Acer saccharinum* L. The acidic soils collected from *B. nigra* communities contained toxic concentrations of exchangeable aluminum and low concentrations of calcium and magnesium. Tree species diversity (Shannon-Weaver index) and species equitability were inversely related to high concentrations of exchangeable aluminum and hydrogen and directly related to high concentrations of exchangeable calcium and magnesium and an increase in soil pH

INTRODUCTION

Strip mining began in Ohio in 1914 and occurs primarily in unglaciated southeastern Ohio which receives approximately 114 cm of rainfall per year. According to Riley (1960) a majority of the spoil banks created by strip mining in Ohio were left ungraded for a period of 25 years subsequent to 1914. The adverse stream chemistry associated with strip mining is due largely to sulfide-bearing compounds such as pyrite, pyritic shales, and marcasite (Blevins et al, 1970). Sulfuric acid produced from oxidation of these compounds may reach the streams by groundwater or surface runoff. Water draining from rock strata associated with coal seams may contain acid salts of aluminum, iron, and manganese (Struthers 1964).

Betula nigra L. has been found along several streams in southeastern Ohio which carry acid coal mine drainage (McClelland and Ungar 1970, Cribben and Ungar 1974). Braun (1961) and Fritts and Kirkland (1960) reported that *B. nigra* was common along streams draining areas with acid soils in Illinois, but absent along streams draining alkaline soils.

The objectives of this research were to: 1) describe and summarize arboreal species within river bottom communities that had low and high importance values for *B. nigra* including edaphic factors within these southeastern Ohio communities, 2) determine the effects of soil pH and other edaphic factors on tree species diversity and evenness, and 3) determine what effects acid mine drainage has had on succession of arboreal species within river bottom communities in southeastern Ohio.

METHODS AND MATERIALS

During the spring and summer of 1970 and 1971, 50 communities of *Betula nigra* were investigated in southeastern Ohio. Quantitative field data for *B.nigra* and other arboreal species were collected in the 50 communities using the quarter method (Cottam and Curtis 1956). Twenty-five points were established in each community with distance and dbh (diameter at breast height, 1.3 m) recorded for 100 trees. The points were approximately 20 m apart and located along the course of a stream. Trees having stem dbh of 2.54 cm or greater were measured at each point. Relative frequency, relative density, relative dominance, and importance values were calculated using techniques described by Phillips (1959) for all arboreal species in each community. Communities were designated group I if importance values for *B.nigra* exceeded 200. Group II communities had importance values for *B. nigra* that were greater than 100 but less than 200, and group III communities had importance values for *B. nigra* that were less than 100. Quantitative data for each of the 50 communities and their locations were described by Cribben and Ungar (1974).

Tree species diversity was calculated for each river bottom community within groups I, II, and III using the importance value for each arboreal species. Tree species diversity (H') and equitability (J') were determined respectively by formulas of Shannon and Weaver (1949) and Pielou (1969) for each of the 50 communities and were summarized in groups I, II, and III.

Three soil samples were collected at depths of 0-10 cm at each of the 50 river bottom communities, and if *Betula nigra* seedlings occurred at the site, the soil samples were taken near the seedlings. The samples were stored in plastic containers, taken to the laboratory, and air-dried for two weeks. Soil samples were than sifted through a 2 mm sieve and stored in plastic containers.

Soils were analyzed for pH and exchangeable calcium, magnesium, potassium, hydrogen, and aluminum concentrations. The pH was measured with a Beckman Expandomatic pH meter using a 1:1 soil-water mixture. These values varied only ± 0.2 from the field moisture measurements of pH. Exchangeable potassium, calcium, and magnesium were extracted with 1N ammonium acetate and exchangeable aluminum and hydrogen were extracted

with 1N potassium chloride using methods of Black (1965). Exchangeable aluminum and hydrogen were determined by titrating with 0.1N sodium hydroxide and 0.1N hydrochloric acid, and exchangeable calcium and magnesium were determined using an EDTA titration method (Black 1965). Exchangeable potassium was determined using a Coleman Flame Photometer as described by Black (1965). All edaphic factors were summarized for communities belonging to groups I, II, and III.

T-values were obtained using the computer program T-Nu at the Ohio University Computer Center, Athens, Ohio. Correlation coefficients were determined using the computer program Correl at the Montclair State College Computer Center, Upper Montclair, New Jersey. This program produced a matrix with nine variables which included species number, diversity, equitability, pH, and exchangeable concentrations of aluminum, calcium, magnesium, hydrogen, and potassium. All programs were run on an IBM system/360 model 44 computer.

RESULTS

River bottom communities belonging to group I were especially evident along the Moxahala and Raccoon Creeks, streams which have been subjected to heavy acid mine drainage from areas that have been extensively strip mined. The 15 group I communities contained a total of 25 arboreal species and averaged six arboreal species per community. Group I communities were dominated by *Betula nigra* (Table I). *Betula nigra* and *Ulmus americana* were the only species with importance values greater than 10.0 (Table I). Thirteen species had importance values less than 2.0 (Table I). A median soil pH of 3.8 and relatively high concentrations of exchangeable aluminum and hydrogen resulted in extremely acid soils within the group I communities (Table II). These soils also contained relatively low concentrations of exchangeable calcium and magnesium (Table II). The stage of succession represented by the Group I communities was characterized by relatively low diversity, low species equitability and low productivity (Table II).

The majority of the group II communities were located on the Raccoon Creek. The 22 group II communities contained a total of 29 arboreal species and averaged eight arboreal species per community. *Betula nigra* was the dominant species in the group II communities (Table III). *Betula nigra, Acer saccharinum, Ulmus americana, Platanus occidentalis, Carpinus caroliniana,* and *Salix nigra* had importance values greater than 10.0 (Table III). With the exception of *B. nigra,* importance values of these species were greater than in the group I communities. Soil pH was higher in the group II communities with lower concentrations of exchangeable hydrogen when compared to the group I communities (Table II). However, concentrations of exchangeable aluminum, calcium, magnesium, and potassium were similar to concentrations in the group I communities (Table II). Soil factors within these group II

TABLE I

Summary of Relative Frequency (RF), Relative Density (RD), Relative Dominance (RDo), and Importance Value (IV) for Arboreal Species Greater than 2.54 cm for 15 Ohio Group I Communities.

SPECIES	RF %	RD %	RDo %	IV
Betula nigra L.	64.6	83.2	85.7	233.5
Ulmus americana L.	5.7	2.7	2.5	10.9
Alnus serrulata (Ait) Willd.	5.7	3.1	0.2	9.0
Acer saccharinum L.	3.6	1.9	2.1	7.6
Platanus occidentalis L.	1.7	0.7	3.8	6.2
Acer rubrum L.	2.2	0.9	0.9	4.0
Prunus serotina Ehrh.	2.2	1.1	0.5	3.8
Acer saccharum Marsh.	2.2	1.0	0.4	3.6
Quercus borealis Michx.	1.9	0.8	0.6	3.3
Salix nigra Marsh.	1.4	0.5	1.1	3.0
Acer negundo L.	1.5	0.7	0.6	2.8
Fraxinus americana L.	1.4	0.6	0.4	2.4
Carya cordiformis (Wang) K. Koch	0.9	0.5	0.3	1.7
Carpinus caroliniana Walt.	1.0	0.5	0.1	1.6
Asimina triloba (L.) Dunal	1.0	0.5	0.0	1.5
Populus grandidentata Michx.	0.7	0.4	0.0	1.1
Quercus imbricaria Michx.	0.3	0.1	0.4	0.8
Populus deltoides Marsh.	0.2	0.1	0.3	0.6
Liriodendron tulipifera L.	0.3	0.1	0.1	0.5
Aesculus octandra Marsh.	0.3	0.1	0.0	0.4
Pyrus malus L.	0.3	0.1	0.0	0.4
Cornus florida L.	0.3	0.1	0.0	0.4
Carya ovata (Mill.) K. Koch	0.2	0.1	0.0	0.3
Morus rubra L.	0.2	0.1	0.0	0.3
Nyssa sylvatica Marsh.	0.2	0.1	0.0	0.3
TOTAL	100.0	100.0	100.0	300.0

Table II. Summary of species diversity (H'), evenness (J'), and productivity (basal area, m^2/hectare) including various edaphic factors for Ohio group I, II, and III communities. Mean cation concentrations were expressed in milliequivalents/ 100 g of soil.

GROUP	H'	J'	BA	pH	Al	Ca	Mg	K	H
I	.3413	.4482	42.4	3.8	2.86	0.62	0.20	0.20	1.33
II	.5882[a]	.6741[a]	80.1[a]	4.7	2.17	0.60	0.17	0.19	0.77[a]
III	.8174[ab]	.7845[ab]	66.5[ab]	5.3	0.78[ab]	1.36[ab]	0.37[ab]	0.25	0.40[ab]

[a]Diversity-evenness values and exchangeable cations were significantly different from group I at the 0.05 level.

[b]Diversity-evenness values and exchangeable cations were significantly different from group II at the 0.05 level.

communities were extreme and comparable to soil factors within the group I communities. Group II communities had significantly greater diversity, species equitability and productivity than group I communities (Table II). The stage of succession represented by the group II communities had a biomass approximately twice that of the group I communities.

The group III communities were located along Wolf, Jonathan, Symmes, Stoney, Big Beaver, South Fork, Rush, and Salt Creeks. These streams had not been subjected to acid mine drainage to the same extent as the Raccoon and Moxahala Creeks. The 13 group III communities contained a total of 39 arboreal species and averaged 11 arboreal species per community. *Acer saccharinum,* was the dominant species in group III communities (Table IV). *Acer saccharinum, Betula nigra, Acer negundo, Platanus occidentalis,* and *Ulmus americana* had importance values greater than 27.0 (Table IV). Soils within the group III communities were less acidic and contained significantly lower concentrations of exchangeable hydrogen and aluminum than the soils within groups I and II communities (Table II). Concentrations of exchangeable calcium and magnesium were significantly higher in the group III communities (Table II). These communities had significantly higher diversity and species equitability than group I and II communities (Table II). The stage of succession represented by the group III communities was characterized by a productivity lower than in the group II communities but higher than in the group I communities (Table II). Certain other species, relatively unimportant in the group I and II communities, were more important in group III (Table IV). These included *Aesculus octandra, Prunus serotina, Liriodendron tulipifera, Ulmus rubra, Fagus grandifolia,* and *Acer saccharum.*

Statistical analysis indicated a direct relationship between diversity (H') and number of species per community ($r = 0.84$; $p = 0.05$), species equitability ($r = 0.86$; $p = 0.05$), exchangeable calcium ($r = 0.36$; $p = 0.05$), exchangeable magnesium ($r = 0.43$; $p = 0.05$), and soil pH ($r = 0.47$; $p = 0.05$). There was an inverse relationship between diversity and exchangeable aluminum ($r = -0.43$; $p = 0.05$) and exchangeable hydrogen ($r = -0.61$; $p = 0.05$).

TABLE III.

Summary of Relative Frequency (RF), Relative Density (RD), Relative Dominance (RDo), and Importance Values (IV) for Arboreal Species Greater than 2.54 cm for 22 Ohio Group II Communities.

SPECIES	RF %	RD %	RDo %	IV
Betula nigra L.	41.5	52.3	58.9	152.7
Acer saccharinum L.	14.8	15.2	24.4	54.4
Ulmus americana L.	8.1	6.8	4.4	19.3
Platanus occidentalis L.	5.4	3.5	5.7	14.6
Carpinus caroliniana Walt.	7.6	5.9	0.8	14.3
Salix nigra Marsh.	5.0	4.2	1.7	10.9
Alnus serrulata (Ait.) Willd	3.7	2.6	0.1	6.4
Asimina triloba (L.) Dunal	2.3	2.4	0.2	4.9
Acer negundo L.	1.9	1.6	0.2	3.7
Quercus borealis Michx.	1.9	1.1	0.7	3.7
Liriodendron tulipifera L.	1.0	0.6	1.0	2.6
Acer saccharum L.	1.1	0.8	0.6	2.5
Prunus serotina Ehrh.	1.2	0.7	0.2	2.1
Fraxinus americana L.	1.0	0.6	0.5	2.1
Sassafras albidum (Nutt.) Nees	0.8	0.5	0.1	1.4
Carya glabra (Mill.) Sweet	0.4	0.3	0.0	0.8
Fagus grandifolia Ehrh.	0.2	0.1	0.3	0.6
Staphylea trifolia L.	0.3	0.3	0.0	0.6
Carya cordiformis (Wang) K. Koch	0.3	0.2	0.0	0.5
Fraxinus pennsylvanica Marsh.	0.3	0.1	0.0	0.4
Aesculus octandra Marsh.	0.2	0.1	0.0	0.3
Cornus amomum Mill.	0.2	0.1	0.0	0.3
Robinia pseudo-acacia L.	0.1	0.0	0.1	0.2
Juglans nigra L.	0.1	0.0	0.0	0.1
Acer rubrum L.	0.1	0.0	0.0	0.1
Celtis occidentalis L.	0.1	0.0	0.0	0.1
Cornus florida L.	0.1	0.0	0.0	0.1
Morus rubra L.	0.1	0.0	0.0	0.1
Quercus alba L.	0.1	0.0	0.0	0.1
Total	100.0	100.0	100.0	300.0

TABLE IV

Summary of Relative Frequency (RF), Relative Density (RD), Relative Dominance (RDo), and Importance Value (IV) for Arboreal Species Greater than 2.54 cm for 13 Ohio Group III Communities.

SPECIES	RF %	RD %	RDo %	IV
Acer saccharinum L.	16.4	27.3	20.3	64.0
Betula nigra L.	14.1	19.3	14.1	47.5
Acer negundo L.	14.6	7.9	18.1	40.6
Platanus occidentalis L.	8.4	17.7	7.2	33.3
Ulmus americana L.	12.3	5.0	10.5	27.8
Salix nigra Marsh.	3.1	2.6	2.3	8.0
Aesculus octandra Marsh.	2.1	1.8	1.9	5.8
Ulmus rubra Muhl.	2.1	0.7	2.9	5.7
Carpinus caroliniana Walt.	2.7	0.4	2.3	5.4
Prunus serotina Ehrh.	2.1	1.4	1.6	5.1
Alnus serrulata (Ait.) Willd.	2.3	0.1	2.5	4.9
Acer saccharum Marsh.	1.8	1.4	1.6	4.8
Fagus grandifolia Ehrh.	0.7	3.6	0.5	4.8
Liriodendron tulipifera L.	1.6	1.6	1.0	4.2
Fraxinus pennsylvanica Marsh.	1.8	0.7	1.2	3.7
Gleditsia triacanthos L.	1.6	0.9	1.2	3.7
Fraxinus americana L.	1.6	0.4	1.5	3.5
Acer rubrum L.	1.4	0.7	1.1	3.2
Quercus alba L.	0.1	3.0	0.1	3.2
Rhus typhina L.	1.4	0.1	1.6	3.1
Asimina triloba (L.) Dunal	1.2	0.1	1.3	2.6
Juglans nigra L.	1.2	0.5	0.8	2.5
Robinia pseudo-acacia L.	0.8	0.7	0.7	2.2
Rhus glabra L.	0.8	0.0	1.0	1.8
Populus deltoides Marsh.	0.3	1.1	0.1	1.5
Salix interior Rowlee	0.4	0.5	0.3	1.2
Ailanthus altissima (Mill.) Swing.	0.4	0.3	0.4	1.1
Quercus borealis Michx.	0.5	0.2	0.3	1.0
Cercis canadensis L.	0.4	0.0	0.2	0.6
Sassafras albidum (Nutt.) Nees	0.4	0.0	0.2	0.6
Viburnum prunifolium L.	0.4	0.0	0.2	0.6
Celtis occidentalis L.	0.3	0.0	0.2	0.5
Staphylea trifolia L.	0.1	0.0	0.2	0.3
Cornus amomum Mill.	0.1	0.0	0.1	0.2
Cornus florida L.	0.1	0.0	0.1	0.2
Crataegus spp.	0.1	0.0	0.1	0.2
Maclura pomifera (Raf.) Schneid.	0.1	0.0	0.1	0.2
Morus rubra L.	0.1	0.0	0.1	0.2
Sambucus canadensis L.	0.1	0.0	0.1	0.2
Total	100.0	100.0	100.0	300.0

A direct relationship existed between species equitability (J') and number of species per community ($r = 0.45$; $p = 0.05$), exchangeable calcium ($r = 0.39$; $p = 0.05$), exchangeable magnesium ($r = 0.36$; $p = 0.05$), and soil pH ($r = 0.57$; $p = 0.05$). There was an inverse relationship between species equitability and exchangeable aluminum ($r = -0.48$; $p = 0.05$) and exchangeable hydrogen ($r = -0.68$; $p = 0.05$).

Biomass as measured by basal area (m^2 per hectare) was directly related to species equitability ($r = 0.29$; $p = 0.05$), but not to diversity or any edaphic factor.

DISCUSSION

River bottom communities along the Moxahala and Raccoon Creeks in southeastern Ohio were very low in diversity and species equitability compared with river bottom communities along streams less affected by acid mine drainage. Productivity was lowest in those communities in which the median soil pH was 3.8, somewhat higher in those communities in which the median soil pH was 5.3, but highest in those communities in which the median soil pH was 4.7. This indicated that the most diverse communities did not have the greatest productivity, an observation which has been noted by Whittaker (1965) and McNaughton (1970).

Betula nigra was the dominant river bottom species along streams which carried acid mine drainage, indicating the high degree of tolerance of this species to low soil pH and accompanying extreme edaphic conditions. *Acer saccharinum, Ulmus americana, Platanus occidentalis,* and *Carpinus caroliniana* were also important along these streams and were tolerant of these edaphic conditions. *Acer negundo, Aesculus octandra, Ulmus rubra, Prunus serotina, Liriodendron tulipifera, Acer saccharum,* and *Fagus grandifolia* had low importance values or were absent along streams which were heavily polluted with acid mine water, suggesting a lower degree of tolerance of these species.

Soils collected from communities located along the Moxahala and Raccoon Creeks had pH values below 5.0, which is characteristic of acid mine affected soils. Similar pH values for acidic soils have been reported by Struthers (1964) and Blevins et al. (1970). In contrast the median pH value of 5.3 obtained for soils collected from communities along other streams was indicative of more moderate edaphic conditions within areas less affected by acid mine drainage.

Struthers (1964) and Blevins et al. (1970) demonstrated that low soil pH was commonly associated with relatively high concentrations of exchangeable hydrogen and aluminum. Our study supported their findings, in that statistical analysis indicated an inverse relationship did exist between soil pH and concentrations of these exchangeable cations. The soils along acid mine affected streams had concentrations of exchange-

able hydrogen and aluminum as high as 1.33 mew/100 g of soil and 2.86 meq/100 g of soil respectively. By contrast the soils along streams not heavily polluted by acid mine drainage had concentrations of 0.40 meq/100 g of soil and 0.78 meq/100 g of soil respectively. Foy (1974a) noted that concentrations of exchangeable aluminum in the soil generally were higher at low pH's, particularly at pH's below 5.0.

Exchangeable calcium and magnesium concentrations were relatively low in the soils most affected by acid mine drainage, but were significantly higher in the soils less affected by acid mine drainage. Low concentrations of these two exchangeable cations is characteristic of acid soils (Blevins et al. 1970).

The toxic effects of aluminum on plant growth have long been known (Hartwell and Pember 1918, Magistrad 1925). Evidence that aluminum is a major growth limiting factor in acid soils was provided by Rorison (1960) who showed that while *Scabiosa columbaria* died in both soil and nutrient solutions with a pH of 4.8 containing aluminum, the species survived in a nutrient solution with a pH of 4.8 containing no aluminum. Clymo (1962) isolated aluminum as a toxic edaphic factor in the growth of *Carex lepidocarpa*. A major factor in the success of a species in acid soil is therefore its degree of aluminum tolerance.

Species differ widely in their tolerance to soil aluminum, and such differences may affect their distribution. Rorison (1969) noted that *Deschampsia flexuosa*, which is extremely tolerant of aluminum, occurred almost exclusively on acid soils, probably because the species grows too slowly to compete with other species on neutral soils. However, the species can tolerate high aluminum concentrations which would eliminate other species from acid soils. The importance of *Betula nigra* along acid mine affected streams in southeastern Ohio may be related to the tolerance of this species to aluminum.

Oosting (1942) reported that *Betula nigra* was a good indicator of secondary succession when occurring in pure stands along streams. He also reported that 14-year old *B. nigra* communities in North Carolina had well-developed overstory trees. The overstory frequencies in these communities were *Betula nigra* (100%), *Platanus occidentalis* (20%), *Salix nigra* (60%), *Pinus taeda* (30%), while understory frequencies were *B. nigra* (100%), *Platanus occidentalis* (50%), *Liquidambar styraciflua* (60%), *Salix nigra* (10%), and *Liriodendron tulipifera* (30%).

In comparison with 14-year old *Betula nigra* communities in North Carolina, we found that a 14-year old site in southeastern Ohio which had been affected by acid mine drainage had overstory frequencies of *B. nigra* (100%), *Fraxinus americana* (16%), *Ulmus americana* (8%), *Alnus serrulata* (12%), *Acer saccharum* (12%), and *Acer saccharinum* (4%). There were few understory species in several 14-year old *B. nigra* communities in Ohio (Cribben, unpublished data). Thus the stage of succession in certain acid mine affected areas in southeastern Ohio differs markedly from the stage of succession described by Oosting (1942).

Margalef (1963), Odum (1969), Whittaker (1970), and Reiners et al. (1971) have indicated that there was a general increase in plant species diversity with succession, at least during the early stages of succession. Some acid mine areas in southeastern Ohio might also increase in species diversity during succession if soil conditions were improved along streams that carry large amounts of acid mine drainage.

High acidity and high aluminum concentrations in acid mine affected soils have provided strong selection pressures in certain southeastern Ohio river bottom communities. These selection pressures might exclude less tolerant species because of the direct and/or synergistic effects of the extreme edaphic conditions existing in these heavily polluted areas. Succession in some Ohio acid mine areas dominated by *Betula nigra* might have been limited to this early stage by these edaphic conditions.

ACKNOWLEDGMENTS

We would like to thank Dr. Thomas Devlin and Ms. Elaine Telewski of the Montclair State College Mathematics Department for their help with the statistical analysis of our data. We would especially like to thank Ms. Gloria Cribben for typing this manuscript.

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IMPACTS OF ACID PRECIPITATION ON CONIFEROUS FOREST ECOSYSTEMS[1]

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ABSTRACT

This paper summarizes the results from current studies in Norway. One main approach is the application of artificial acid "rain" and of lime to field plots and lysimeters. Application during two growth seasons of 50 mm per month of "rain water" of pH 3 to a podzol soil increased the acidity of the humus and decreased the base saturation. The reduction in base saturation was mainly due to leaching of calcium and magnesium. Laboratory experiments revealed that decomposition of pine needles was not affected by any acid "rain" treatment of the field plots. Liming slightly retarded the decomposition. No nitrification occurred in unlimed soils (pH 4.4 - 4.1). Liming increased nitrification. The soil enchytraeid (*Oligochaeta*) fauna was not much affected by the acidification. Germination of spruce seeds in acidified mineral soil was negatively affected when soil pH was 4.0 or lower. Seedling establishment was even more sensitive to increasing soil acidity. Analysis of throughfall and stemflow water in southernmost Norway reveals that the total deposition of sulphuric acid beneath spruce and pine is approximately two times the deposition in open terrain. A large part of this increase is probably due to dry deposition. Increased acidity of the rain seems to increase the leaching of cations from the tree crowns. Tree-ring analysis of spruce (*Picea abies* (L.) Karst.) and pine *Pinus sylvestris* L.) has been based on comparisons between regions differently stressed by acid precipitation and also between sites presumed to differ in sensitivity to acidification. No effect that can be related to acid precipitation has yet been detected on diameter growth.

