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

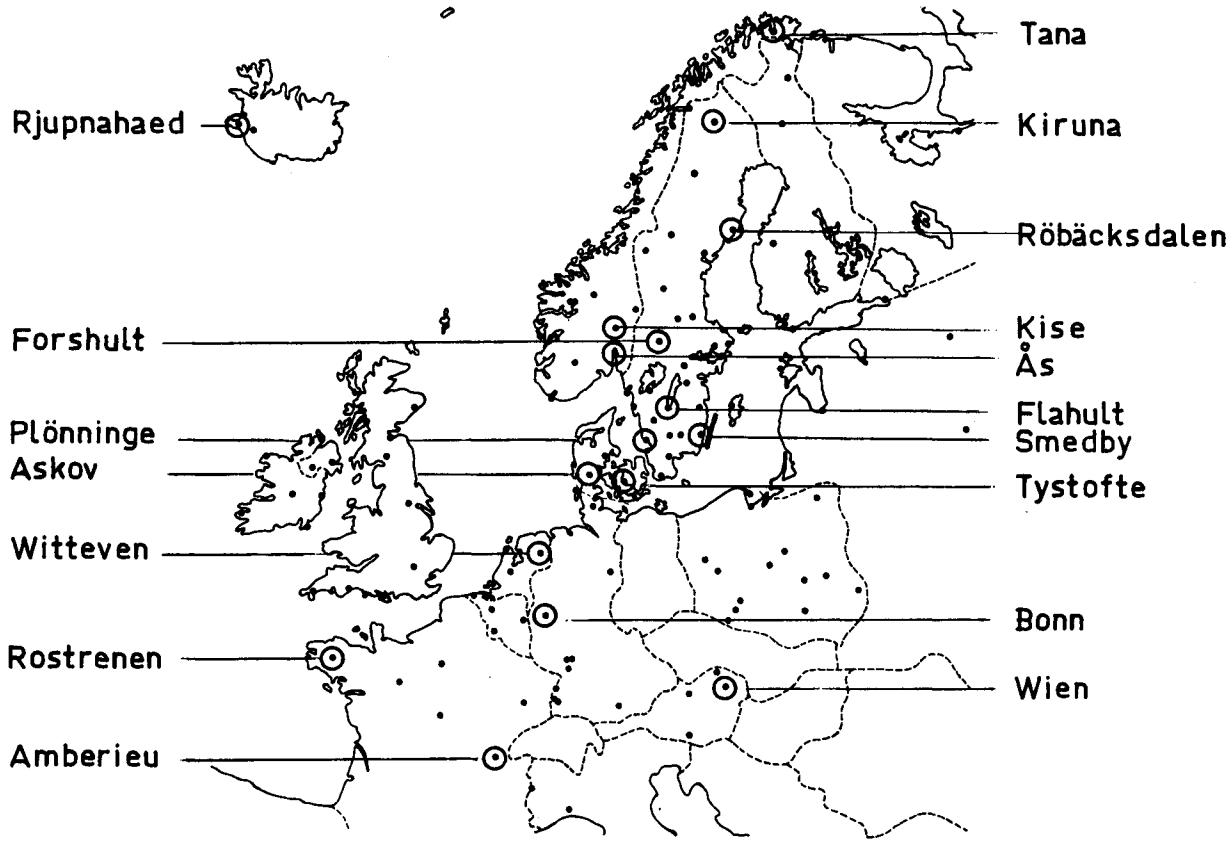


Figure 1. Each dot on the map represents a sampling station for precipitation and air. Long-term data are available for the circled stations. Part of the network is coordinated by the International Meteorological Institute in Stockholm.

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

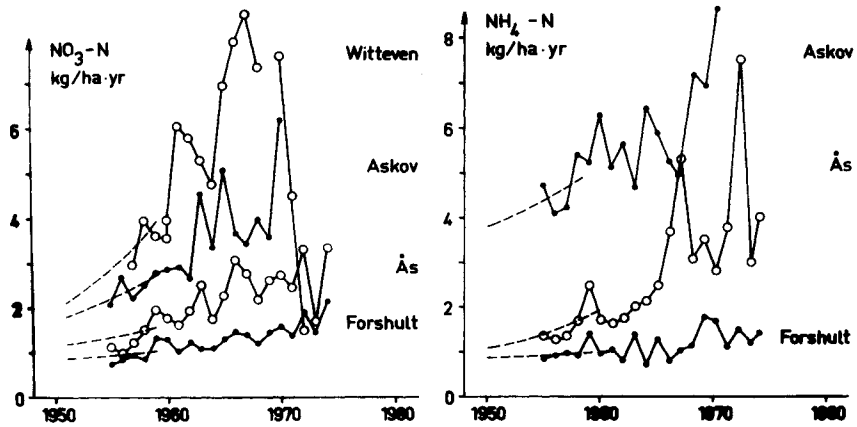


Figure 2. Time records of the wet fallout of nitrate and ammonia at some stations of the European network. The stations vary latitudinally from 60° N (Ås and Forshult) to 53° N (Witteven). See Figure 1 for location of each station.

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

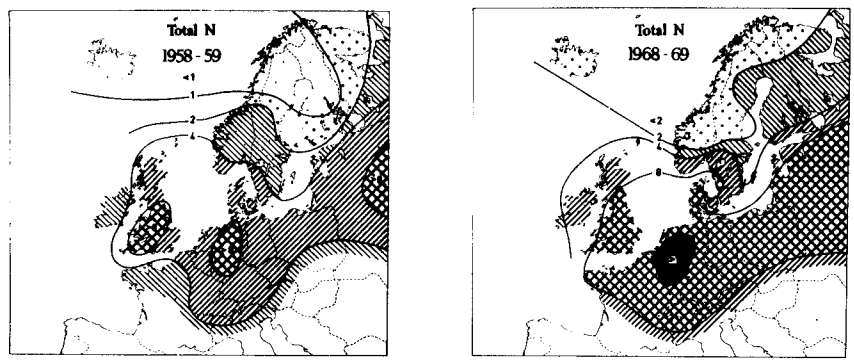


Figure 3. The maps show the geographical distribution of the wet fallout of total nitrogen (NO_3-N and NH_4-N) averaged for the period 1958-59 in comparison with 1968-69. Figures are given in kg/ha/year.

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).