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[1]SNSF-contribution FA 1/75

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1. INTRODUCTION

Southern Norway receives acidic pollutants with air and precipitation far in excess of what could be expected from the emissions within the region. The monthly mean pH of the precipitation varies between 4 and 5.

The deposition of acids represents a possible threat to forest and fresh-water ecosystems. An increasing number of rivers and lakes are becoming too acidic for trout (Jensen & Snekvik 1972). Occasional mass-dying of trout has been observed. Estimates of an anticipated reduction in forest growth have been given (Dahl & Skre 1971). Lysimeter studies have indicated a dramatic increase in the leaching of calcium from soil when the percolating water pH drops below 3 (Overrein 1972).

The great concern over these problems in Norway has resulted in the establishment of a large nationwide project named "Acid Precipitation - Effects on Forest and Fish" (Overrein & Abrahamsen 1975). The aim of the forest-research portion of this project is primarily to study the effects of acid precipitation on forest growth and development, secondly to study the effects on main processes influencing forest growth and development. The present paper summarizes the main approaches, and the results obtained so far, without comprehensive discussion.

2. EFFECTS ON SOIL

The effects of acid precipitation on soil properties and processes are undoubtedly very complicated. Experiments with simplified systems in the laboratory must therefore be controlled by field experiments where the complex interaction of climate, organisms, and organic and inorganic matter are largely undisturbed. Because most field experiments have to be pursued over a long period of time, these experiments have been given priority in the starting phase of the project.

The soil studies include investigations on soil fauna, decomposition and soil chemistry.

2.1. Experimental design

The soil studies are based on the application of lime and of simulated acid rain, to field plots and lysimeters. The aim of these experiments is to obtain information on the effect of acid precipitation on soil properties, soil processes, and plant growth. At present, results from one plot experiment and one lysimeter study, both started in 1972, are available. These particular experiments were located in a

semipodzolic soil (intermediate profile between podzol and brown earth), developed in a sandy, glacifluvial sediment. Soil chemical characteristics appear in Table 1. The experimental area, which is situated

Table 1. Soil chemical characteristics of the field experiments.

Soil horizon	Soil depth cm	Soil chemical properties ($\bar{x} \pm s$)				
		Loss on ignition %	pH (H_2O)	Cation exchange capacity meq/100 g	Base saturation %	N in % of oven-dry material
A_0	0-ca. 3	28 ± 10	4.4 ± 0.1	39 ± 13	25 ± 3	1.27
A_2	3-6	7.3 ± 0.9	4.4 ± 0.1	17 ± 2	15 ± 4	0.14
B	9-12	4.3 ± 0.4	4.7 ± 0.1	11 ± 1	7 ± 2	0.06

approximately 40 km north of Oslo, was clear cut about 1960 and reforested with *Pinus contorta* Douglas, in 1965. In 1974 the trees were between 2 and 4 m high. The ground flora is completely dominated by *Deschampsia flexuosa* (L.) Trin.

Three by four meter plots were treated with lime and "rain" of various acidity (Table 2). "Rain water" quality was adjusted with sulphuric acid. The simulated rain was applied in addition to the natural precipitation, and was applied once a month in the non-frozen period of the year.

The lysimeters are 29.5 cm wide and 45 cm high fiberglass cylinders. Each is filled with an undisturbed soil monolith according to the procedure described by Overrein (1968). Treatments appear in Table 2.

The leachate from the lysimeters was collected in 5-liter plastic containers. Each week, 100 ml of the leachate was analysed for pH, conductivity and colour.

The remaining leachate was stored in the field and preserved by adding HCl (10 ml per l). At the end of each month, one liter of the preserved leachate for the month was used for chemical analysis.

Table 2. Treatment of the field plot (P) and the lysimeter (L) experiment. Lime was applied as ground limestone. Experimental design: Complete randomization with 3 replicates in the plot experiment and 2 in the lysimeter study.

Liming	IRRIGATION							
	No irrigation	25 mm per month			50 mm per month			
		pH 5.7	pH 4	pH 3	pH 5.7	pH 4	pH 3
No lime	P	P L	P L	P L	P	P	P
1500 kg CaO/ha				P			
3000 " "		P	P	P			
6000 " "				P			

2.2. Soil zoology

Soil samples collected from the field experiment in October 1974 were extracted for enchytraeids (*Oligochaeta*) which is one of the most abundant groups of animals in coniferous forest soils. The procedures used in sampling, extraction, etc. are described elsewhere (Abrahamsen 1972). Other groups of soil animals were not considered.

Statistical analyses did not reveal any significant influence of the various treatments on the total abundance of enchytraeids. The three main species, however, seem to respond differently to the various treatments. *Cognettia spagnetorum* (Vejdovsky, 1877) is a dominant species in acidic raw-humus habitats (e.g. Abrahamsen 1972). Populations of this organism were significantly reduced by liming, but not by the "acid rain". *Enchytronia parva* Nielsen & Christensen, 1959, is confined to more fertile soils (Abrahamsen 1972). This organism increased in numbers with increasing acidity of the rain at a high lime concentration and decreased with increasing acidity at a low lime concentration. (Significant interaction at 1% level). The abundance of the third main species, *Enchytraeus norvegicus* Abrahamsen, 1969, has not been significantly influenced by any treatment.

2.3. Soil microbiology

Studies on microbiological processes have been focused on the decomposition of organic matter, nitrification and nitrogen fixation. No results are yet available for nitrogen fixation.

Decomposition has been studied on needles of *Pinus contorta* (Ishac & Hovland 1975). The needles were collected from the field in 1973 and

1974 in the month of November. They were incubated at 15° and 25° on moistened glass-wool in conical flasks. Weight loss was measured after 90 days.

Decomposition was significantly increased by increasing temperature from 15° to 25° C, significantly decreased by liming (3000 kg CaO per ha) and not significantly influenced by the acidity (pH 5.7 and pH 3) of the "rain".

Decomposition was also examined on needles from the control plots. The needles were moistened with various dilutions of sulphuric acid. The experiment showed that the decomposition rate (weight loss) was significantly ($P<0.05$) increased when the initial pH was increased from 1.8 to 3.5 (Figure 1). No difference was found between pH 3.5 and 4.

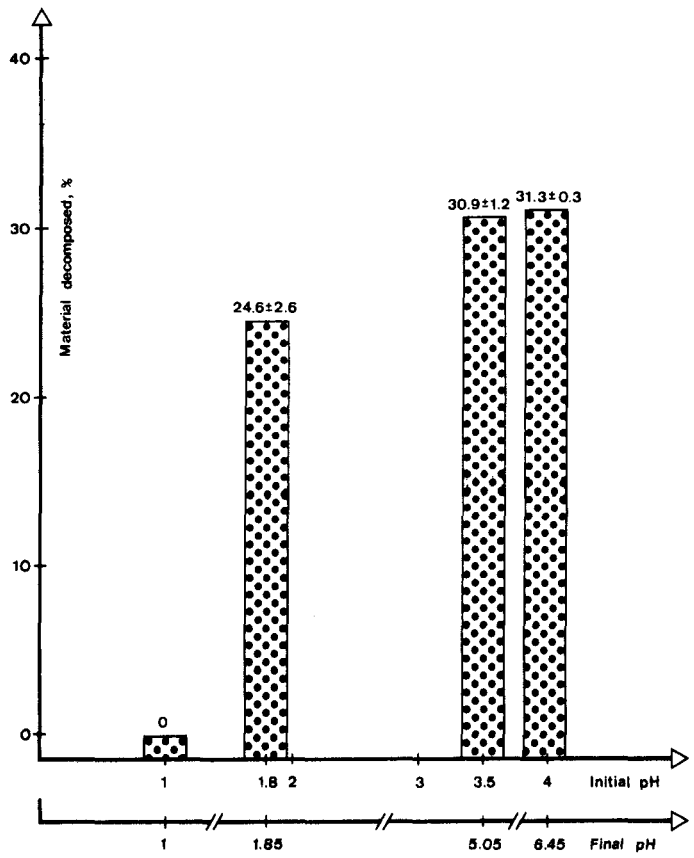

Figure 1. Effect of pH on the decomposition (weight loss after 105 days) of pine needles (*Pinus contorta*). pH of the substrate was adjusted by dilute H_2SO_4.

At pH 1 no decomposition took place.

Humus samples collected in October 1974 from the field plot experiment (Table 2) were used for nitrification experiments in the laboratory (Hovland & Ishac 1975). The experiment was carried out using a perfusion technique with the addition of $(NH_4)_2SO_4$. No nitrification occurred in humus from the unlimed plots. Liming on the other hand significantly increased the nitrification. The amount of nitrate formed was almost proportional to the quantity of lime added to the soil. No interaction was found between liming and pH. The experiment shows that in this particular soil (Table 1), the formation of nitrate is of small ecological importance probably due to the high acidity.

2.4. Soil chemistry

Soil cores sampled from the plot experiment (Table 2) in October, 1974, and the leachate of the lysimeters were analysed for chemical properties by standard methods.

Soil reaction and the amount of soluble and exchangeable nutrients in the soil of the various experimental plots are given in Tables 3 and 4. Table 3 shows the main effect of liming independently of the treatment with acid "rain". This can be given since acid "rain" had no effect on soil characteristics at the lowest rain level where lime had been applied. Liming had on the other hand highly significant effects on soil chemical properties. The decrease in potassium by increased liming must be explained by ion exchange of the two elements. The decrease in the amount of soluble and exchangable manganese is on the other hand explained by a transition to water-insoluble manganese compounds.

Effects of "rain" acidity were only observed at the highest "rain" level where no lime was applied (Table 4). Rain of pH 3 applied at a rate of 50 mm per month resulted in a significant reduction ($P < 0.01$) of the degree of base saturation. The interaction between the amount and the acidity of the "rain" was also highly significant ($P < 0.005$). The decrease in base saturation at the highest "rain" level results from the decreasing content of soluble and exchangable cations that occur in the soil when the pH of the "rain" drops from 4 to 3. The decrease in the amount of the individual cations was not, however, large enough to be statistically significant.

No effect due to the acidity of the "rain" was found on soil chemical properties in the field plots treated with 25 mm "rain" per month. However, acid "rain" applied at the same rate to the lysimeters significantly increased the leaching of calcium and magnesium (Table 5). The figures given in the table are relative, meaning that the amount of calcium or magnesium leached in 1973 at pH 5.7 is designated 1.0 and the other values are designated relative to this one. Increased leaching by increased acidity of the "rain" has not been observed for other

TABLE 3. EFFECT OF LIMING (GROUND LIMESTONE) ON SOIL CHEMICAL PROPERTIES. DATA FROM THE LOWEST "RAIN" LEVEL ONLY (25 MM PER MONTH).

Soil layer and depth cm	Kg CaO/ha 0	1500	3000	6000
			$pH_{(H_2O)}$	
Humus ca. 3 cm	4.27	5.92	6.54	6.65
Mineral soil 0-3 cm	4.31	4.75	4.85	5.14
Mineral soil 6-9 cm	4.68	4.71	4.70	4.92
			K meq/100 g	
Humus ca. 3 cm	1.15	0.87	0.73	0.85
Mineral soil 0-3 cm	0.13	0.12	0.11	0.10
Mineral soil 6-9 cm	0.06	0.06	0.06	0.05
			Ca meq/100 g	
Humus ca. 3 cm	4.8	24.1	40.6	57.6
Mineral soil 0-3 cm	1.2	4.1	5.0	7.1
Mineral soil 6-9 cm	0.4	0.8	0.6	1.1
			Mn meq/100 g	
Humus ca. 3 cm	1.07	0.58	0.50	0.53
Mineral soil 0-3 cm	0.19	0.16	0.11	0.11
Mineral soil 6-9 cm	0.04	0.05	0.04	0.03
			Base saturation %	
Humus ca. 3 cm	22	77	100	100
Mineral soil 0-3 cm	12	26	31	40
Mineral soil 6-9 cm	7	9	8	12

cations, nitrate or organic nitrogen. Nor has the acidity of the leachate been influenced by the treatment. Other lysimeter experiments in operation indicate, however, very significant increases in the leaching of most cations when the amount of rain increases and especially when it becomes more acidic than pH 3.

Table 4. The effect of the quantity and acidity of the "rain" on soil chemical properties. Data from unlimed plots only.

	25 mm/month			50 mm/month		
	pH 5.7	pH 4	pH 3	pH 5.7	pH 4	pH 3
			pH			
Humus ca. 3 cm	4.4	4.1	4.3	4.4	4.6	4.1
Mineral soil 0-3 cm	4.3	4.2	4.4	4.5	4.4	4.2
" " 6-9 cm	4.8	4.6	4.7	4.7	4.7	4.7
			Na Meq/100 g			
Humus ca. 3 cm	0.15	0.17	0.14	0.11	0.10	0.09
Mineral soil 0-3 cm	0.05	0.05	0.04	0.06	0.05	0.05
" " 6-9 cm	0.04	0.04	0.04	0.04	0.04	0.04
			K Meq/100 g			
Humus ca. 3 cm	1.14	1.32	1.00	0.99	0.85	0.87
Mineral soil 0-3 cm	0.13	0.13	0.13	0.14	0.16	0.13
" " 6-9 cm	0.06	0.07	0.07	0.06	0.07	0.06
			Ca Meq/100 g			
Humus ca. 3 cm	4.3	5.4	4.7	6.1	4.9	2.8
Mineral soil 0-3 cm	1.3	0.9	1.3	1.2	1.2	0.8
Mineral soil 6-9 cm	0.5	0.3	0.4	0.6	0.4	0.4
			Mg Meq/100 g			
Humus ca. 3 cm	1.38	1.45	1.15	1.55	1.12	0.81
Mineral soil 0-3 cm	0.39	0.30	0.30	0.39	0.34	0.23
Mineral soil 6-9 cm	0.12	0.06	0.13	0.11	0.09	0.09
			Mn Meq/100 g			
Humus ca. 3 cm	1.20	0.87	1.16	1.31	0.94	0.73
Mineral soil 0-3 cm	0.20	0.15	0.22	0.22	0.21	0.19
Mineral soil 6-9 cm	0.03	0.04	0.04	0.06	0.04	0.03
			Base saturation %			
Humus ca. 3 cm	24	19	23	25	27	18
Mineral soil 0-3 cm	14	9	13	14	11	8
Mineral soil 6-9 cm	9	5	7	7	6	6

3. EFFECTS ON TREES

3.1. Washing and leaching of tree crowns

When penetrating tree crowns, the chemical composition of the rain is altered, mainly due to the washing of absorbed deposits ("dry" deposits), and the leaching of excreted metabolites.

Table 5. The effect of acid "rain" on the relative leaching of Ca and Mg. "Rain" quantity: 25 mm per month. Leaching in 1973, pH 5.7 is designated 1.0. Differences in leaching due to different treatments are significant at the 0.1 % level.

Element	Year	pH of "rain"		
		5.7	4	3
Ca	1973	1.0	1.4	1.4
	1974	1.3	2.9	4.5
Mg	1973	1.0	1.2	1.4
	1974	1.2	1.9	2.4

The chemical composition of incident rainfall, throughfall and to a lesser degree, stemflow has been studied during three summer and autumn periods in Birkenes, South Norway, and one period in Målselv, North Norway.

Throughfall collectors were placed halfway between the stem and the perimeter of the crown projection. Incident rainfall was measured in open terrain. Stemflow was collected by means of a collar nailed to the tree.

The results (Table 6) show that the deposition of most chemical substances was higher in South Norway than in North Norway. Note, however, that the sampling period is shorter and the amount of precipitation less in North Norway. Further, the throughfall enrichment of sulphate, calcium, and potassium was greater in South Norway than in North Norway. In South Norway, the tree crowns seem to have absorbed nitrate and ammonium from rainwater. Throughfall beneath spruce and pine, in contrast to birch, contained more strong acid than did incident rainfall. In North Norway, the amounts of strong acid were negligible.

The concentrations of the different substances were in general negatively, but not significantly, correlated with the amount of rainfall or throughfall. In incident rainfall, chloride, sodium, and magnesium (mainly derived from sea salt) constituted one group of correlated ions, and ammonium, nitrate, calcium, sulphate, and strong acid constituted another. In throughfall, chloride, sodium, magnesium, ammonium, nitrate, calcium, sulphate, and potassium were correlated.

Table 6. Amount and chemical composition of incident rainfall and throughfall in Birkenes, (58°23'N, 8°15'E), South Norway (average of 1973 and 1974) and Målselv, (69°03'N, 19°20'E), North Norway (1973).

Location and Species	Period	Precip. mm	Total deposition (mg/m²) Cl.	NO3-N	NH4-N	PO4-P	SO4-S	Ca	Mg	Na	K	Strong acid	Average pH
Birkenes													
Spruce	June-Nov.	270	2560	20	20	7	990	550	220	1210	1060	50	4.4
Pine	"	370	2900	60	40	2	950	490	470	1620	770	60	4.4
Birch	"	400	1700	80	60	15	650	340	178	880	700	14	4.7
Open	"	470	990	160	140	2	490	90	70	600	60	25	4.3
Målselv													
Spruce	July-Oct.	70	740	20	110	25	110	70	70	400	450	0	5.9
Pine	"	100	890	20	60	21	110	100	80	540	410	2	5.7
Birch	"	90	210	10	30	14	50	60	30	120	250	0	5.9
Open	"	150	170	20	20	9	90	30	20	100	60	1	5.2

The lack of correlation between strong acid and the other ions in throughfall was most consistent beneath birch.

When the net removal of chemical substances from the tree crowns (throughfall minus incident rainfall values) in North Norway and South Norway is compared to values obtained from southern Sweden and from Germany (Table 7), a certain pattern appears. The removal of chloride

Table 7. Net removal of selected elements by rain from spruce crowns in different areas of Europe.

Location	km from the coast	S	Cl	Ca	Mg	Na	K	Reference
				kg/ha/year				
Målselv, N. Norway	60	0.6	17	1	1	9	12	Present paper. Data extrapolated to annual values
Birkenes, S. Norway	20	10	30	9	3	12	20	Do.
Scania, S. Sweden	15	34	35	11	4	17	21	NIHLGÅRD (1970)
Solling, BRD	200	174	-	49	7	5	45	ULRICH (1968)

and sodium reflects the distance from the coast to the study areas. The removal of potassium, magnesium, calcium and, most distinguishably, sulphur shows a considerable increase from north to south. The increase in sulphur and calcium is probably caused by a greater dry deposition, cf. the wet deposition pattern in Europe (Oden 1971, Royal Ministry for Foreign Affairs & Royal Ministry of Agriculture 1971).

The amount of stemflow increased in the order: spruce < pine < birch (Table 8). The concentration of strong acid, sulphate, chloride, calcium, and magnesium was roughly two times greater in stemflow than in throughfall. Sodium and potassium differed less. In birch the stem bark or epiphytes absorbed a considerable amount of nitrate and

Table 8. Amount and chemical compostion of stemflow. Values significantly higher (h), or lower (l), than the corresponding throughfall values are indicated. Birkenes, Norway, 1974.

Species	ml/tree	mg per l. Cl	NO_3	NH_4	PO_4	SO_4	Ca	Mg	Na	K	Strong acid	pH
Spruce	10-300	8.5	0.2	1.4	0.94h	11.7	3.5h	1.0h	4.7	4.0 l	0.07	4.9 h
Pine	50->3500	21.2h	0.3	0.3	0.03	20.3h	4.8h	1.7h	10.3h	3.7 h	0.42	3.8
Birch	800->3500	11.4h	0.1 l	0.1 l	0.13	15.0h	2.3h	1.2h	4.6	1.5	0.34h	3.7 l

ammonium. It is further noteworthy that while birch throughfall was less acidic than incident rainfall, stemflow was more acidic.

A conclusive interpretation of the results appears to be impossible at present. It is probable that a larger part of the throughfall enrichment in chloride, sulphate, calcium, sodium, and hydrogen ions in Birkenes is derived from dry deposits than from leached metabolites. Further, hydrogen ions from dry and/or wet deposits might replace other cations in the tree crowns.

3.2. Germination and establishment

The results presented here are based experiments carried out with seeds of spruce (*Picea abies* (L.) Karst.) and pine (*Pinus sylvestris* L.) in artificially acidified mineral soil (Teigen 1975).

Soils of different pH were obtained by percolating mineral soil with 1500 mm water of different pH values. Additional soil pH levels were obtained by liming. The soil used was derived from a podzolized morainic soil with a low content of plant nutrients (cation exchange capacity 10 meq/100 g and base saturation 2 per cent).

Seeds from one open pollinated tree of each species were transferred to the acidified soils. An adequate moisture regime was obtained by adding distilled water. The number of germinated seeds and established seedlings was recorded after 7 weeks. Seeds were defined to have germinated when the emerged embryo was at least 3 mm long. Seedlings were defined as established when the primary needles were developed.

The experiments with pine covered a soil pH range of 4.0 to 4.6. No effects upon germination or establishment were found within this range.

The experiments with spruce covered a soil pH range of 3.8 to 5.6. Significant effects of soil pH upon both germination and establishment were demonstrated (Figures 2 and 3). Germination seems to have a rather broad optimum around pH 4.8. Establishment seems to have a more narrow optimum around pH 4.9. About 80 per cent of the seeds did not develop

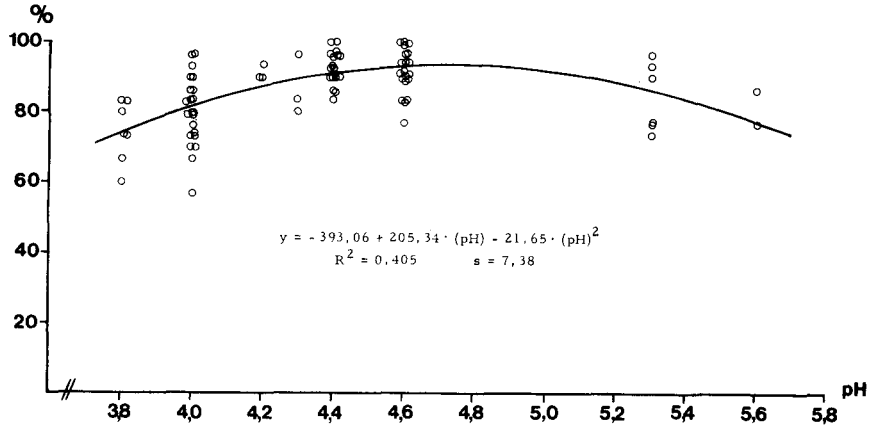

Figure 2. Relation between soil reaction and percentage of spruce seed germination.

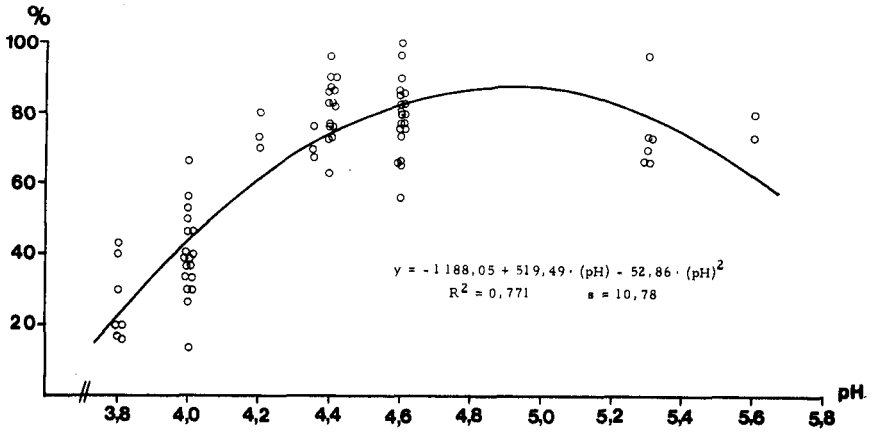

Figure 3. Relation between soil reaction and percentage of spruce seedlings established.

normal seedlings at pH 3.8. A large number of these plants had developed roots, but the roots did not penetrate into the soil. Variations in the nutrient content of the soils had no apparent effect upon germination or establishment.

3.3. Tree growth

Possible effects of acid precipitation upon tree growth are partly being studied in field experiments with simulated acid rain and partly by analysing past tree growth in different regions and on different sites. At present only preliminary results from tree ring analyses are available.

Tree ring analyses have been used in studies of air pollution effects around local emission sources (e.g. Pollanschutz 1971, Sundberg 1974). As far as we know the only attempt to use this approach in analyses of regional acidification effects has been made by Jonsson & Sundberg (1972).

Our approach and models lean heavily upon the Swedish study of Jonsson & Sundberg (1972). Tree ring development is compared: 1) between regions presumed or known to have different inputs of acid precipitation and 2) within regions between sites supposed to differ in sensitivity owing to soil properties. Increment cores of spruce (*Picea abies* (L.) Karst.) and pine (*Pinus sylvestris* L.) are obtained from the National Forest Survey which annually collects information about the Norwegian forests according to a systematic clustered sampling scheme. Sample plot information is used to stratify the material into site or regional groups.

It is necessary in the models used to have a reference period before the acidification effects started. At this stage of the study, the period from the year 1927 and onwards has mainly been investigated. Trees of the same species covering the whole investigation period are put together within sample plots to form an average-plot tree-ring series. In the models adopted, the factors influencing growth are supposed to act multiplicatively. Additive models are obtained by using logarithmic ring width as the dependent variable.

Plots within the same region or site group are combined to form average tree ring series for the separate groups. Two groups are further compared by forming a difference series which shows the relative tree ring development of the groups. The difference series are analysed for possible trend changes.

The analyses are complicated by a number of factors. Ideally there should be a negligible interaction between group and growth year. This is probably not the case in comparisons between geographically separated regions or in comparisons between regions which are extreme in ecological factors. Autocorrelation in the time series is another factor which decreases the sensitivity of the analyses. Other complicating factors are possible differences in cutting practices and intensity, stand history, and the normal time-trend between regions or site groups that are compared. The effect of these factors must be evaluated in addition to the time series analyses.

Figures 4 and 5 show the average tree ring development in pine and spruce in two geographic regions - Sørlandet and Østlandet, in South Norway and East Norway respectively - as well as the difference series between the regions. Sørlandet receives more acid precipitation and is also supposed to be more sensitive to acidification due to shallow soils.

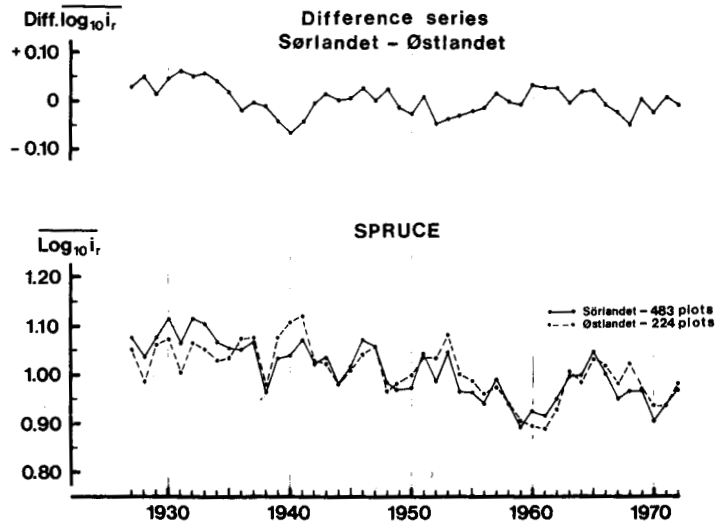

Figure 4. Tree ring development of spruce in different regions and a difference series between the regions.

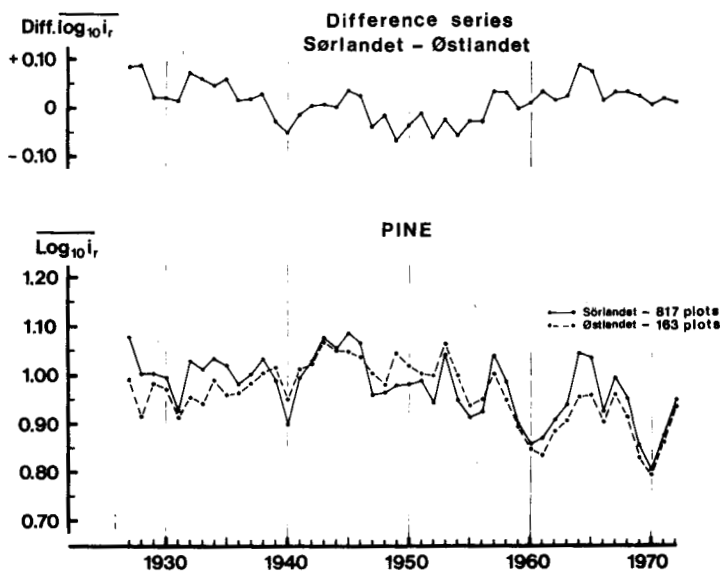

Figure 5. Tree ring development of pine in different regions and a difference series between the regions.

The main features of ring-width development are similar in the two regions pointing back to common components of climatic growth factors and time trends. The difference series reveal some fluctuations in the relative tree ring development. Interactios between region and year

seem to be a main component of these fluctuations according to preliminary analyses. These interactions decrease the sensitivity of analyses of trend changes. The year 1950 has been used as a starting point for possible acidification effects in the Swedish study. There are, however, no indications of a relatively slower growth within Sørlandet after this year. The region Østlandet is, on the other hand, also influenced by acid precipitation and does not give an ideal reference.

The data from one region (Sørlandet) have been more fully analysed in an attempt to elucidate the possible effect of different productivity (the site-class concept in forest terminology), vegetation type, water regime, soil depth, and tree species in relation to the acidification problem. Although the analyses are not completed, the difference series between extreme groups do not support the hypotheses that less productive sites, poor vegetation types, ombrogen sites, or shallow soils should be more sensitive to acidification. Neither does an analysis of the development of spruce relative to pine support the hypothesis that spruce is more sensitive to acidification when growing on poor sites. Figure 6 shows as an example the tree ring development

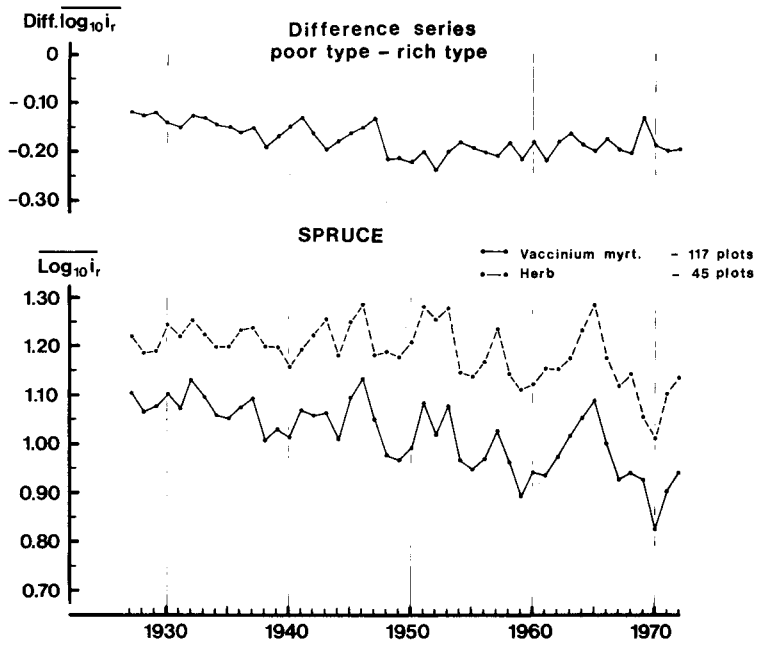

Figure 6. Tree ring development of spruce within different vegetation types and a difference series between the types. Stands from Sørlandet (South Norway) below 300 m altitude.

of spruce within two groups of vegetation types (a *Vaccinium myrtillus* type and a herb-rich type) from stands within Sørlandet and below 300 m alt. Figure 7 shows finally the development of pine on two groups of

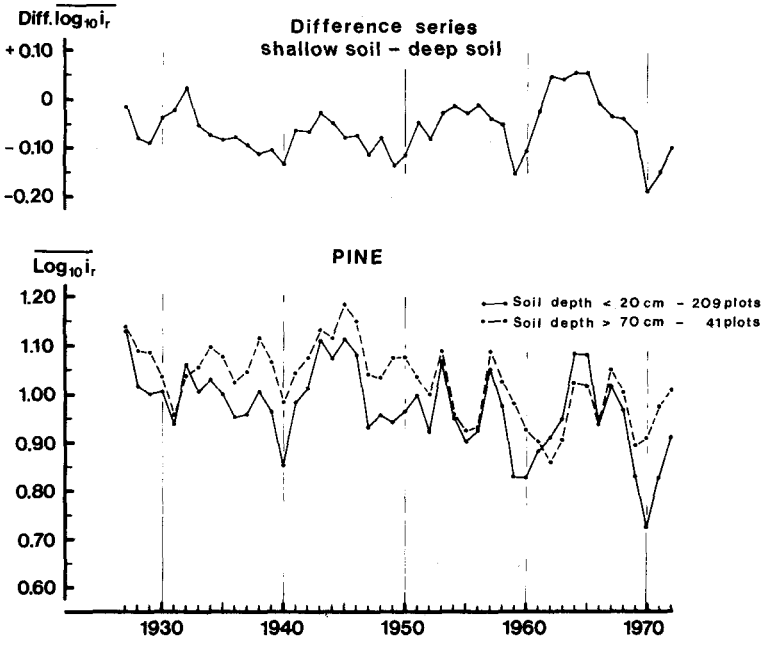

Figure 7. Tree ring development of pine on different soil depth groups and a difference series between the groups. Stands from Sørlandet (South Norway) below 300 m altitude.

soil depths (< 20 cm and > 70 cm) within the same region and height zone.

The reason for the apparent lack of relationship between tree ring development and the hypotheses about acid precipitation effects can be many-fold. The effects may be masked by other factors which are not satisfactorily isolated by the approach. The hypotheses about possible effects are based upon meagre facts and may be false. More data may be needed. It also may be that no large effects of acid precipitation upon tree growth have yet occurred.

4. SUMMARY AND CONCLUSION

The present paper summarizes the current results of ongoing studies in Norway on the impact of acid precipitation and dry deposits on coniferous forest ecosystems. These studies include investigations on soil,

leaching from tree crowns, germination, establishment of seedlings and tree ring analyses.

The soil studies are entirely based on simulated acid rainfall (pH range 5.7 - 3.0) and the application of lime, in field plots and lysimeters. Results from these experiments are at present available from an experiment running since September 1972. The results concern soil fauna, decomposition of organic matter, and soil chemistry.

The abundance of one important group of the soil fauna - the Enchytraeidae has been studied. Two species had not been influenced by the acid rain. One species decreased in abundance with increasing acidity of the "rain" at a low lime level and increased in abundance at a high lime level.

Laboratory experiments with pine needles (*Pinus contorta*) from the field plots have not revealed any influence of acid "rain" (pH range 5.7 - 3.0) on decomposition. Liming on the other hand, has reduced the decomposition rate significantly.

During the period from September 1972 to October 1974 significant reduction in the degree of base saturation has occurred in the topmost layer of the soil of the plots where the highest amounts of acid have been applied. This reduction is reflected by the increased leaching of Ca and Mg in the lysimeter experiments.

Leaching from tree crowns has been studied in Birkenes, South Norway, being heavily exposed to long transported air pollutants, and in Målselv, North Norway, which is supposed to serve as a control area.

Both the amount of various chemical components in throughfall and the ratio between concentration in throughfall and in incident rainfall are significantly higher in Birkenes than in Målselv. Conclusive interpretation of these results is impossible at present. However, the high concentrations in Birkenes may derive from dry deposition, the leaching of metabolites and the exchange of ions between plant tissue and deposited pollutants.

Green-house experiments with spruce (*Picea abies*) on artificially leached (with dilute sulphuric acid) mineral soil indicate that germination and especially establishment are negatively affected when soil reaction drops below pH 4.0 - 4.2.

Regions supposed to differ in exposure to acid deposition have been compared with regard to tree ring development. So far no differences have been found that can be related to the pollution. Nor have clear effects of acid precipitation been observed on sites supposed to be most sensitive to acidification (poor vegetation types, shallow soils, etc.).

The experiments described in the present paper indicate that severe negative influences on soil and organisms are not to be expected over a period of a few years when the acidity of the rain is above ca. pH 4. Since the acidity of the precipitation in southern Norway varies greatly between pH 3.5 and 5.7 with a prevailing pH of ca. 4.5 (1974) it seems likely that possible effects on tree growth up to now have been too small to be detected by tree ring analysis. However, longer exposure time and increased acidity of the precipitation seem to be a severe threat to soil conditions, the health of vegetation, and finally to forest production.

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EFFECTS OF APPLICATION OF SULPHURIC ACID TO POOR PINE FORESTS

C. O. TAMM, G. WIKLANDER AND B. POPOVIĆ

The department of plant ecology and soils of the College of Forestry has been interested in the problem of the acid rain as an environmental factor since the discussion of this problem started in the late 1960's (Odén 1968).

FIELD EXPERIMENTS

(by C. O. Tamm)

A field experiment was started in 1969 in a young pine forest growing on a glacifluvial eskar at Lisselbo, 160 km north of Stockholm. The experiment consisted in watering out sulphuric acid in dilute solution to plots 30 × 30 m. The treatment was given in two dosages: Acid 1 corresponding to 50 kg H_2SO_4 per hectare and year and Acid 2 twice as much. The treatment Acid 1 was not started until 1970. Both treatments were tried both alone and combined with a NPK fertilizer treatment and in the same experiment also irrigation and liming were tested with and without fertilizer. There were further experiments laid out in the same site, a nitrogen dosage experiment with and without a PK treatment and a third experiment with a balanced block design to test the effect of other nutrients PK, S, Mg and a combination of micronutrients in the presence of nitrogen (Tamm et al. 1974).

The source of nitrogen in the Lisselbo experiment was amonium nitrate and this fertilizer was added every year, first in amounts corresponding to 60 (N1), 120 (N2) and 180 (N3) kg N per hectare. After two years the fertilizer amount was lowered to 40, 80 and 120 kg N per hectare and year. The other elements have been applied at somewhat larger intervals.

The Lisselbo experiments have been revised twice and the results conclusively prove that nitrogen is a factor limiting forest growth on this site. No positive effect has been established for any of the other nutrient additions. The higher nitrogen levels appear to be supra-optimum and an optimum curve for growth in relation to nitrogen percentage in the pine foliage has been established (Fig. 1). There have been some needle injuries and shoot dieback which have been attributed to

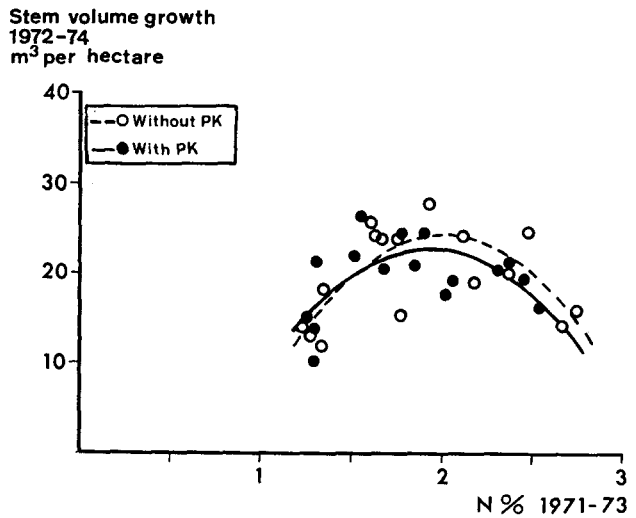


Figure 1. Stem volume growth as a function of the nitrogen concentration in current needles. Expt. E40 Lisselbo, fertilized from 1969 onwards with ammonium nitrate and in 1969, 1972 with a PK fertilizer.

frost damage (Aronsson, in preparation). These injuries have been particulary frequent on the plots receiving nitrogen. Trees on plots receiving both lime and fertilizer have been damaged particularly. Nitrogen fertilization has increased basal-area growth much more than height growth which appears to be almost unaffected by fertilization (except for the mentioned negative effect of lime). The only treatment except nitrogen application which has increased growth appears to be irrigation even if the results are not statistically significant due to the small number of replicates in the experiment (only two). Irrigation of unfertilized plots, however, had no measurable effect.

The application of sulphuric acid, particularly the treatment Acid 2, has killed much of the ground vegetation (mosses, lichens and the dwarf shrub *Calluna vulgaris*) but there is no evidence of a negative growth effect on the trees so far (Fig. 2). However, measurements of volume or basal area growth for a tree stand are relatively crude measurements so a smaller change in growth would not be detectable by the measurement method used.

Soil studies have been made within the area but the results will be briefly reported in section 3 of this paper.

The second acidification experiment started in 1971 at Norrliden 100 km northwest of Umeå in north Sweden. The site is located at about

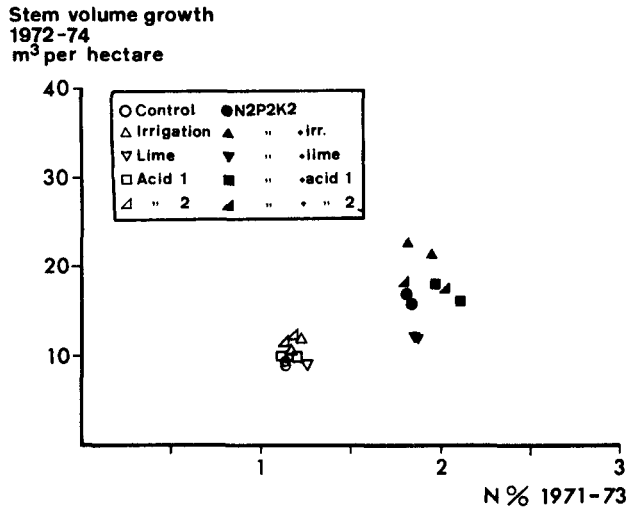


Figure 2. Stem volume growth as a function of the nitrogen concentration in current needles. Excpt. E42 Lisselbo. Treatments from 1969 onwards (cf. Fig. 1).

250 meters altitude and the soil is a glacial till. The design of the experiment is similar to that of the Lisselbo experiment although one higher level of acid was included (Acid 3, 150 kg H_2SO_4 per hectare and year). There were three replicates of each treatment in this experiment but no irrigation plots within the same experiment. However, irrigation was tested in another experiment on the same site and seemed to give a slight positive effect also here. Fertilization was also tried on the same site as in the Lisselbo experiments. The first revision of the Norrliden experiment was made in the autumn of 1974 and showed here as at Lisselbo a very clear effect of nitrogen fertilization but small effects of the other nutrient additions including the acidification (Fig. 3, 4).

LYSIMETER EXPERIMENTS

(by G Wiklander)

In the Lisselbo experimental area a lysimeter installation was made and an experiment started in May 1972. The lysimeters consisted of about 40 cm deep polyethylene buckets containing soil (medium sand) from the site. Ground vegetation and top soil were disturbed as little as possible at the installation. The buckets were drained with plastic tubes containing wicks of terylene to polyethylene flasks. The percolate was analysed at intervals. The lysimeters received the same

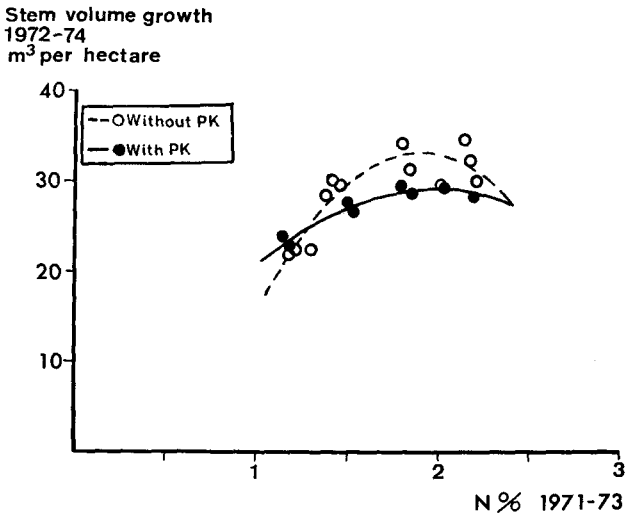


Figure 3. Stem volume growth as a function of the nitrogen concentration in current needles. Expt. E55 Norrliden, fertilized from 1971 onwards with ammonium nitrate and in 1971, 1974 with a PK fertilizer.

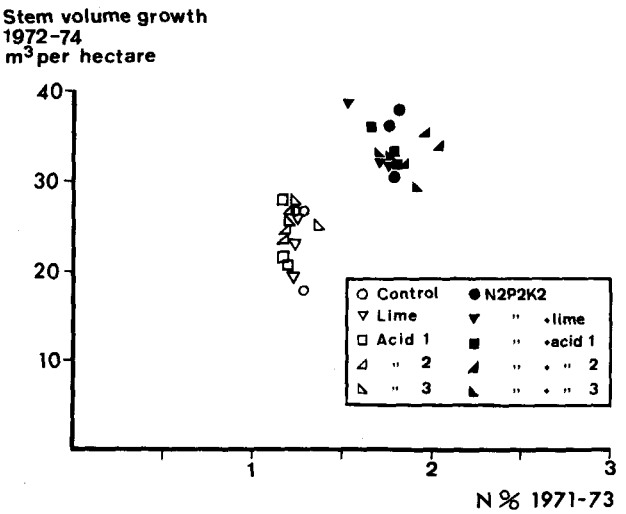


Figure 4. Stem volume growth as a function of the nitrogen concentration in current needles. Expt. E57 Norrliden. Treatments from 1971 onwards (cf. Fig. 3).

treatments as the field plots with four replicates; Control, Acid 2, N2P2K2 and the combination of these treatments. Acid 2 means 100 kg H_2SO_4 per hectare and year applied as 50 + 50 kg at an interval of one month. N2P2K2 means 120 kg N per hectare and year as ammonium nitrate and 40 kg P + 76 kg K per hectare the first year as a commercial PK fertilizer. The PK fertilizer contains also other elements, e.g. calcium (13 per cent) and sulphur (6-7 per cent).

Just after the first treatment in June 1972 there was an exceptionally heavy rain (about 90 mm) which immediately carried down a relatively large proportion of the added acid and nutrients (Fig. 5-7).

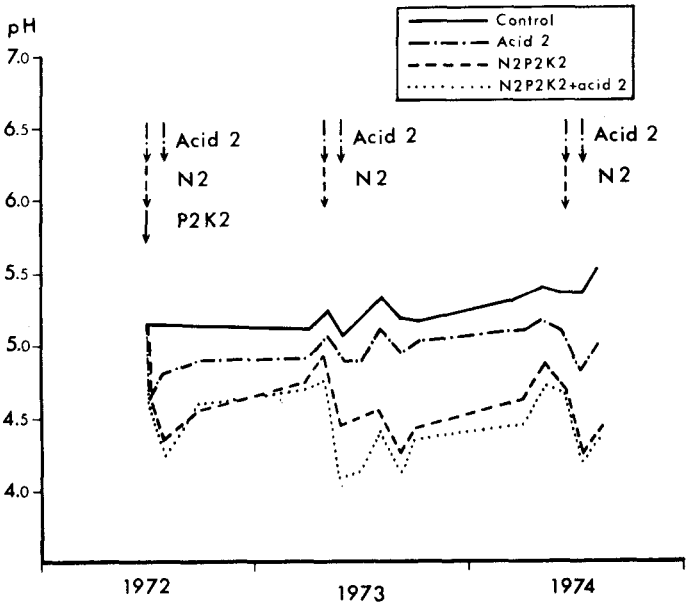


Figure 5. Lisselbo, pH of lysimeters percolates. Mean values of four repititions. Acid 2 means 50+50 kg H_2SO_4/ha, N2 means 120 kg N/ha as ammonium nitrate and P2K2 means 40 kg P/ha + 76 kg K/ha as a PK fertilizer.

However, both sulphate ions and much of the cations were retained in the soil and further leaching was rather slow. The next addition of ammonium nitrate in fertilized lysimeters led to an increased leaching of hydrogen ions and cations (Fig. 5,7). It appears as if ammonium nitrate application had a higher leaching and acidifying effect than sulphuric acid but it then has to be remembered that the number of equivalents given was considerably higher in the case of ammonium nitrate than in the case of sulphuric acid. Although sulphuric acid as well as addition of soluble salts, ammonium nitrate in particular, has an acidifying

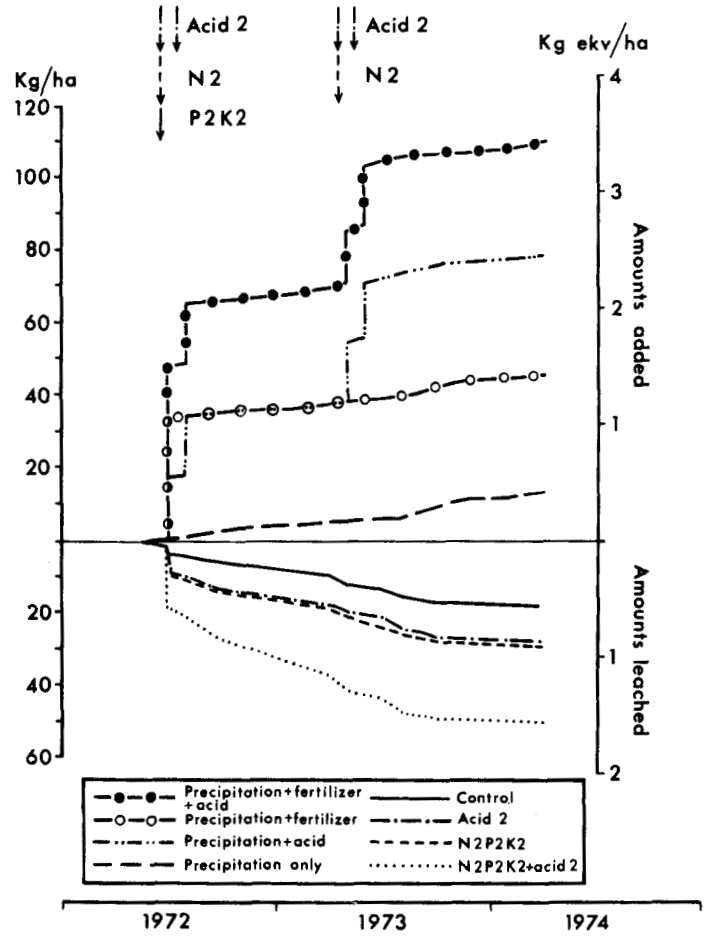


Figure 6. Lisselbo. Addition and leaching of sulphur from lysimeters (Cumulative data). Mean values of four repetitions. Amounts corresponding to Acid 2 and N2P2K2 as in Fig. 5.

effect on the leachate and also increases leaching of cations, this acid soil has an ability to retain for a considerable time a large proportion of the added ions. The leaching of cations which can be attributed to the addition of hydrogen ions as sulphuric acid is only a small proportion of the addition (Fig. 8).

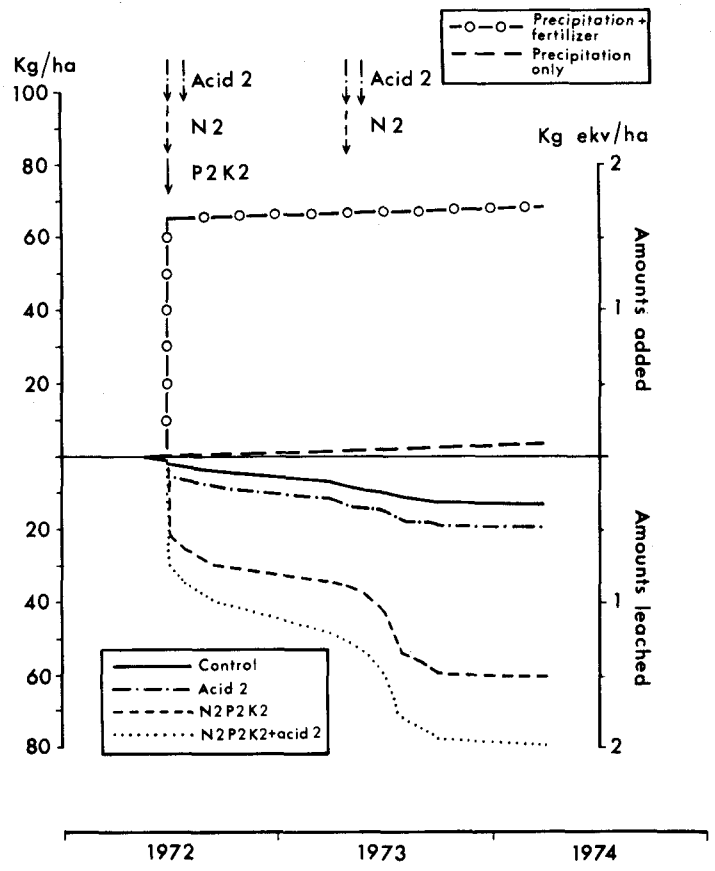


Figure 7. Lisselbo. Addition and leaching of calcium from lysimeters (Cumulative data). Mean values of four repititions. Amounts corresponding to Acid 2 and N2P2K2 as in Fig. 5.

SOIL INCUBATION EXPERIMENTS
(by B. Popović)

Soil samples (A_O horizon) have been collected from the various plots in both the Lisselbo and the Norrliden experiments. They have then been incubated in the laboratory and the release of nitrogen has been measured after intervals of six to nine weeks. There have also been model experiments carried out with humus samples from untreated areas of the experiments (both Lisselbo, Norrliden and a new experimental area where an acidification experiment was started in 1973, Åseda, northeast of Växjö in south Sweden).

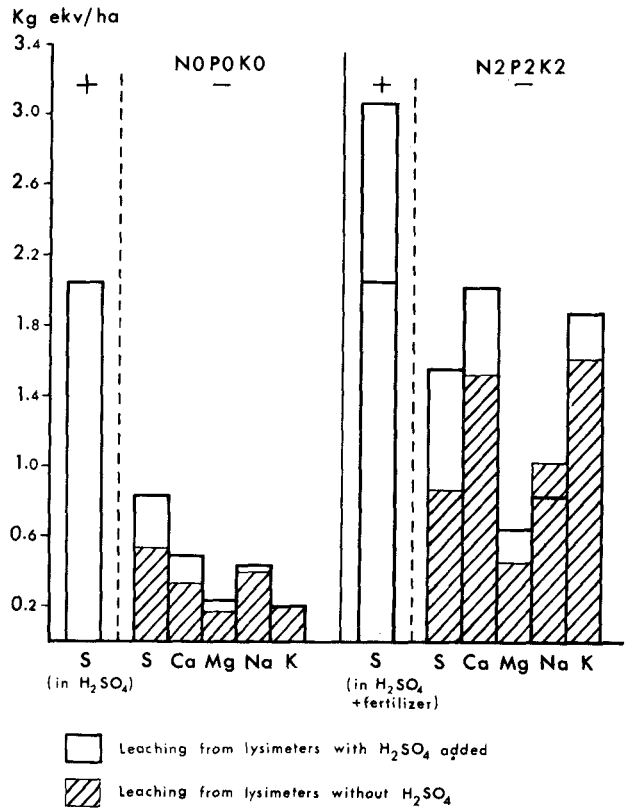
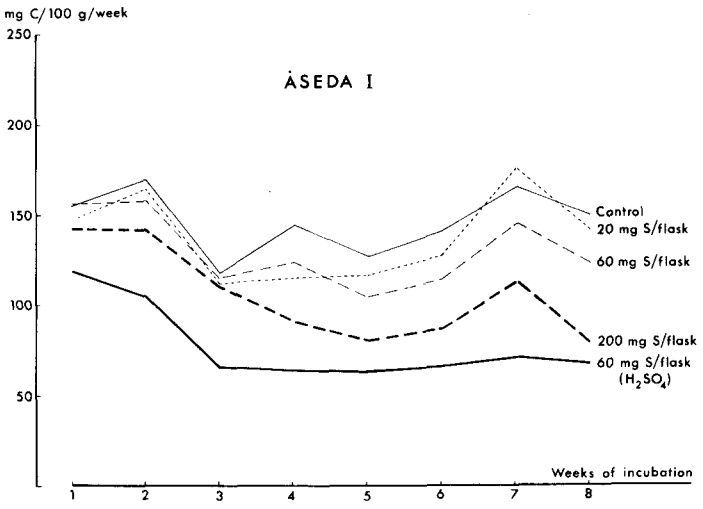
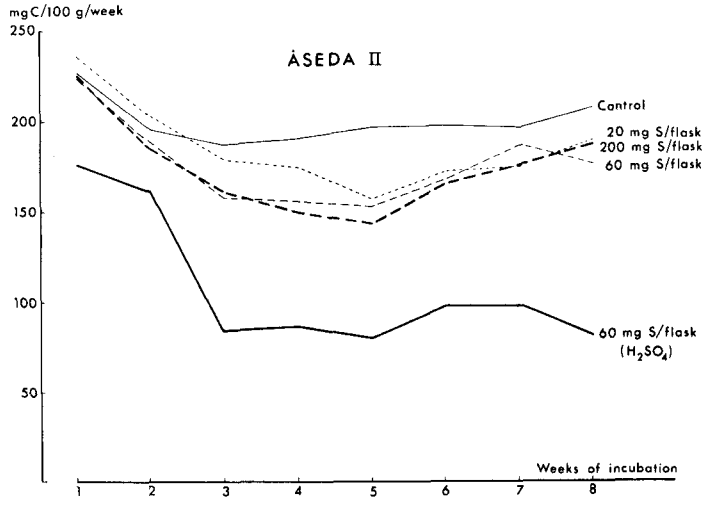


Figure 8. Lisselbo. The effect of addition of H_2SO_4 on the leaching of various elements. Mean values of four repetitions.

The incubation experiment of soil samples were carried out at a temperature of 20°C and soil moisture adjusted to 60% WHC. In some experiments the carbon evolution during the incubation experiment was measured with a technique recommended by Nömmik (1971).

The results from the model experiments in the laboratory are more consistent than the incubation experiments with samples from field plots. There always is a local variation between plots which causes a scattering in the results. We therefore first report the results from the experiment with the Åseda samples which were from two different sites representing different experimental blocks in the field experiment. In both cases an addition of either sulphuric acid or powdered sulphur caused a distinct depression of the release of carbon dioxide during the incubation period (Fig. 9, 10). Sulphuric acid was more effective than sulphur in this respect. pH measurements showed that the lowest addition of sulphur iad no depressing effect on pH, while 60 mg S as sulphuric acid lowered pH in flask with half a pH unit. The same amount

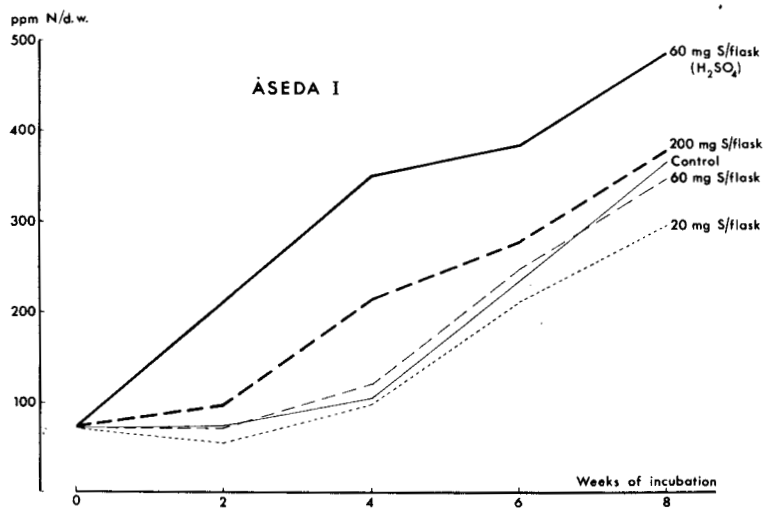


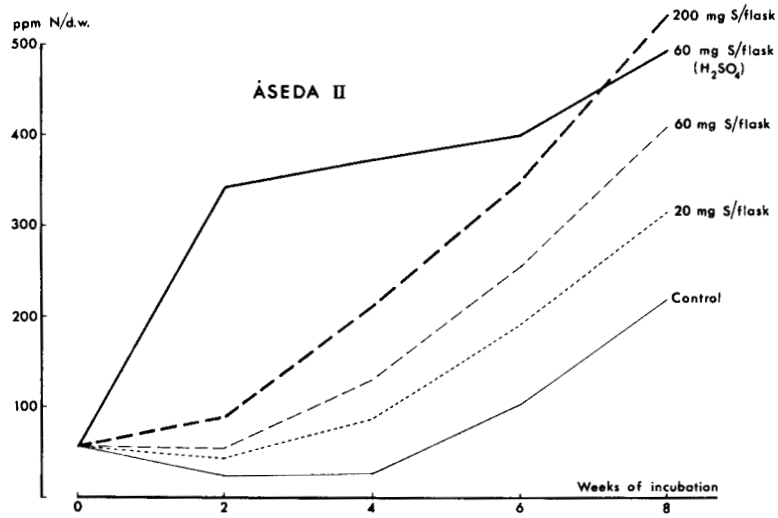


Figures 9 and 10. Respired quantity of CO_2 in mg C/100 g D. W. per week during incubation of humus samples pretreated with different doses of powdered sulphur or sulphuric acid. Experimental area Åseda I and Åseda II. Mean values of three repetitions.

as powdered sulphur had no measurable effect on pH but depressed carbon dioxide evolution, 200 mg S in powdered form depressed carbon dioxide evolution even more and lowered pH about two tenths of a unit. All these comparisons concern differences between control flasks and

treated flasks; pH increased from 4.1 - 4.2 at start to 4.4 - 4.5 at end in the controls. In the case of release of mineral nitrogen the tendency was opposite (Fig. 11, 12). The additions of sulphur usually





Figures 11 and 12. Accumulation of inorganic nitrogen content in humus samples during eight weeks' incubation and pretreatment by different doses of powdered sulphur or sulphuric acid. Sampling at two weeks' interval. Experimental area Åseda I and Åseda II. Mean values of three repetitions.

increased the amount of mineral nitrogen in the samples (most pronounced for the addition as sulphuric acid), but lowered the amount of nitrate (Fig. 13-16).

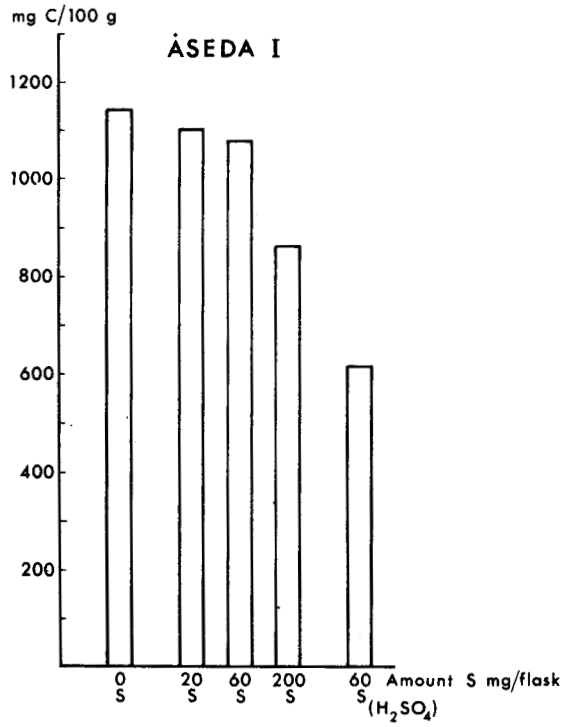


Figure 13. Total amount of CO_2 (mg C/100 g initial d.w.) respired during eight weeks incubation. Experimental area Åseda I. Mean values of three repetitions.

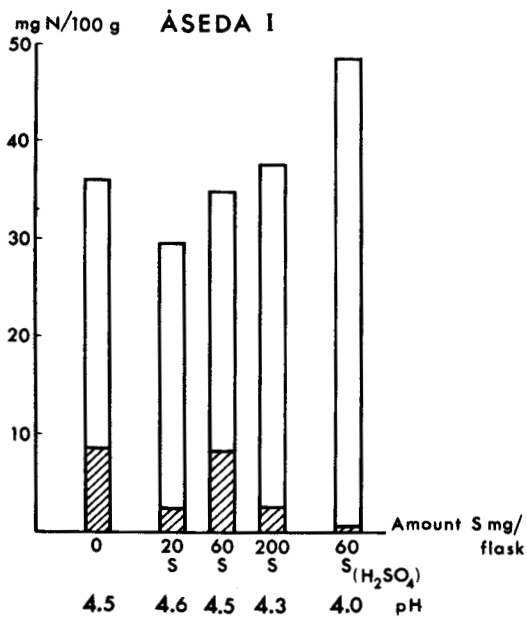


Figure 14. Total amount of inorganic nitrogen (mg N per 100 g) after eight weeks' incubation in humus samples pretreated in different ways from experimental area Åseda I. Mean values of three repetitions. Hatched area refers to nitrate nitrogen.

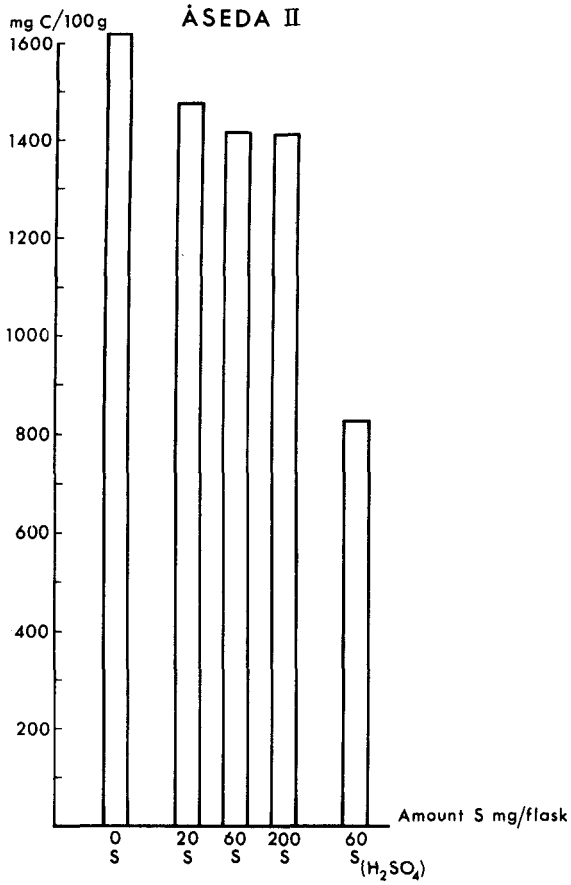


Figure 15. Total amount of CO_2 (mg C/100 g initial d.w.) respired during eight weeks' incubation. Experimental area Åseda II. Mean values of three repetitions.

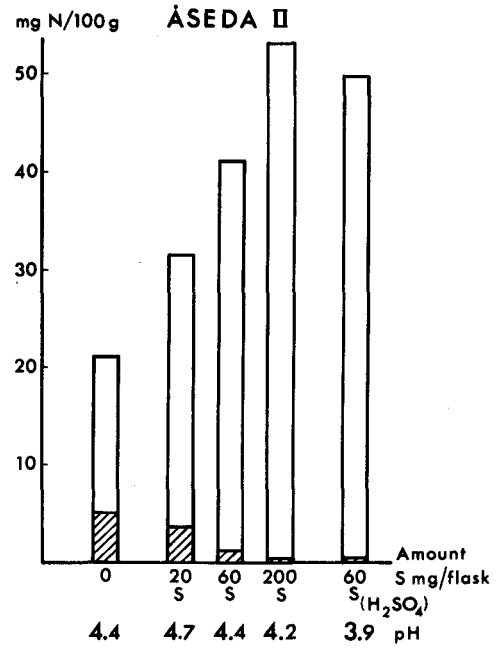


Figure 16. Total amount of inorganic nitrogen (mg N per 100 g) after eight weeks' incubation in humus samples pretreated in different ways from experimental area Åseda II. Mean values of three repetitions. Hatched area refers to nitrate nitrogen.

A similar increase in mineral nitrogen after acidification had also been established in experiments with soil from the Lisselbo experimental areas. In the absence of data on carbon dioxide evolution we had difficulties to explain the results of the earlier experiments. However, with CO_2 data available it seems safe to conclude that an acidification of the soil decreases microorganism activity in the samples and that this decrease is apparently more pronounced as regards the immobilization processes (including microbial growth) than in the case of decomposition processes. The increased availability of nitrogen in the samples should probably be looked upon as a result of a disturbance rather than as a positive effect.

As said before, rather variable results have been obtained in incubation experiments with samples from the various plots treated in the field. Table 1, where the six first lines represent composite samples from six different plots, gives an idea of the variability of the soil. In the Norrliden experimental series, which is the most extensive one, there seems to be a tendency to release of less available nitrogen in samples from acidified plots than from controls, an observation valid for both unfertilized and fertilized plots. The samples for the incubation experiment were taken after four applications of sulphuric acid. Liming also decreased mobilisation of nitrogen but probably for the opposite reason (when compared with sulphuric acid). Liming is known to favour micro-biological immobilisation of soluble nitrogen in agricultural soils and also in some forest soils.

TABLE 1 NORRLIDEN. BASE EXCHANGE PROPERTIES OF SOME SAMPLES

SAMPLE AND TREATMENT	APPROXIMATE DRY WEIGHT KG/HA · 10^3	EXCHANGEABLE CATIONS (OTHER THAN H_3O^+) KG E/HA	TITRATABLE ACIDITY (H_3O^+) KG E/HA	CATION EXCHANGE CAPACITY KG E/HA	DEGREE OF "BASE SATURATION" %	pH
NORRLIDEN, CONTROL	30	4.4	20.0	24.4	18	3.8
A_0 SAMPLES	30	9.6	16.3	25.9	37	4.7
	30	4.6	16.9	21.5	21	4.2
NORRLIDEN, ACID 3	30	4.7	28.5	33.2	14	3.6
A_0 SAMPLES	30	7.0	17.6	24.5	28	4.3
	30	3.0	22.5	25.5	12	3.8
NORRLIDEN, CONTROL						
SOIL PROFILE A_0	30	5.9	16.8	22.7	26	3.8
A_2	840	16.0	57.1	73.1	22	3.5
B	1300	12.2	162.0	174.2	7	4.4
C	1400	9.8	103.6	113.4	9	4.8
	(PER 10 CM)					

GENERAL CONCLUSIONS

Further acidification of already acid forest soils by air pollutants is a slow process and it probably takes a considerable time before growth effects can be established. However, there are obvious effects of even moderate additions of sulphuric acid or sulphur on soil biological processes, nitrogen turn-over in particular.

These changes may have far-reaching consequences on soil fertility in the long run, and it is imperative that these processes are studied in greater detail and over a longer range of sites before the acid rain has affected our soils much longer.

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RADIAL GROWTH AND WOOD DENSITY OF WHITE PINE IN RELATION TO FOSSIL-FIRED POWER PLANT OPERATIONS

W. T. LAWHON, Battelle Columbus Laboratory and F. W. WOODS, The University of Tennessee.

ABSTRACT

The objectives of this study were twofold: (1) to develop a gamma densitometry technique for measuring the relative wood density and radial growth of trees from 12 mm increment cores; and (2) to determine whether changes in the relative wood density and radial growth of "resistant" eastern white pine (Pinus strobus L.) occurred after initiation of operations of the Kingston and Bull Run steam plants in eastern Tennessee. The study area was surveyed by air to determine the distribution of white pine around the Kingston and Bull Run steam plants. It was found that white pine was distributed into roughly three "groups" (11 sampling locations): Group 1, located west of Bull Run Steam Plant; Group 2, located northeast of the Kingston Steam Plant; and Group 3, located southwest of the Kingston Steam Plant. These groups served as the basis for subsequent analyses. Two 12 mm increment cores were taken from each of 89 dominant or codominant eastern white pine for analysis using the gamma densitometry technique. Within each core, two five-year periods were analyzed for: (1) relative wood density, (2) radial growth, (3) percent earlywood, and (4) percent latewood. One five-year period was designated as the "pre-impact" (before steam plant operations) period and the other was designated as the "post-impact" period (after steam plant operations). The annual ring for the year of steam plant start up was not included in this study. Four questions were asked: (1) was there a difference in the pre- and post-impact relative wood density and radial growth of eastern white pine in the vicinity of the Kingston and Bull Run steam plants, (2) were there any difference in the pre- and post-impact relative wood density and radial growth among groups, (3) if so, did distance and azimuth from each location to the nearest steam plant influence the difference between the pre- and post-impact relative wood density and radial wood growth at each location, and (4) could differences between pre- and post-impact relative wood density and radial growth at each location be described by age or certain environmental variables.

There was a significant difference ($P < 0.01$) between the relative wood density (average of 5-year periods) of the wood formed before (pre-impact) and after initiation of operations (post-impact) at the Kingston and Bull Run steam plants. At ten of eleven sampling locations, the relative wood density was greater after steam plant operations started. Orthogonal comparisons of 8 locations within groups indicate no significant differences ($P < 0.10$) in relative average density. The effects of azimuth and distance on the relative density of the pre- and post-impact wood samples were significant ($P < 0.10$). Of the variation found in the estimated relative density differences at each location, about 48 percent is related to the distance and azimuth from the nearest steam plant. The partial regression coefficients for distance and azimuth were negative, with the partial regression coefficient of distance being significant ($P < 0.10$). Thus, as the distance from the steam plants increases, there was a corresponding decrease in the relative density differences between the pre- and post-impact wood. Although the partial regression coefficient of azimuth is not significant, it was negative which suggested that as the direction from the steam plant changes relative to the prevailing winds, the influence of the steam plant is reduced. The following environmental variables were not significantly related ($P < 0.10$) to relative wood density after the effects of distance and azimuth were removed: (1) available moisture holding capacity of the soil at each location; (2) the average maximum, average minimum, and mean monthly temperature by month; (3) the mean number of drought days by month at each location; (4) the mean number of excess moisture days by month at each location; and (5) the cambial age at breast height of the pre- and post-impact wood samples.

There were significant differences ($P < 0.10$) between the percentage of earlywood and latewood formed before and after initiation of operations at the Kingston and Bull Run steam plants. At nine of eleven sampling locations (3 groups), percent earlywood decreased and percent latewood increased after initiation of steam plant operations. An orthogonal contrast between group 1 and groups 2 and 3 indicates that a significant difference ($P < 0.10$) in percent early wood and percent latewood existed. Of the variation found in the group mean differences, about 44 percent can be attributed to the grouping of trees around the steam plants. The effects of azimuth, distance, and the aforementioned environmental variables on the differences in pre- and post-impact percent earlywood and percent latewood at each location (within groups) were not significant ($P < 0.10$). No significant difference was found in radial growth between the pre- and post-impact samples.
No significant difference was found in radial growth between the pre- and post-impact samples.

THE EFFECT OF ACID PRECIPITATION ON TREE GROWTH IN EASTERN NORTH AMERICA[1]

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ABSTRACT

Detailed study of the history of forest tree growth by tree-ring analysis is used to assess the effect of acid precipitation. The pattern and historical trends of acid precipitation deposition are compared with growth trends from mature forest stands in New Hampshire and Tennessee. No clear indication of a regional, synchronized decrease in tree growth was found. The residual variation of relative tree growth responses, after removal of variation due to weather, shows no recent time-dependent trend. Due to the unknown initiation date of acid precipitation and to the large variation of tree growth estimates, a correlation of forest growth and acid precipitation in eastern North America cannot be established at the present time.

INTRODUCTION

Although the interaction between acidic precipitation and actual forest growth is complex, involving many types and extents of interaction, it is useful to look at forests for several reasons. First, they are widespread and constantly exposed, second, they contain a growth history in tree-rings, and third, they are economically and biologically important. I have studied tree growth in order to

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[1]This study was supported with funds from the National Science Foundation and the E. I. DuPont de Nemours and Co.

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determine if acidic precipitation and forest growth histories are correlated (see Jonsson and Sundberg 1972, Whittaker et al. 1974). The nature of the interaction is undefined, but could involve depletion of soil nutrients (Overrein 1972), fertilization effects, foliage leaching (Eaton et al. 1973), metabolic disruption in leaf tissue (Wood and Bormann 1974), and/or other effects.

SITES AND METHODS

Two forest sites were carefully selected for old aged, mature stands with a minimal history of disturbance. A New Hampshire site was located in the Bowl Natural Area of the White Mountain National Forest. Boring for tree-ring analysis (Fritts 1961) was carried out in August 1972 by W. B. Leak in the northern hardwood plots described in Leak (1973). A Tennessee site was in the Great Smoky Mountains National Park and increment cores were taken in June 1973 in the spruce-fir forest around Newfound Gap. Both sites are in mountainous areas, on acid soils, and in isolated areas removed from local sources of pollution. Yearly growth chronologies for the dominant species were derived from increment cores obtained from scattered trees in each stand.

One site (the Bowl) is near the center of the acid precipitation region while the other site (Smokies) is at the periphery of the acid pattern. The Bowl site was probably acidified (pH <4.52) sometime before 1955 and today has an average acidity in precipitation of pH 4.10. Meanwhile, the Smokies site has become acidified from an annual average pH of about 5.2 in 1955 to a present-day pH of 4.4 (Cogbill and Likens 1974).

Response indices (ratio of yearly growth to previous 10 year average) give an indication of relative growth of a stand (Fritts 1961). These indices are then used as the dependent variable in a multiple stepwise linear regression against precipitation and temperature variables in the growing season. The residual variation of these regressions indicate growth trends not accounted for by weather variables.

RESULTS

The radial growth chronologies for beech *(Fagus grandifolia)*, birch *(Betula lutea)*, and maple *(Acer saccharum)* at the Bowl are shown in Figure 1. Beech growth shows a maximum in the 1940's, possibly in response to release by the hurricane of September 1938. Growth in

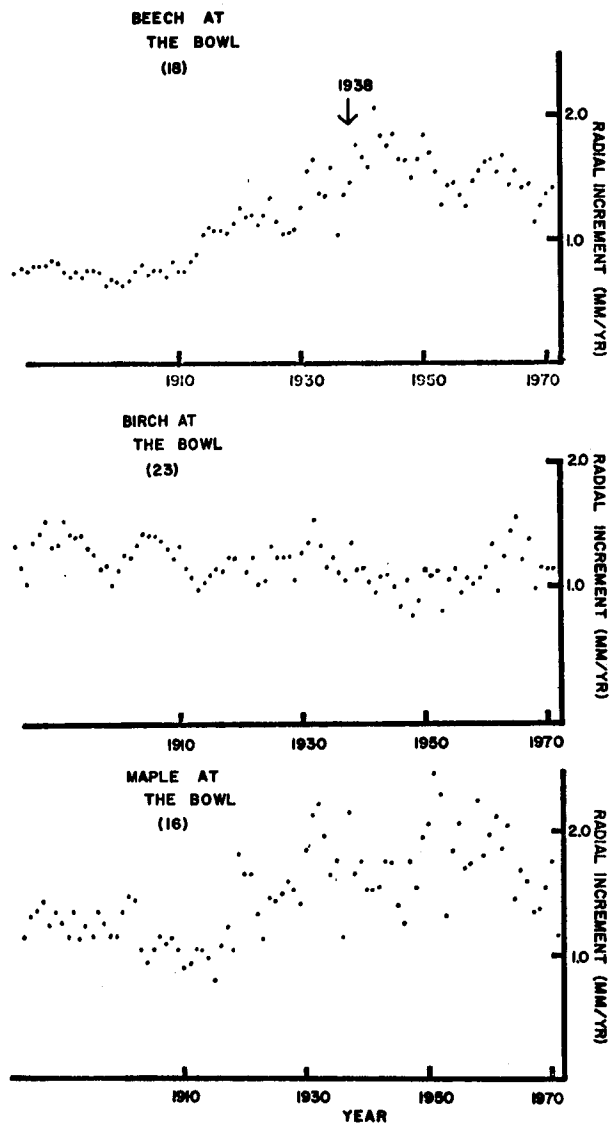

Figure 1. Tree-ring chronologies at the Bowl. The number of trees included in the chronology is in parentheses.

beech was significantly decreasing ($p<.001$ for a linear fit) from 1940 to 1970, but not significantly different from 0 slope ($p>.05$) from 1950 to 1970. Birch had fairly consistent growth with significant increases ($p<.05$) both from 1940 to 1970 and from 1950 to 1970. Maple had irregular growth which was not significantly decreasing ($p>.05$) from 1940 to 1970, but was statistically decreasing ($p<.05$) from 1950 to 1970.

The inclusion of different size trees in chronologies and the general tendency to decrease radial increment as a tree becomes older and larger somewhat biases trends gleaned from radial increment curves. Since basal-area increment is a fair estimate of total productivity regardless of tree size, the basal-area increment chronologies for the

Bowl are shown in Figure 2. All species show a general increase in

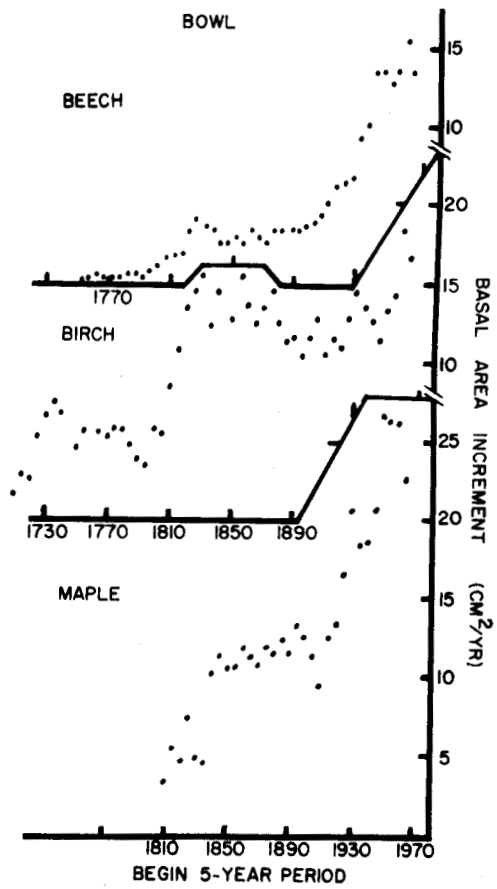

Figure 2. Basal area growth at the Bowl.

basal-area increment with time, as all trees are growing in size. Recent irregular growth has no consistent breakpoint, particularly any downward shift originating before 1955.

The chronology for red spruce *(Picea rubens)* in the Smokies (Figure 3) is similar to those seen in the Bowl, particularly on birch. Irregular decreasing growth is statistically significant ($p<.05$ different from 0 slope) from 1910, 1940, and/or 1950 to 1970. Despite being affected by acid precipitation since 1955, there seems to be no unusual change in growth pattern after this time.

Although both the magnitude and time sequence of acid deposition vary from New York to Tennessee no substantial difference in forest growth was found. At neither site was there a residual downward trend in the response indices after reduction of weather variance by multiple regression techniques. The auto-correlation of these

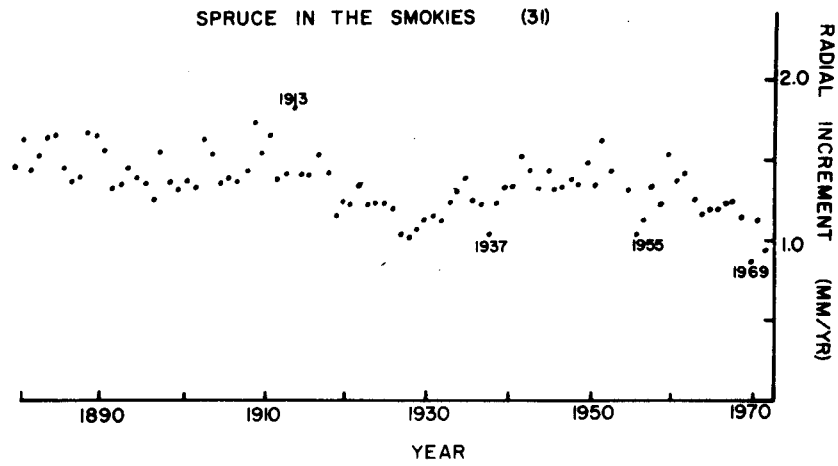

Figure 3. Tree-ring chronology for spruce in the Smokies. The number of trees included in the chronology is in parentheses.

residual indices were not significant ($p>.05$), indicating that no unaccounted for time-dependent variable was left after growth response and weather variance were taken into account.

CONCLUSIONS

No regional, synchronized decrease in radial increment growth was evident in the two mature stands studied in the eastern United States. Despite different acid precipitation regimes, these two stands displayed similar growth patterns. Slight recent decreases in basal area increment in the mature stands were neither dramatic nor without precedent, but acid precipitation cannot be eliminated as their cause. Weather, stand dynamics, and determination error are probable contributory causes. Thus, due to the unknown initiation date of acid precipitation and to the large variance of tree growth estimates with no breakpoint, a correlation of forest growth and acid precipitation in eastern North America cannot be established at the present time.

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FIELD STUDIES OF PINE, SPRUCE AND ASPEN PERIODICALLY SUBJECTED TO SULFUR GAS EMISSIONS

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ABSTRACT

Field studies of photosynthesis in *Pinus contorta/Pinus banksiana* (lodgpole pine/jack pine) hybrids, *Picea glauca* (white spruce) and *Populus tremuloides* (aspen) subjected to SO_2 and H_2S from a nearby natural gas processing plant were initiated near Whitecourt, Alberta, Canada during the summer of 1974. The site was characterized as a *Pinus-Picea glauca/Arctostaphylos uva-ursi* association (pine-white spruce/bearberry). A 15 meter high scaffold was used as access to mid-crown foliage in the pines while the spruce and aspen were accessible from the ground. Net assimilation rates, transpiration rates and leaf resistances were calculated and water deficits were monitored. Photosynthetic rates measured were in a low range for the conifers studied, with pine having a maximum of 3.28 mg dm^{-2} hr^{-1} and white spruce a maximum value of 2.3 mg dm^{-2} hr^{-1}. The low maximum photosynthetic rate determined for aspen is thought to be attributable to the onset of autumn. Chemical analyses for SO_4-sulfur using the methylene blue colorimetric method of Johnson and Nishita (1952) showed levels of 300-700 ppm, with the older foliage showing slightly higher values. Visible chronic SO_2 symptoms had a pronounced sun, or upward, orientation. Ambient SO_2, H_2S and total S were measured using á Tracor 270HA Atmospheric Sulfur Analyzer (chromatographic method) and trends in ambient SO_2 concentrations using an Envirometrics SO_2 Analyzer (polarographic method). Concentration was found to be variable for SO_2 and generally below 0.05 ppm. A concentration gradient of SO_2 was found to exist in the lodgepole pine/jack pine stand with the SO_2 values above the canopy generally higher than below the canopy (0.1 ppm above and 0.05 ppm below). This condition was occasionally reversed. The plant canopy is considered to act as a barrier to downward diffusion of the sulfur emissions in the first case and also a barrier to upward diffusion of sulfur

emissions present due to advection in the stand in the second case. The vegetative environment surrounding the Windfall Gas Plant is definitely affected by sulfur gas emissions but the extent remains to be determined.

INTRODUCTION

Specific damage and even elimination of plant species from areas exposed to sulfur gas emissions such as SO_2 have often been documented (Scheffer and Hedgecock, 1955; Bowen, 1965; Westman, 1974; Skorepa and Vitt, 1975). Air quality sampling trailers are used extensively today to monitor air pollutants. It is difficult if not impossible, however, to estimate "damage" or impact from air pollutants upon vegetation without a knowledge of the many environmental variables, in addition to pollutant dose, that can modify plant response. An extensive research effort is needed to determine the short term and long term effects of high and low concentrations of sulfur gas emissions on vegetation in the field.

The main objective of this study was to begin answering specific questions about the effects of sulfur gas emissions on several dominant plant species periodically exposed to a point source in the field:

(1) What is the nature of the plant communities surrounding the point source emission?

(2) What is the ecophysiological status of several dominant plant species *Pinus contorta/Pinus banksiana* (lodgepole pine/jack pine), *Picea glauca* (white spruce) and *Populus tremuloides* (aspen) under "as it is" field conditions?

(3) What is the nature and composition of the ambient atmosphere in terms of SO_2 and H_2S using the methods of gas chromatography and polarography?

The experimental site is located approximately one-half mile east of the AMOCO Windfall Gas Plant in the Whitecourt area of the sour gas corridor of western Alberta and is shown in plate 1 and plate 2. This area was chosen for study for several important reasons:

(1) presence on the vegetation of classic symptoms indicating stress from sulfur gas emissions;

(2) extensive background data already available for the area;

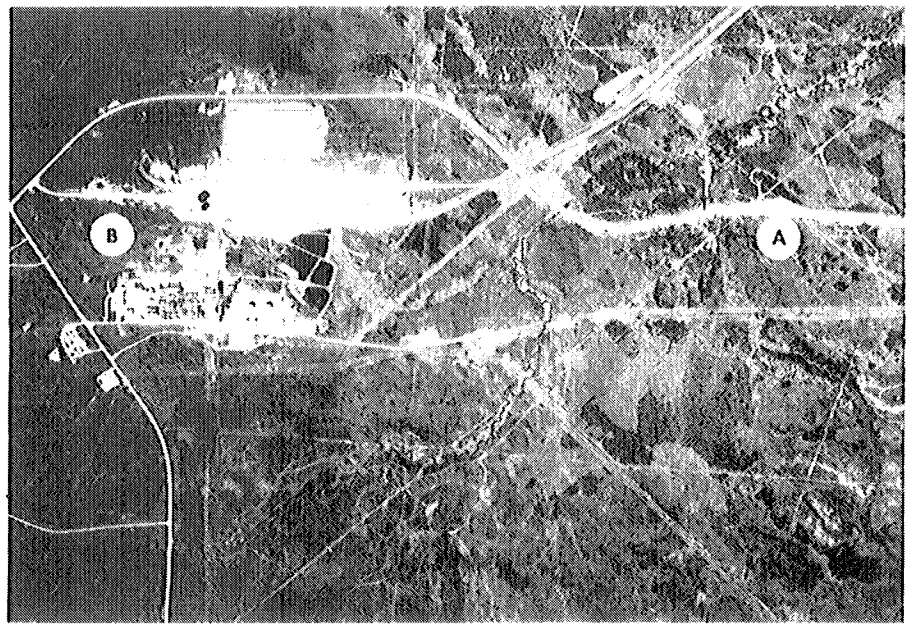

Plate 1. False color infrared aerial photograph showing spatial relationship between experimental ecophysiological test site on sand dune (A) and the AMOCO Windfall Gas Plant (B). The study area is east of the gas plant. The effects of the 1956 fire are readily identifiable by the patchwork nature of the vegetation.
Scale: 1:30,000
Imagery supplied by INTERA Environmental Consultants Ltd.

(3) similarity in plant species composition between this site and similar areas in the region of the Athabasca Tar Sands, thus making the data generated transferrable;

(4) availability of line power; and

(5) excellent cooperation with the gas processing industry via the Whitecourt Environmental Study Group member companies.

Since the study area is located near the Windfall Gas Plant, it must be remembered that the primary point sources were the flare stacks rather than the incinerator stacks.

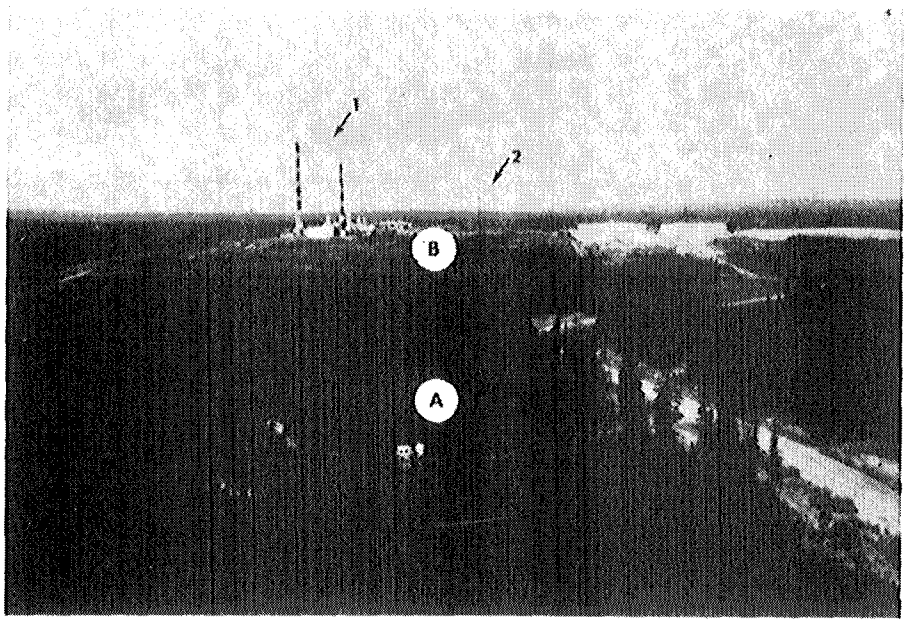

Plate 2. Aerial color oblique showing relationship between experimental ecophysiological test site (A), instrument trailer, 15 meter access tower to mid-crown foliage of lodgepole pine/jack pine hybrids in the foreground and the AMOCO Windfall Gas Plant (B) in the background and to the west. The red and white striped incinerator stacks are indicated by (1) and the flare stacks by (2). Note the undulating nature of the topography.

SITE CLASSIFICATION AND DESCRIPTION

The vegetation of the Whitecourt, Alberta area is included in the "predominantly forest" subregion of the Boreal Forest Region of Canada by Halliday (1937). Rowe (1972) has further subdivided the Boreal Forest Region into 45 distinct geographic areas with the Whitecourt area located in the Lower Foothills area (B.19a). This area is characterized as a transition forest area between the Boreal and the Subalpine Forest Regions. The transitional nature of the vegetation is emphasized by the fact that two common species of trees occurring in the area are actually represented by populations of hybrid individuals between *Pinus contorta* and *Pinus banksiana* while the true fir in the area represents hybrids between *Abies lasiocarpa* and *Abies balsamea*.

Variability in natural plant communities in the Whitecourt area in the vicinity of the Windfall Gas Plant is naturally complex, but this complexity has been intensified due to past disturbance of the area by fire in 1956 and by seismic exploration. The subdued undulating topography also contributes to gradual environmental gradients causing subtle variation in community composition and structure from location to location (plate 2). Two distinct sites offer fairly uniform and repeatable habitats for vegetative community development. These are well-drained vegetated sand dune sites and moist bogs. These two sites exhibit plant communities that are remarkably uniform and repeat themselves consistently across the landscape. Only the sand dune site, one-half mile east of the AMOCO Windfall Gas Plant, will be described in detail since it was the location of the ecophysiological analysis during the late summer of 1974 (plate 3).

Plate 3. Experimental test site one-half mile east of the AMOCO Windfall Gas Plant showing the mature stand of *Pinus contorta/Pinus banksiana* hybrids with 15 meter access tower scaffolding and instrument trailer. Note the open nature of the stand and the dominance of the pine.

The plant association occurring on this sand dune site has been characterized following standard phytosociological techniques (Daubenmire, 1968). Table 1 shows the overstory and understory in this single-layered, even-aged stand. Pine and spruce reproduction are both moderately light, and since the pine is clearly dominating

Table 1: Phytosociological analysis of a pine stand on a sand dune near the Windfall Gas Plant, Whitecourt, Alberta.

Overstory Components

Species	Stems/hectare	Diameter (cm.)
Picea glauca (white spruce)	400	18.4
Pinus contorta P. banksiana (lodgepole × jack pine)	533	22.7
Picea reproduction	1680	---
Pinus reproduction	3680	---
TOTAL	6293	

Understory Components

Species	Percent cover	Percent presence
Vaccinium vitis-idaea (bog cranberry)	40.0	100
Vaccinium myrtilloides (blueberry)	8.7	92
Arctostaphylos uva-ursi (bearberry)	8.1	46
Elymus innovatus (hairy wild rye)	3.8	77
Lycopodium complanatum (ground cedar)	5.8	31
Cornus canadensis (bunchberry)	+	15
Ledum groenlandicum (Labrador tea)	1.5	87
Campanula rotundifolia (bluebell)	+	23
Amelanchier alnifolia (Saskatoon berry)	+	15
Maianthemum canadense (lily-of-the-valley)	+	++
Solidago canadensis (goldenrod)	+	++
Lonicera involucrata (bracted hyneysuckle)	+	++
Potentilla tridentata (three-toothed cinquefoil)	+	++
Geocaulon lividum (fern)	+	++
Galium boreale (northern bedstraw)	+	++
Dicranum polysetum	+	++
Pleurozium schreberi	+	++
TOTAL	67.9	---

+ = less than 1% cover
++ = present in only one microplot

here, it seems that an edaphic climax community of pine is developing on this well-drained dune. The five indicator species of this pine-spruce/bearberry association (*Pinus-Picea glauca/Arctostaphylos uva-ursi* association) are pine *(Pinus contorta x P. banksiana)*, white spruce *(Picea glauca)*, bearberry *(Arctostaphylos uva-ursi)*, hairy wild rye *(Elymus innovatus)*, and blueberry *(Vaccinium myrtilloides)*.

With bog cranberry *(Vaccinium vitis-idaea)* dominating the understory at this particular site one is led to believe that this site has higher moisture holding capacity, at least in the A horizon, than is common for this association in other areas where blueberry *(Vaccinium myrtilloides)* is clearly dominant over *V. vitis-idaea*. The soil on this site is a rapidly drained sand. Several samples show the subsoil to be more than 90 per cent sand, 5-8 per cent silt and 1 per cent or less clay. The surface soil, however, has a loamy sand texture. The soil can be classed as a degraded eutric Brunisol, indicating a comparatively high base saturation for this soil.

In terms of forest productivity measured as basal area, this site is very low on the scale with a value of approximately 35 m^2/ha. Other workers have computed basal area values for conifers at other

sites in North America and these range from highs of 145 m^2/ha to lows of 56 m^2/ha (Daubenmire, 1968; Whittaker, 1956). Daubenmire (1968) has also shown basal area to be closely correlated with ecological site classification. When sites are carefully chosen based upon homogeneity of vegetation composition and structure, this close relationship is apparent. Not only does total productivity vary according to ecological units of vegetation classification but also individual species vary in productivity from site to site. This concept is illustrated utilizing lodgepole pine/jack pine from the Windfall area.

Figure 1 shows the annual increment in basal area production for

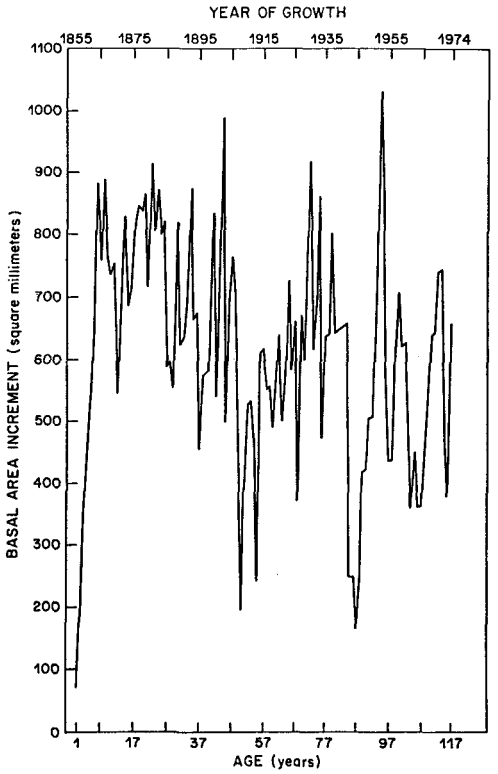

Figure 1. Hybrid lodgepole pine/jack pine annual basal area increment of growth in the *Pinus-Picea/Arctostaphylos uva-ursi* (pine-spruce/bearberry) plant association on the experimental sand dune site. Note the fluctuation around a long term basal area increment average.

pine at the experimental dune site where it is a dominant part of the overstory. Figure 2 shows the same annual increment in basal area for pine in a *Picea mariana/Ledum-Sphagnum* (black spruce/Labrador tea-sphagnum) bog site adjacent to the sand dune site where the pine is only occasional in its occurrence. The growth increments are significantly different at the 0.1 per cent level of probability (average annual increment = 620 mm^2/year for the tree in figure 1 and 272 mm^2/year for the tree in figure 2). Although the sample size is too small to say that this relationship holds throughout both plant associations, it is thought that both trees studied represent the

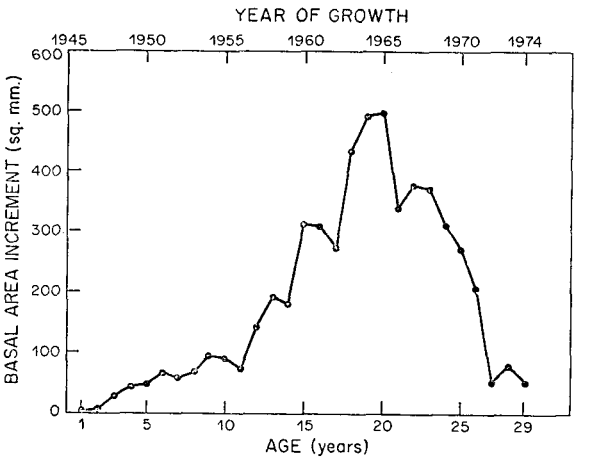

Figure 2. Hybrid lodgepole pine/jack pine annual basal area increment of growth in *Picea mariana/ Ledum-Sphagnum* (black spruce/Labrador tea-sphagnum) bog plant association, adjacent to *Pinus-Picea/ Arctostaphylos uva-ursi* (pine-spruce/bearberry) sand dune plant association. Pine only rarely occurs in this black spruce plant association. In contrast to the pine illustrated in figure 1, productivity as measured by basal area increment is less than half that of the pine growing in the sand dune site. The pronounced decrease in basal area increment after 1965 is probably due to unfavorable moisture conditions (excess water) rather than the presence of sulfur gas emissions.

common pattern of growth for pine in each plant association.

Within the black spruce bog are small mounds which support some pine and blueberry *(Vaccinium myrtilloides)*. These microtopographic rises are better drained than the black spruce bog itself. As a consequence pine growth more closely approximates that on the dune site (as shown when figure 3 is compared to figure 1). Average annual increment for the pine in figure 3 is 700 mm^2/year while that for the tree in figure 1 is 620 mm^2/year (no significant difference in growth detected).

Another factor of large importance when comparisons of growth before and after some outside influence or stress is placed on a plant is the natural change in growth patterns throughout the life span of any given plant. Net photosynthetic rates as well as the amount of photosynthate utilized in construction of woody tissues in conifers will vary with the age of the plant, time of year and environmental factors. This fact is illustrated in figure 1 by comparing the first few years of growth. A rapid increase in basal area increment for

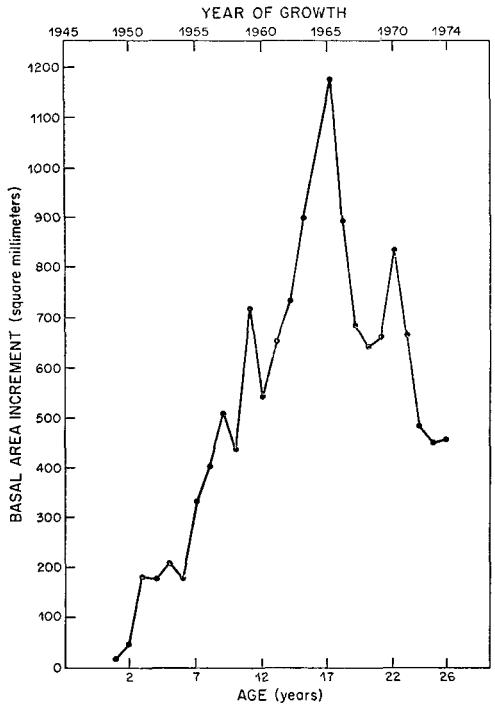

Figure 3. Hybrid lodgepole pine/ jack pine annual basal area increment of growth on a mounded inclusion of *Pinus-Picea/ Arctostaphylos uva-ursi* (pine-spruce/bearberry) association vegetation in a *Picea mariana/ Ledum-Sphagnum* (black spruce/ Labrador tea-sphagnum) association. The more than 100 per cent increase in basal area increment of this pine in contrast to the pine illustrated in figure 2 drastically illustrates the effect of microsite on plant productivity. The pronounced decrease in basal area increment after 1965 is probably due to unfavorable moisture conditions (excess water) rather than the presence of sulfur gas emissions.

this 117 year old tree is seen in the first 10 to 15 years of growth, followed by growth rates which begin to level off and fluctuate around a long-term average. Senility does not appear to have begun in the oldest trees on the dune site (see figure 1) despite the presence of white pocket rot *(Fomes pini)*. Lodgepole pine is known to reach ages of several hundred years in other areas although none of that age are common in the Boreal Forest Region.

Older trees such as the one illustrated in figure 1 are the only trees that provide a long enough record of yearly growth rates to make comparisons prior to and after any given date once the first 15-20 years of early growth are eliminated. Young pines (40-50 years old) do not provide acceptable working material for making these comparisons. The tree illustrated in figure 1 does, however, assuming that the last few years growth has not been affected by any consequences of senility. No significant difference in growth prior to 1961 and after 1961, when the Windfall Gas Plant began operations, is detected from the data graphed in figure 1. However, only minor biological significance can be placed on this study for two major reasons: (1) the sampling site is much too small and (2) no control areas (similar ecological sites unaffected by the Windfall Plant) were compared to the affected site.

These few examples describe the complexity of the "growth" response (measured as basal area increment per year) in the same species over several different environmental conditions (i.e. different

ecological conditions). Not only does the environment in which a seedling is established affect the growth rate of that seedling but also the genotypic makeup exerts controls on photosynthesis rates and thus basal area increment. The genetic controls of growth rates and patterns of growth will vary for the same species from site to site. Any organism, whether it be plant or animal, is a product of its genotype-environment interaction and the organism is continually exposed to simultaneous changes in many environmental parameters.

This initial study, aimed at describing the plant community on which the physiological experiments were conducted during the summer of 1974, has pointed to two recommendations for further study. These should be undertaken to provide the data to aid in assessing whether or not plant life in the vicinity of the Windfall plant has been affected by the sulfur gas emissions.

The first is to conduct paired plot studies of basal area growth rates in black spruce, white spruce, birch, and/or aspen. Pine cannot be used, as ecologically similar sites are probably not available both in affected and unaffected locations. Plots would be paired based on ecological similarity of sites as determined by detailed phyto-sociological analysis of selected sites. Growth rates would be analyzed and compared prior to 1961 and after 1961.

The other method would also be based upon paired plot studies. The object of the study would be mosses, liverworts and lichens epiphytic on given tree species. Many studies have shown the sensitivity of these plants to atmospheric contaminants. The plot to be studied would be whole trees of a given height, age, diameter and growing in a given plant community. Similarity indices based on the cryptogamic flora and productivity of that flora would be compared in affected and unaffected sites. This sampling design would follow that of Pike et al. (unpubl. manuscript).

SULFUR DIOXIDE AND VEGETATION

SULFUR DIOXIDE AS AN ENVIRONMENTAL VARIABLE

Several reviews have considered the effects of SO_2 on plants (Thomas, 1961; Daines, 1968; Tamm and Aronsson, 1972). They indicate that most studies have attempted to correlate dosage with measurable visible damage. Assuming comparable exposure conditions, it is generally accepted that for each plant there is a threshold value for the development of injury by SO_2 (Thomas, 1961; Guderian and Van Haut, 1970).

Two distinct types of visible SO_2 plant damage have been recognized by most workers: acute damage that occurs with high dosages (over 1.0 ppm) of short duration and chronic damage that appears after long periods at low or intermittently low dosage (less than 0.2 ppm or between 0.2 and 1.0 ppm). More recently, however, in a report to the Whitecourt Environmental Study Group (1973, Section 1: Surface Environment; B. Foliar symptoms as a monitor of environmental stress, 1-8 through 1-17) visible SO_2 symptomology was divided into three types: transient, chronic and acute. This division is much more realistic as it describes symptoms in terms of longevity as well as degree. It works well in describing the status of the vegetation under field conditions exposed to sulfur gas emissions. It is impossible at present, however, to assign a meaningful concentration of a pollutant or pollutants under field conditions which will elicit these symptoms. This may be possible in the future when air quality trailers are monitoring environmental parameters other than pollutants, wind speed and direction, and temperature (next to or above the trailer) such as relative humidity (or absolute water content of air), photosynthetically active radiation (PAR) and soil moisture. It is further critical to determine what plant communities are exposed to in terms of pollutants and their concentration. Research on the meaningfulness of monitoring techniques is urgently needed.

Certain environmental parameters, such as high relative humidity and soil moisture, with moderate light intensity and temperature (above 5°C), will make vegetation more susceptible to damage from air pollutants. The extent of SO_2 injury is primarily determined by the status of the stomatal pores (Scheffer and Hedgecock, 1955; Stratmann, 1960; Meidner and Mansfield, 1968; Lopushinsky and Klock, 1974). The degree to which these pores are open or closed (stomatal aperture) controls the rate of gas transfer (CO_2 and SO_2) to and from the external ambient environment and the internal plant environment. The SO_2 which enters the plant through the stomatal pores readily enters solution in the thin layer of water surrounding the mesophyll cells (outer layer of internal cells) and is slowly oxidized from sulfite and bisulfite, the more damaging forms, to sulfate (Thomas and Hill, 1937). Tanaka *et al.* (1974), using alfalfa leaf homogenate, showed a 50 per cent decrease in $^{14}CO_2$ fixation caused by a 3×10^{-2} M concentration of sulfite ion, but no effect from the same concentration of sulfate ion. They attributed this reduction to an inhibition of the enzyme ribulose-1, 5-diphosphate carboxylase by sulfonation of its -SH groups.

Although sulfite is more inhibitory than sulfate in short-term exposures, evidence indicates (Thomas *et al.*, 1950) that over long exposures to excess sulfur, sulfate buildup in the tissues is damaging. Thus, although chlorosis and early leaf loss are recognized as symptoms of chronic SO_2 damage, detection of high levels of sulfate-sulfur by plant-tissue analysis is a more reliable indicator of potentially damaging sulfur (Ulrich *et al.*, 1967).

GAS-EXCHANGE METHODOLOGY

For photosynthesis under controlled-environment conditions, optimal levels of light, temperature, soil moisture and relative humidity have been determined for many species using CO_2 gas-exchange methodology. Among these studies was the work done on species associated with the mixed forests of west central Alberta by Dykstra (1974) who studied *Pinus contorta* (lodgepole pine) and Van Zinderen Bakker (1974) who worked with *Picea mariana* (black spruce). This work provides essential background information for the Whitecourt area.

The gas-exchange technique has only recently been applied to the study of the effects of air pollutants on plant life under controlled conditions in the laboratory. Hickling (1974) working on *Pseudotsunga menziesii* (Douglas fir) reported both inhibitory and stimulatory effects of low levels of SO_2 on net assimilation and transpiration with short-term exposures. SO_2 was shown to have a direct effect on the degree of opening of stomata by Majernik and Mansfield (1970; 1971) in *Vicia faba* (broad bean). These workers showed that levels of SO_2 above 0.5 ppm caused stomatal closure while levels below 0.5 ppm prevented complete stomatal closure.

Legge (1973) and Legge and Harvey (1974), working with seedlings of *Pinus contorta*, acclimated to a low growing temperature (11°C), to an optimal growing temperature (17.5°C), and to a high growing temperature (27.5°C) prior to SO_2 exposure (0.5 ppm for 12 hours), predisposed the test plants to an increase in transpirational water loss with increasing temperature. Relative humidity was maintained at 35-40 per cent in all these experiments. Acute symptoms appeared only on the optimally grown seedlings subjected to SO_2, with all seedlings surviving. Seedlings of *Pinus contorta* subjected to dark stress (increase in length of dark period) and optimal growing temperature (17.5°C) prior to exposure to SO_2 (0.5 ppm, 24 hours) also displayed an increase in transpirational water loss and acute visible SO_2 damage, but resulted in death.

Although there is variability in photosynthetic performance within a plant species, this laboratory work is essential for verification and comparison with photosynthetic performance of plant species in the field.

CO_2 GAS-EXCHANGE SYSTEM

The basic open CO_2 gas-exchange system developed by Salo (1974) for studies of photosynthetic performance of Douglas-fir in the field was utilized at the Windfall site. This system was modified, however, to allow for the analysis of sulfur gas emissions (specifically SO_2 and H_2S) as well as CO_2. Ambient air was drawn from a height of 20 meters at the top of the canopy and was conducted to a mixing vessel through

FEP (Fluorinated-ethylenepropylene) teflon which has been shown to have a very low adsorptivity coefficient for SO_2 (Legge and Harvey, 1974). After leaving the mixing vessel which had a variable volume of from 3 to 9 liters, the air was continuously pumped to each of 3 net assimilation chambers or cuvettes (plate 4). Two of the cuvettes

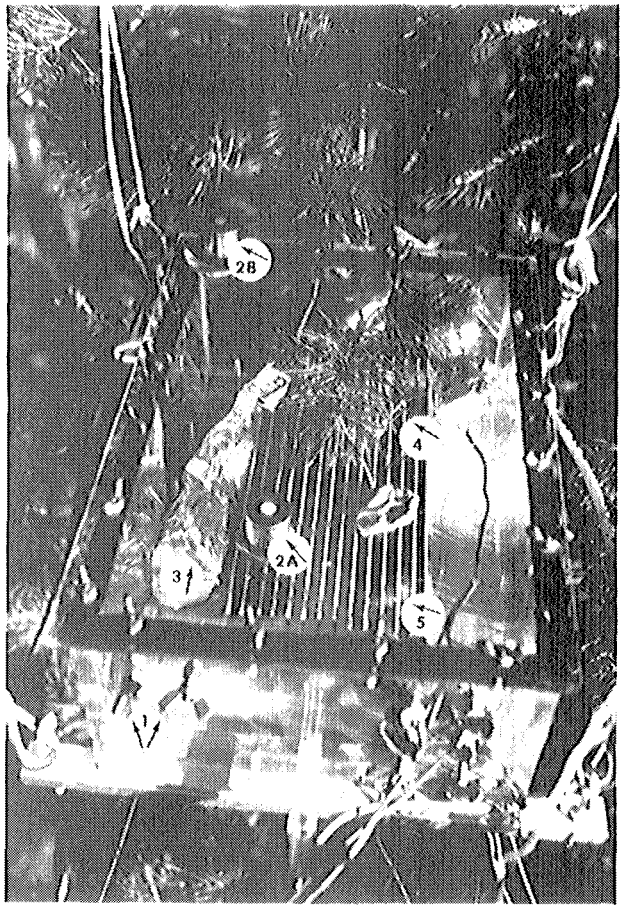

Plate 4. Assimilation chamber (cuvette) for gas-exchange measurements surrounding a branch of *Pinus contorta/P. banksiana* (lodgepole pine/jack pine) hybrid at a height of 15 meters using the access tower scaffolding.

(1) Cuvette for enclosing pine branch and measuring gas-exchange capability.
(2) Quantum sensors for measuring light:
A - internal
B - external
(3) Shielded ambient air thermocouple.
(4) Clip-on thermocouple for measuring needle temperature on enclosed branch.
(5) Peltier block for maintaining and controlling temperature within cuvette to the temperature outside the cuvette.

contained tree branches (live plant material) and the third cuvette served as a control. The assimilation chambers used were manufactured following the design of Salo *et al.* (1972). An electric switching system was developed which permitted automatic sampling of each cuvette, thus allowing the outflow from a single cuvette to be sampled at any predetermined sampling frequency. The switching system could also be operated manually.

The air stream being monitored was passed through a temperature stabilized vessel which contained a Hygrodynamics LiCl water vapor sensor and from there passed to a wet bulb/dry bulb psychrometer (described in Bierhuizen and Slatyer, 1964). The water vapor was then

removed by a Siemens water vapor trap and passed through a Beckman LB 15A absolute infrared gas analyzer. Flow rate was measured at the outlet by a Brooks precision flow meter.

By using the blank cuvette as an ambient control, the differences in CO_2 and water vapor concentrations were monitored in the two sample cuvettes and net CO_2 assimilation (= net photosynthesis), transpiration and leaf resistances could be calculated.

In each assimilation chamber internal ambient air temperatures and external ambient air temperatures were monitored, with Peltier cooling plates being used to maintain cuvette temperatures equal to those outside the chambers. Photosynthetically active radiation (PAR) was monitored with Lambda quantum sensors, while thermocouples were used for temperature measurements. A clip-on thermocouple (Fry, 1965) was used for the conifer needles, while fine wire thermocouple junctions were pressed against the underside of the aspen leaves.

BIOMETEOROLOGY AND PLANT WATER STATUS

Wind speed and direction were monitored at the top of the tree canopy from the access tower scaffolding. Three sampling points were available for monitoring air quality in terms of total S, H_2S and SO_2. These were located above the canopy (at 20 meters), at mid-canopy (10 meters) and one meter above the ground.

Air was drawn from each sample point via FEP teflon tubing through a manually controlled glass manifold and two atmospheric sulfur gas analyzers. The 20-meter sampling point also served as the primary air intake for the CO_2 open gas-exchange system. A branch line of FEP tubing, preceding the mixing vessels, lead to the glass manifold for the 20-meter ambient sample point.

The three cuvettes in the CO_2 gas-exchange system were also connected to the sulfur analyzers via the glass manifold. Since this manifold system was manually operated, however, only air from a single sampling point (cuvette or ambient air) could be analyzed at any one time.

The two sulfur gas analyzers used were coupled together to optimize the advantages and reduce the disadvantages of each instrument. The first instrument was a Tracor model 270HA Atmospheric Sulfur Analyzer using the gas chromatographic method of analysis and a flame photometric detector (FPD). This unit automatically takes a 10cc air sample every 3 minutes and 45 seconds, and, between sampling periods, the internal instrument pumping system is bypassing air in preparation for a new sample injection. (For background information on

the flexibility of this system for analyzing sulfur compounds other than SO_2 see Brody and Chaney, 1966).

The second instrument was an Envirometrics SO_2 analyzer using the polarographic method of analysis. The principle advantage of the polarographic analyzer was the capability of continuous measurement of SO_2 concentration at a flow rate of 0.5 liters/minute and a response time of 30-60 seconds, depending on the age of the analytical cell or "Faristor." The main disadvantage of this analysis is the interference of H_2S to a level of 15 per cent with SO_2, thus giving an apparently higher level of SO_2 than is actually present in the atmosphere at the time of sampling.

The gas chromatograph permitted sensitive chromatographic separation of SO_2 and H_2S in concentration ranges of 0-100 ppb and 0-1 ppm as well as a measure of total sulfur, total SO_2, and total H_2S in both high and low ranges in the sample. On the other hand, the continuous SO_2 monitor enabled detection of sharp changes in SO_2 concentration in the selected ranges 0-1 ppm, 0-5 ppm or 0-10 ppm possibly missed by the gas chromatograph due to the 3 minute 45 second delay between samples.

The water status of a plant is indicated by its water potential, which can be estimated from Scholander chamber pressures measured on excised shoot samples (with the + value changed to - by convention) (Waring and Cleary, 1967). These values are reported in bars and reflect the chemical potential of free water in a plant system. Pure water is assigned a chemical potential of "0" and as solutes are added or the turgor pressure (water pressure on cell walls) of the plant cells decreases, this potential declines. Therefore more negative values of the water potential are indicative of decreasing chemical potential which reflects the increasing water deficit. Thus plant water deficits increase when water is lost from the plant faster than it can be resupplied by the roots. It follows that if the Scholander pressure is 17 bars, the water potential is taken to be -17 bars. If there is sufficient decrease in water potential of the leaves, stomata will start to close, resulting in a reduction of transpiration. When the stomata are completely closed, transpirational water loss is negligible.

Leaf surface areas were measured using the glass bead technique of Thompson and Leyton (1971). All photosynthetic rates presented in this report were calculated on the basis of total leaf surface area.

Plant samples from all three species on which photosynthesis was determined (lodgepole pine/jack pine, white spruce and aspen) and from plants with severe damage located at or near the Windfall site were returned to the University of Washington laboratory for analysis of sulfate-sulfur content.

RESULTS

Scaffolding and power had been installed at the Windfall study site by the time most of the equipment arrived on 9 August 1974, and the first data were collected within 12 days. The mobility of the cuvettes and the connecting lines helped to speed the initial set-up and subsequent transfer to new foliage.

PINE STUDIES, CASE I

On 1 September a small 3 meter pine located 25 m west of the instrument trailer was sampled (figure 4). Net assimilation (NA), or

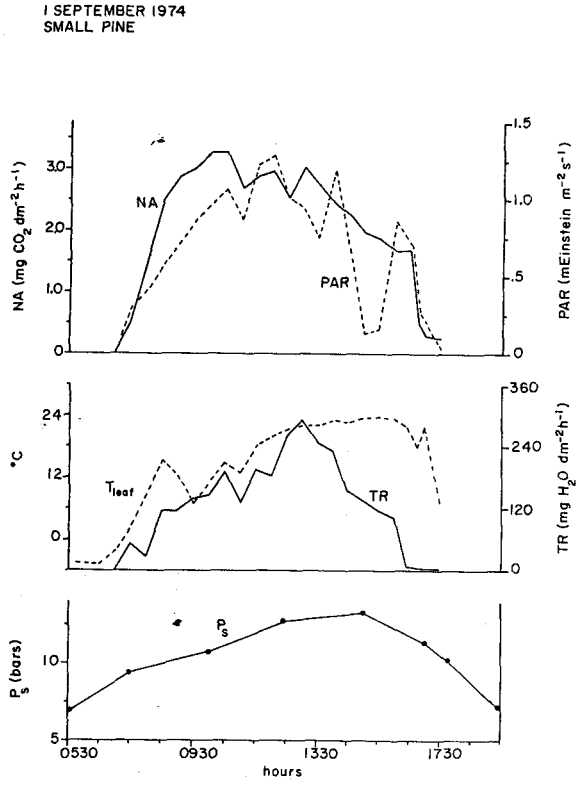

Figure 4. Net CO_2 assimilation (NA) of a young 3 meter *Pinus contorta/Pinus banksiana* (lodgepole pine/jack pine) hybrid located 25 m from the instrument trailer through the course of a low temperature high solar radiation day (1 September 1974) in relation to:

(1) PAR (Photosynthetically active radiation--400-700 nm)
(2) TR (Transpiration)
(3) T_{leaf} (Leaf temperature)
(4) P_s (Scholander pressure chamber values on twigs)

Note that this low temperature high radiation day prolonged the time period during which the plant would be more susceptible to air-borne pollutants since there was inadequate energy for excessive transpiration (TR).

uptake of CO_2 by the plant, peaked early in the morning at approximately 1030 hours although the photosynthetically active radiation (PAR) was not at the maximum recorded for the day. Air temperatures had dropped to -5°C just prior to sunrise and leaf temperatures remained low to moderate until late morning. Transpiration (TR) increased all morning with increasing leaf temperature. The transpiration peak occurred at 1300 hours or 2.5 hours after maximum net assimilation (NA) even though the photosynthetically active radiation

was greatest at 1200 hours. This suggests partial stomatal closure but not enough to inhibit greater transpiration (TR) associated with the higher afternoon temperatures. Plant water potential (P_s) dropped to less than -13 bars at 1500 hours due to substantial transpiration (TR) still taking place at that time. By 1700 hours, however, the water potential had risen by over 1.5 bars with both net assimilation (NA) and transpiration (TR) proceeding at negligible rates, indicating stomatal closure. It is not known if the low early morning temperature had any effect on net assimilation through increased mesophyll resistance (decrease in internal plant air space). The low early morning temperatures allowed for good net assimilation (NA) rates while not supplying adequate energy to drive a great amount of transpiration (TR), therefore the stomata were open longer. This low temperature high radiation day, as a result, allowed for greater photosynthate production on an area basis, but as a consequence, prolonged the time period during which the plant would be more susceptible to air-borne pollutants. The SO_2 analyzers were not yet available at the site.

PINE STUDIES, CASE II

Two dominant pines approximately 20 meters tall were monitored throughout the course of the study. Scaffolding was used as access to foliage on both trees. This allowed sampling of foliage with either a south-facing or north-facing exposure and facilitated collecting the many samples needed for monitoring plant water potentials (see plate 5).

The study site experienced an SO_2 episode during daylight hours on 13 September, by which time the Tracor 270HA and Envirometrics analyzers had been delivered to the site, tested and were operational. The early morning temperature on that day was near 0°C, but leaf temperatures increased rapidly and maximum transpiration (250 mg dm^{-2} hr^{-1}) was reached between 0830 and 0930 hours. Though low levels of H_2S and SO_2 (20 ppb and 0.1 ppm respectively) were measured with the Tracor unit during the previous night, only SO_2 was present during this exposure which occurred at approximately 0845 (figure 5).

The cuvette was located on foliage in the north tree so that at 0930 hours the south tree began shading the foliage causing a decrease in irradiance, net CO_2 assimilation and transpiration (TR). The levels of SO_2 never exceeded 0.1 ppm and it is doubtful that this low concentration for such a short period of time had any effect. If there was an effect from the SO_2, it was masked by the marked decrease in light. Early morning transpiration was high enough for plant water potential to drop to -14 bars and remain at that level until 1600 hours when it began to increase. The decrease in both transpiration and net CO_2 assimilation after 1100 hours indicated partial stomatal closure. Photosynthesis did not decrease as much as transpiration because of increased irradiance in the afternoon. Had there been more light in the morning the decline in photosynthesis no doubt would have been

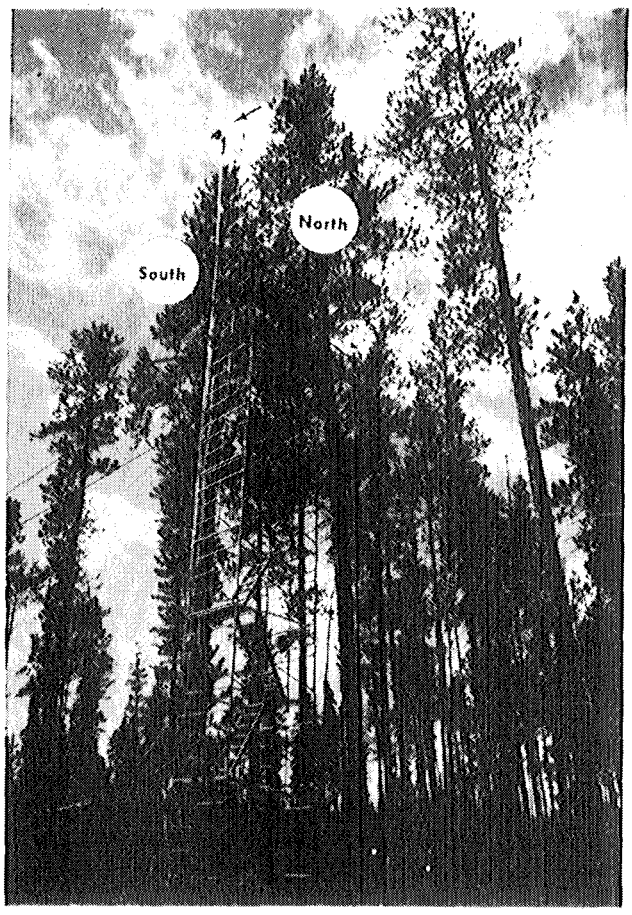

Plate 5. Fifteen meter access tower scaffolding to lodgepole pine/jack pine hybrids at the AMOCO Windfall Gas Plant experimental test site. The north-south orientation of the test trees is noted. The Windfall Gas Plant is to the right (west) in the photograph. The air intake for the three cuvettes is located just under the wind speed and direction instrumentation (noted by the arrow) at 20 meters.

greater. [Note: water potentials in the pines never dropped below -15 bars during the course of the field work.]

SPRUCE STUDIES

A 3 meter spruce located 30 m from the instrument trailer was studied on 2 September (figure 6). The decline in net CO_2 assimilation (NA) between 0930 hours and 1000 hours was caused by a decrease in irradiance (PAR) due to shading from adjacent pines. However, even with increased irradiance after 1100 hours, net assimilation did not regain its previous rate of 2.3 mg dm^{-2} hr^{-1}. Transpiration, calculated but not plotted in figure 6, reached a maximum rate (205 mg dm^{-2} hr^{-1}) at 1000 hours and had declined to less than half that value by 1100. This drop in transpiration even when there was a 3°C rise in leaf temperature and a 5 mb increase in vapor pressure deficit, indicated that stomata were closing. Plant water potential decreased to -17 bars (1 bar = 0.987 atm) by 1330 hours from a predawn value of -10 bars and remained at that level for at least an hour during which

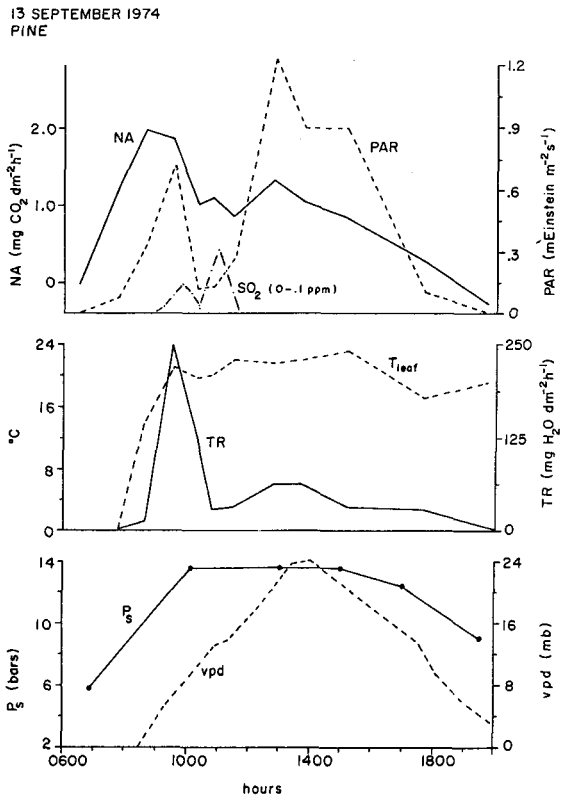

Figure 5. Net CO_2 assimilation (NA) at the 15 meter level in a *Pinus contorta/Pinus banksiana* (lodgepole pine/jack pine) hybrid through the course of a high temperature moderate solar radiation (scattered clouds) day (13 September 1974) in relation to:

(1) PAR (Photosynthetically active radiation--400-700 nm)
(2) SO_2 (in the cuvette air)
(3) TR (Transpiration)
(4) T_{leaf} (Leaf temperature)
(5) vpd (Water vapor pressure deficit in the air)
(6) P_s (Scholander pressure chamber values on twigs)

Stomatal closure is indicated by the rapid decrease in transpiration (TR) rate beginning at 0900 hours. The stomata were mostly closed during the remainder of the day. Despite the fact that clouds covered the sun during the SO_2 episode as indicated by the rapid decrease of photosynthetically active radiation (PAR), it is doubtful that this low concentration of SO_2 for such a short period of time had any effect. The stomata were also closing at this same time.

time transpiration had virtually ceased. By mid-afternoon, however, water uptake by the tree had resupplied enough water to decrease the plant water deficit by 2 bars.

ASPEN STUDIES

A 2 meter aspen located 30 m from the instrument trailer was studied on 22 August (figure 7). Net assimilation (NA) and leaf temperature (T_{leaf}) clearly followed irradiance through the course of the day, indicating that photosynthesis was light limited most of the day. The maximum value of net assimilation was 3 mg dm^{-2} hr^{-1}. Scholander readings were not taken on the aspen at this time, but early morning readings on the pines showed water potentials above -5 bars

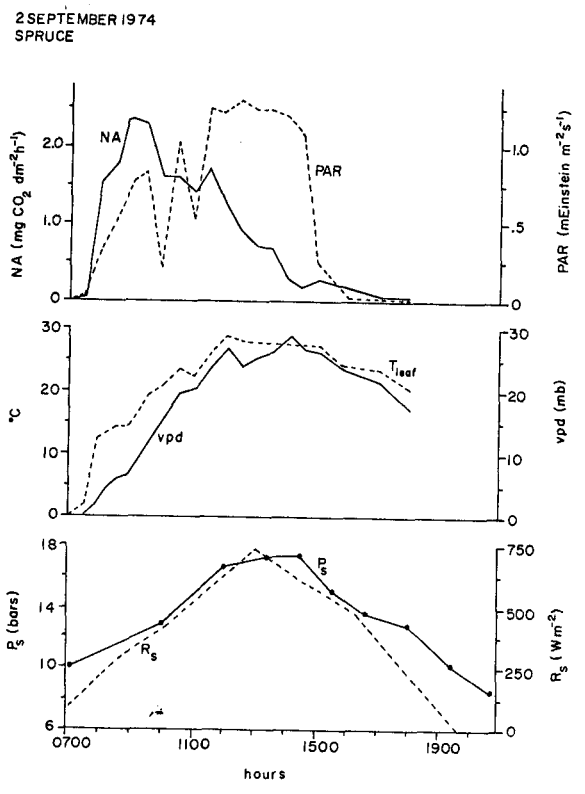

Figure 6. Net CO_2 assimilation (NA) of a *Picea glauca* (White spruce) sapling through the course of a moderate to low solar radiation and high temperature day (2 September 1974) in relation to:

(1) PAR (Photosynthetically active radiation--400-700 nm)

(2) R_s (Total solar energy at top of stand)

(3) T_{leaf} (Leaf temperature)

(4) vpd (Water vapor pressure deficit in the air)

(5) P_s (Scholander pressure chamber values on twigs)

Note the initial rapid increase in net assimilation (NA) and the gradual drop in NA throughout the remainder of the day despite adequate photosynthetically active radiation (PAR). This tree is in a condition of marginal water stress at this time.

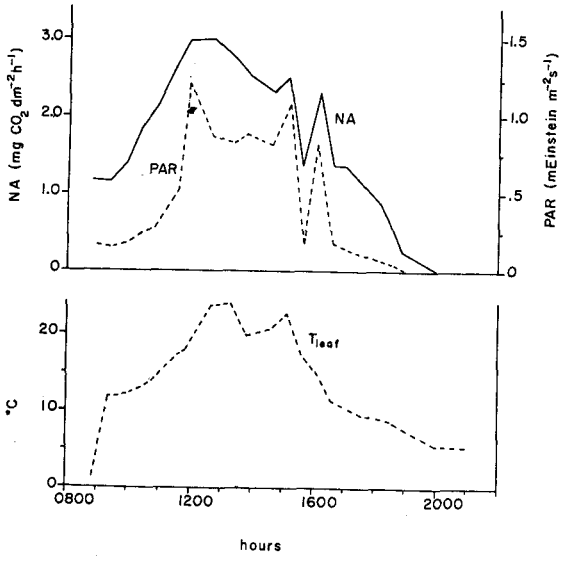

Figure 7. Net CO_2 assimilation (NA) of an aspen *(Populus tremuloides)* through the course of a high solar radiation low temperature day (22 August 1974) in relation to:

(1) PAR (Photosynthetically active radiation--400-700 nm)

(2) T_{leaf} (Leaf temperature)

Note that net assimilation (NA) and leaf temperature (T_{leaf}) follow photosynthetically active radiation (PAR).

which indicated adequate soil moisture. Ample soil moisture and relatively low air temperatures would aid in maintaining a wide stomatal aperture for most of the day.

FOLIAR SULFATE ANALYSIS

Foliage samples were taken from each of the plants monitored with the CO_2 gas-exchange system and from others which showed severe damage. These samples were dried and tested for sulfate-sulfur using the methylene blue colorimetric method of Johnson and Nishita (1952). Results have indicated high sulfate-sulfur levels (between 300 and 700 ppm), but too few samples were collected and analyzed to establish the relationship between sulfate accumulation and time. In one instance in which two age classes from the same branch were tested, the older foliage had a somewhat higher sulfate-sulfur concentration than the younger foliage. More research is required in this area to determine the role of sulfate build-up in plant tissues and sulfate toxicity.

PLANT CANOPY AND SULFUR GAS EMISSIONS

An SO_2 concentration gradient was detected using the three-point ambient air sampling system affixed to the 15 meter access scaffolding in the lodgepole pine/jack pine study site. During a fumigation concentrations of SO_2 were generally greater in the upper portion of the canopy (0.1 ppm above and 0.05 below). Under these conditions the stand crown was providing an adequate barrier to dispersal of emissions throughout the stand. This situation was reversed on several occasions with the lower sample point being 0.1 ppm and the value above the canopy being 0.05 ppm or below. The relationship can best be explained by advection of sulfur gas emissions from the gas plant into the leading edge of the stand. With little or no convection and the semi-closed nature of the plant canopy the SO_2 was removed by further advection and subsequent dilution.

DISCUSSION

For any plant to grow and maintain itself it must have a good rate of net CO_2 assimilation. This CO_2 uptake can be limited by different environmental factors acting on the photosynthetic apparatus and stomata. It is known that soil moisture, relative humidity, temperature and irradiance all affect photosynthesis through changes in stomatal aperture and it is therefore imperative that these environmental variables be monitored at all times when assessing net CO_2 assimilation.

Little information is available on how SO_2 affects photosynthesis, although it has been suggested that direct effects occur through enzyme-SO_2 interactions (Tanaka *et al.*, 1974; Zeigler, 1974). A majority of workers supports the position that low levels of SO_2 for short periods of time are relatively harmless, and at times can supply needed sulfur, but when long time intervals are involved with multiple exposures, the probability of visual damage or decline in CO_2 assimilation (limited photosynthetic capacity and hence decreased productivity) is enhanced.

The vegetation at the Windfall site is quite chlorotic and much of the foliage is being cast earlier than normal for both the pine and spruce (see plate 6). Several of the trees nearest the gas plant show

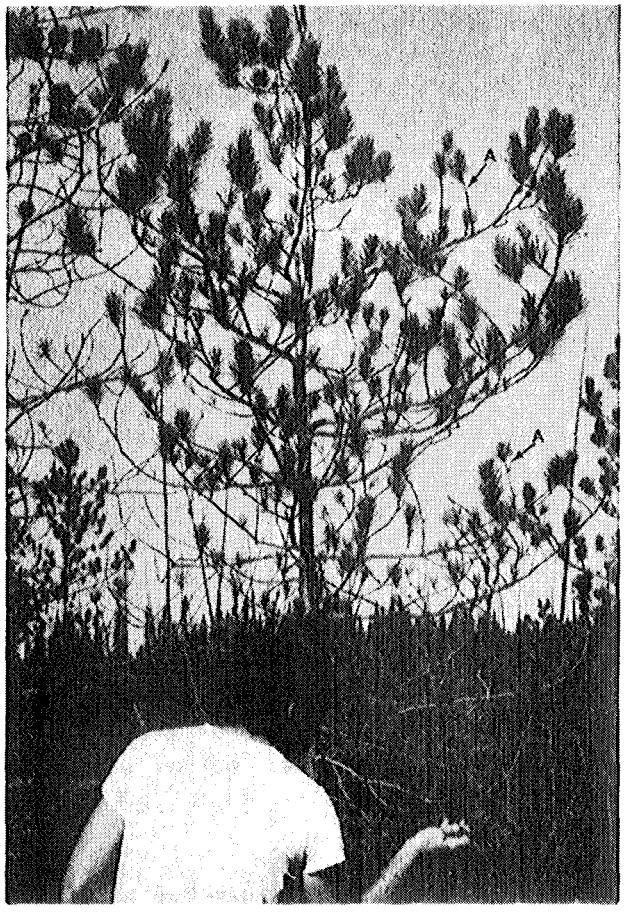

Plate 6. *Pinus contorta/P. banksiana* (lodgepole pine/jack pine) hybrid on windward (west) side of experimental site relative to the Windfall Gas Plant showing SO_2 symptoms such as premature needle drop (A) and growth retardation.

signs of acute SO_2 damage with severe growth retardation. There apparently is either a filtering action by the leading edge of the stand (biological sink) or, more likely, the stand limits air flow from the direction of the gas plant and thus reduces the number and/or severity of exposures.

Dykstra (1974) reported maximum net photosynthetic rates of 10 mg dm^{-2} hr^{-1} (projected needle area basis) in *Pinus contorta* seedlings. Direct comparison of his values with those reported here based on total surface area are misleading. A conservative conversion of Dykstra's values to total area would place the maximum rates between 4-5 mg dm^{-2} hr^{-1}. The maximum photosynthetic rate monitored in the pines at the Windfall site was 3.28 mg dm^{-2} hr^{-1}. Van Zindern Bakker (1974) observed a maximum rate in the field of 6 mg gDW^{-1} hr^{-1} for black spruce. Since the ratio of grams to dm^2 in conifer foliage is normally less than one, converting a rate from a dry weight to an area basis would decrease the magnitude of the rate. The highest rate calculated for the spruce at the Windfall site was 2.3 mg dm^{-2} hr^{-1}. All of the samples showed less than expected photosynthetic rates, but due to the approach of autumn it is possible that senescence was a factor in the low rates for aspen (3 mg dm^{-2} hr^{-1}). It is doubtful that the conifers were influenced by the onset of dormancy, but Van Zinderen Bakker (1974) observed that photosynthesis can be reduced when low temperatures (less than -2 C) occur, even during the summer. Neilson *et al.* (1972) working on Sitka spruce *(Picea sitchensis* (Beng.) Carr.) attributed such drops in photosynthesis to increases in mesophyll resistance.

Throughout the course of the field study plant water potentials in pine did not fall below -15 bars, while plant water potentials of -18 bars were recorded for spruce. At those minimum plant water potentials, transpiration in both species was greatly reduced. These results agree with those of Lopushinsky and Klock (1974) who found that the stomata of pines are more sensitive to decreasing leaf water potentials than the spruce. On days of high evaporative demand, the stomata of pine tend to close earlier than those of spruce and are less susceptible to air-borne pollutants under these conditions.

CONCLUSION

This preliminary investigation was seen as an extension of the controlled laboratory SO_2 fumigation experiments conducted by the Environmental Sciences Centre (Kananaskis), University of Calgary, for the Whitecourt Environmental Study Group.

Initial results from the field research indicate the following:

(1) The vegetation around the Windfall Gas Plant is basically characterized by two habitat types which repeat themselves across the landscape. These are the moist bogs and well-drained sand dune sites which are classified phytosociologically as a *Pinus-Picea glauca/ Arctostaphylos uva-ursi* (pine-white spruce/bearberry) association and a *Picea mariana/Ledum-Sphagnum* (black spruce/Labrador tea-sphagnum) bog association.

(2) SO_2 and H_2S in the atmosphere were found to be extremely variable with levels generally below ambient air quality standards.

(3) A concentration gradient of SO_2 was found to exist in the lodgepole pine/jack pine stand where the gas-exchange experiments were undertaken, with the SO_2 values above the plant canopy generally higher than levels below the plant canopy (0.1 ppm above and 0.05 below). This relationship was occasionally reversed.

(4) Lower than expected photosynthetic rates were observed for lodgepole pine, spruce and aspen.

(5) Unusually high sulfate-sulfur levels were found in plant material of lodgepole pine.

(6) Visible chronic SO_2 symptoms on plant material were more common on the windward side of the experimental site relative to the Windfall Gas Plant.

(7) Visible chronic SO_2 symptoms had a pronounced sun, or upward, orientation. This fact was experimentally verified in the laboratory.

The vegetative environment around the Windfall Gas Plant is definitely affected by sulfur gas emissions, but the extent remains to be determined.

RECOMMENDATIONS

It is critical that further research place particular emphasis on the transfer processes that affect the movement of sulfur gas emissions from their source to their contact with the vegetation through the stomata down to the molecular level. When it is known how these processes are modified and under what conditions, we can begin to estimate the effect.

Specific recommendations for further studies into the effects of sulfur gas emissions on vegetation are:

(1) Air quality monitoring trailers need to monitor environmental parameters which modify plant response such as soil moisture, relative humidity and photosynthetically active radiation (PAR) in addition to wind speed/direction, concentration of pollutants and temperature.

(2) Paired plot studies based on ecologically similar sites, determined by phytosociological analysis, between affected and unaffected locations of basal area growth rates in black spruce, white spruce, birch and/or aspen should be undertaken. A similar study

should also be done with mosses, liverworts and lichens epiphytic on given tree species.

(3) Analysis of plant macronutrients, particularly nitrogen and phosphorous, should be conducted. At present nitrogen dificiency cannot be eliminated as a possible contributing factor to the general chlorotic condition of the vegetation around the Windfall plant.

(4) Controlled SO_2 fumigations of plant species under field conditions to determine on-site responses should be undertaken.

(5) Key plant metabolites such as chlorophyll (total chlorophyll, chlorophyll a, and chlorophyll b) pigments, carotenoid pigments, Adenosine triphosphate (ATP), soluble sugars, amino acids, total sulfur and sulfate-sulfur should be monitored to determine the metabolic status of vegetation exposed to sulfur-gas emissions

(6) Plant water and soil water relations should be monitored seasonally to determine plant and soil water flux.

(7) Micrometeorology and its relation to sulfur-gas emissions should be studied to obtain a measure of the SO_2/H_2S concentration to which a defined plant canopy is exposed and the major environmental parameter fluctuations during this exposure.

ACKNOWLEDGEMENTS

This work would not have been possible without grants from the following agencies to the Environmental Sciences Centre (Kananaskis), University of Calgary:

(1) Whitecourt Environmental Study Group,
(2) Research Secretariat, Alberta Environment,
(3) Oil Sands Environmental Study Group, and
(4) UNISUL (University of Calgary Interdisciplinary Sulfur Research Group).

In addition to data collected at the study site, air quality data were made available by AMOCO from their Windfall Gas Plant and at the Whitecourt headquarters. Thanks are extended to Mr. Byron G. Scott for valuable technical assistance, and to Dr. David J. Salo for indispensable advice on equipment and methodology.

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DEVELOPING REGULATORY PROGRAMS FOR THE CONTROL OF ACID PRECIPITATION

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ABSTRACT

The U.S. Clean Air Act provides mechanisms by which the public welfare may be protected from "any known or anticipated adverse effects associated with the presence of (an) air pollutant in the ambient air." The history of the U.S. Environment Protection Agency's (EPA) efforts to establish and defend a secondary ambient air quality standard for sulfur oxides is reviewed. The role of acid rain in producing "welfare effects" is described. Emphasis is given to the fact that a wide range of effects not simply limited to forest vegetation must be considered when designing pollution control programs.

The possible effects of ignoring acid rain in developing control strategies to meet health related standards for sulfur oxides, nitrogen oxides and particulates are mentioned. Researchers need to be aware of the kinds of information which are needed by regulatory agencies before a regulatory program can be designed for alleviating the threat. Concern and speculation are not adequate. Accurate dose-response information and cumulative damage estimates are needed to quantify the effects of acid rain. Of vital importance are: (1) discovery of pollutant concentrations, mechanisms, and atmospheric conditions which lead to harmful effects: and (2) identification of major sources of the pollutant. The effect such information could have on techniques for meeting ground-level air-quality standards such as tall stacks and Intermittant Control Systems (ICS) is discussed. The desirability of an integrated research effort in this area to answer these needs is stressed. EPA efforts in this regard are mentioned.

Recent reviews of available data (1,2,3) indicate that precipitation in a large region of the United States is highly acidic when compared to the expected pH value of 5.7 for pure rainwater. Figure 1

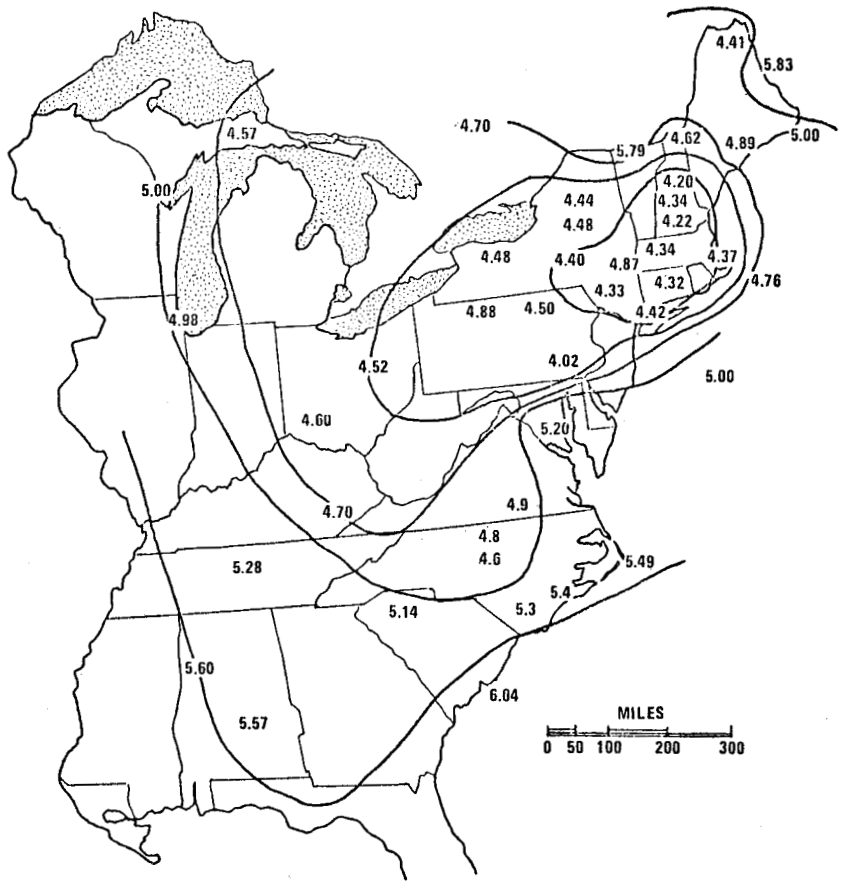

Figure 1. Rainfall acidity, 1965 - 1966 (pH units).[1]

shows that the average pH of precipitation in the northeastern U.S. was routinely less than 4.7 in the mid 1960's. More recent information indicates that in this area, pH's between 3.0 and 4.0 are observed during individual storms.(3,4) Analyses of historical trends suggest that the regional acid rain phenomenon began to develop in the early 1950's and has widened and intensified to some extent since that time. (1,3) The causes of this situation are not well understood, but it has been suggested that acid rain is related to regional emissions of acid forming air pollutants, chiefly sulfur oxides and nitrogen oxides.(3,5)

A growing body of evidence suggests that acid rain may be responsible for substantial adverse effects on the public welfare. Such effects may include acidification of lakes, rivers and groundwaters, with resultant damage to fish and other components of aquatic ecosystems;(6) acidification and demineralization of soils,(7) reduction of forest productivity,(8) damage to crops, and deterioration of man-made materials.(2) These effects may be subject to cumulative build-up as a result of years of exposure to acidic precipitation but some may also result from "peak" acidity episodes.

It is of great importance that the causes and consequences of acid precipitation become more fully understood in the near future so that corrective measures can be taken to minimize any deleterious effects. This paper will briefly outline the regulatory options available in the United States for implementing control programs designed to protect public welfare. It will also discuss some of the past experiences with such programs with regard to the importance of developing a sound data base to support regulatory strategies. In addition, emission projections are presented to indicate the trends in precipitation acidity over the next several years under current Federal and State control programs. Also, important areas for further research leading to the establishment of a regulatory program for acid rain are suggested.

THE CLEAN AIR ACT

The Clean Air Act as amended in 1970 and 1974 is the basic U.S. Federal Law for controlling the adverse effects of air pollution. Air-pollution control organizations must determine how much of the acid precipitation problem will or can be solved through current regulatory mechanisms provided under this Act. The first task of establishing any pollution-control program is the analysis of available scientific information. In this analysis, knowledge of a pollution threat is matched with regulatory options available for controlling the pollution problem. The entire problem/regulatory option-assessment is called "a prefered standards path analysis."

As provided by the Clean Air Act, air pollution can be controlled in several ways. The basic regulatory options available are: (1) National Ambient Air Quality Standards, (2) Performance Standards for New Sources, (3) National Emission Standards for Hazardous Pollutants, (4) National Emission Standards for Mobile Sources, (5) Regulation of Fuels and Fuel Additives, and (6) Abatement Conferences.

The National Ambient Air Quality Standards (NAAQS) (Section 108 of the Act) specify an ambient concentration of a pollutant over a prescribed time period which cannot be exceeded. There are two types of NAAQS: the primary standards which are designed to protect public health and the secondary standards which are designed to protect the

public welfare. In general, a pollutant is considered a likely candidate for NAAQS if its presence in the air is the result of numerous and diverse mobile and stationary sources.

New Source Performance Standards (NSPS) (Section 111 of the Act) are emission limitations for new or modified sources which contribute significantly to air pollution which causes or contributes to the endangerment of public health or welfare. The NSPS for any specified pollutant must be based on the best degree of control, including the consideration of cost, and must be adequately demonstrated. Also, no new source, even if it meets NSPS, can be operated if it will cause a violation of a National Ambient Air Quality Standard.

National Emission Standards for Hazardous Pollutants (NESHAP) (Section 112 of the Act) are established for pollutants for which there is no NAAQS and which may cause an increase in mortality or serious irreversible, or incapacitating reversible illness in men. Pollutants for which these standards are established are a more serious threat to the public health than pollutants controlled by the NAAQS. To date, hazardous emission standards have been established for significant sources of atmospheric mercury, asbestos, and beryllium.

Standards are established for pollutants emitted from mobile sources (Section 202 of the Act) which harm public health or welfare. Mobile source emission reductions for CO, HC, and NO_x as mandated by the 1970 Clean Air Act require a 90 percent reduction from 1970 levels for each of the pollutants.

Section 211 of the Clean Air Act provides for the registration and control of any fuel or fuel additive. Under this section of the Act, manufacturers may be required to give the name of any additive, the concentration of the additive in the fuel, the purpose of the additive, and the chemical composition of the additive. Also, the law provides that the manufacturer conduct tests to determine the possible health effect of any additive or the emissions resulting from the use of the additive.

Interstate or international air-pollution problems are addressed under the Abatement Conference Section of the Clean Air Act (Section 115). As a result of conference recommendations addressing problems which span state or national boundaries, the law provides authority to seek court relief to ensure abatement.

POTENTIAL APPLICATION OF REGULATORY OPTIONS TO ACID RAIN

The characteristics of the potential acid-precipitation problem are somewhat unique. It is hypothesized that atmospheric emissions of precursors such as SO_2 and NO_2 are transformed into strong acids before

or during transferal between air and rainfall. The precipitation then plays an important role in concentrating and delivering the pollutants in a form in which they can be more damaging than if they were present as gases dispersed throughout the mixing layer. The connection between emissions, atmospheric concentrations, and effects is thus mediated through precipitation removal processes. Nevertheless, a strategy for acid-precipitation control could be applied under existing clean air options. The most effective means for control would probably center around a set of strategies based on the attainment of National Ambient Air Quality Standards and New Source Performance Standards for acid precursor pollutants.

Previous experiences with the establishment of ambient air quality standards have pointed to a need to have a sound scientific basis. When the SO_x standards were first promulgated in 1971, the scientific basis for the annual 60 micrograms per cubic meter ($\mu g/m^3$) standard was successfully challenged by industry. In a defense of the need for the standard, it could not be shown that the annual 60 $\mu g/m^3$ level specified by the standard would prevent any specific environmental effect. As a result, the standard was revoked. The lesson which was learned pertaining to any future air quality standards related to acid rain, is that soundly quantified scientific evidence is clearly needed. In addition, the scientific community must be willing to stand behind standards, many times calling upon their scientific judgment, to render support. This is especially important when considering the many hard-to-quantify effects which are apparently caused by acidic precipitation.

Table 1 lists the National Ambient Air Quality Standards for acid

Table 1

U.S. AMBIENT AIR QUALITY STANDARDS

POLLUTANT	AVERAGING TIME	PRIMARY STANDARDS	SECONDARY STANDARDS
SULFUR OXIDES	ANNUAL (ARITHMETIC MEAN)	80 $\mu g/m^3$ (0.03 ppm)	—
	24 - HOUR	365 $\mu g/m^3$ (0.14 ppm)	—
	3 - HOUR	—	1300 $\mu g/m^3$ (0.5 ppm)
NO_2	ANNUAL (ARITHMETIC MEAN)	100 $\mu g/m^3$ (0.05 ppm)	(SAME AS PRIMARY)

precursor pollutants. All 55 States and territories are required to have plans which provide for the attainment and maintenance of these as well as the other National Ambient Air Quality Standards.

At the present time, only a three hour secondary standard for SO_2 exists for the prevention of damages in the same category as those caused by acidic precipitation. However, when compared to the many effects caused by acid precipitation, the basis for this current secondary standard is rather unimpressive. For example, the reason for the standard is prevention of leaf spotting on vegetation. Reasons for preventing acid precipitation could conceivably surpass this in many respects. Compared to the research effort and information being collected around the world on health effects, research to date concerning the adverse effects of acidic precipitation is extremely limited.

The control of acid precipitation through the attainment and maintenance of Air Quality Standards is possible only if the standards are met through emission reduction. One convenient way for meeting an air quality standard is obviously through the use of dilution techniques such as tall stacks and intermittent control systems. But if one accepts the notion that acid rain is a potentially serious regional and ecological problem that may be related to regional emissions of acid precursors, then total sulfur and nitrogen loading of the atmosphere must be controlled. Identifying the environmental damages resulting from acid rain provides yet another reason for limiting dilution strategies and encouraging the use of control devices and fuels which reduce the total sulfur and nitrogen loading of the atmosphere.

One viable means of countering the growth of gaseous acid precursors is through the establishment of additional New Source Performance Standards. Table 2 shows some typical acid presursor emitting

Table 2

SOME OF THE NEW SOURCE PERFORMANCE STANDARDS

BEST AVAILABLE CONTROL TECHNOLOGY
FOR
STEAM GENERATORS (SO_2, NO_2, TSP)
SULFURIC ACID PLANTS (SO_2)
NITRIC ACID PLANTS (NO_2)
PETROLEUM REFINERIES

sources for which NSPS are currently in effect. Standards for sources such as these not only provide for the attainment of the NAAQS, but in the long-run, as existing sources die out, could provide for a downward trend in regional pollutant emissions causing atmospheric acid formation.

TRENDS AND PROJECTIONS

Some authors (2,3) have expressed the concern that regional acid precipitation may markedly increase over the next several years due primarily to increased SO_x and NO_x emissions resulting from coal combustion. The region of greatest concern is the northeastern quadrant of the nation. This region is also of importance with respect to investigation of atmospheric suspended sulfates and their effect upon public health. Based on suspended sulfate measurements, a 24-state area (Figure 2) had significantly higher sulfate concentrations than the rest

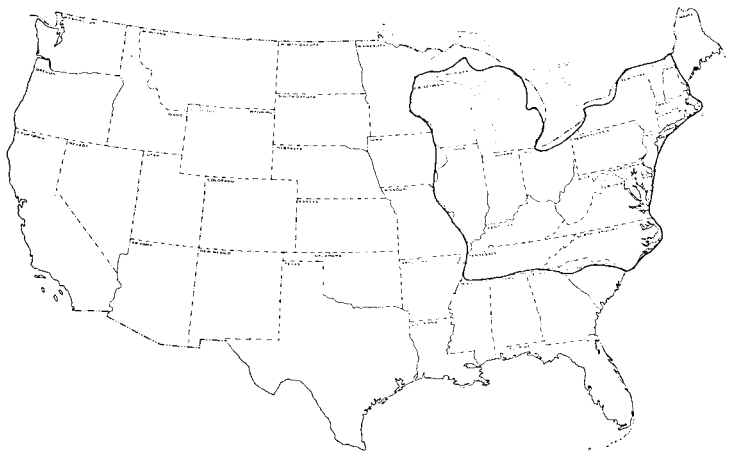

Figure 2. High sulfates 24 State Region

of the nation. Comparison of Figure 2 with Figure 1 indicates that this region is quite similar to that impacted by precipitation of pH5 or less. Some information on the likely trends for acid precipitation can be obtained from examination of emissions projections originally made to project trends in acid sulfate aerosol levels.(9) SO_2 emissions for this region from 1969 projected through 1980 are presented in Figure 3.

These projections assume that current State and Federal SO_2 emission limits are successfully implemented through the 24-State Region. Assuming that SO_2 is one of the more important agents in forming the regional acid precipitation, a dramatic increase in sulfuric acid related precipitation over the next few years is not anticipated.

It is interesting to note that in the time period 1969 to 1974 which the historical data covers, that SO_2 emissions remain essentially constant. This seems to be in agreement with the results of the Hubbard Brook Work (3,1) where the sulfate in precipitation remained about constant during the same time period.

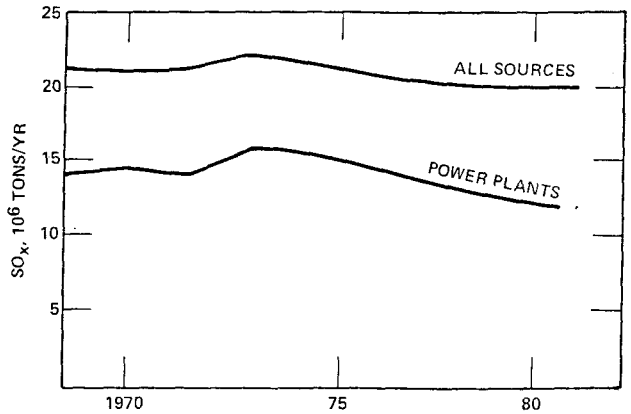

Figure 3. Projected SO_x Emissions, 24 State Region.

The historical NO_x emissions data base is less reliable than that for SO_2. However, based on projections by the National Academy of Sciences (10) and 1972 data compiled by the National Emissions Data System of EPA, NO_x emissions in this 24-State Region might increase from 15×10^6 tons in 1972 to about 18×10^6 in 1980.

Although SO_2 emissions will be limited to the extent necessary to attain and maintain the National Ambient Air Quality Standards, they may not be doing much to alleviate the cumulative effects of acid precipitation. A feeling exists that acid rain causes an adverse buildup in the environment. Feelings or speculations are not enough, however. More hard, conclusive evidence of the acid rain's relation to air pollution are needed before regulatory programs can be established.

RESEARCH NEEDS

The most basic need for establishing a regulatory program for acid precipitation is to be able to intelligently relate the sources which can be regulated to damages caused by acid rain.

Some of the more specific elements of these basic research needs are posed in the following questions:

What pollutants and levels of those pollutants significantly contribute acid rain? (SO_2, NO_2, HCl, etc.?)

What is the relation between pollution concentration and environmental damage? Is the old approach to measuring ground-level concentrations satisfactory?

What is the relationship between pollutant emissions and environmental damages? (Transport and Transformation Models)

Where are the regions most affected?

What kinds of sources predominate in those regions?
What is the natural composition of and potential for environmental damage in those regions?
What emission controls are available?
What is the most efficient control strategy?
What are the benefits of preventing acid precipitation?
Are the proposed control strategies enforceable?
Are goals for controlling acid rain realistic?

In summary, acid rain may be a serious environmental problem which will require regulation within the next few years. Past experience has taught air quality regulators that a sound scientific base is a necessary ingredient for developing effective regulatory control programs. The information base must be broad in nature and cross the boundaries of different disciplines. The acid-rain problem must be understood all the way from the sources which emit acid pollutants through the varying atmospheric transformations and on into an affected environment. Concerned citizens, scientists, government regulatory agencies, and industry must cooperate to the address the acid-rain problem.

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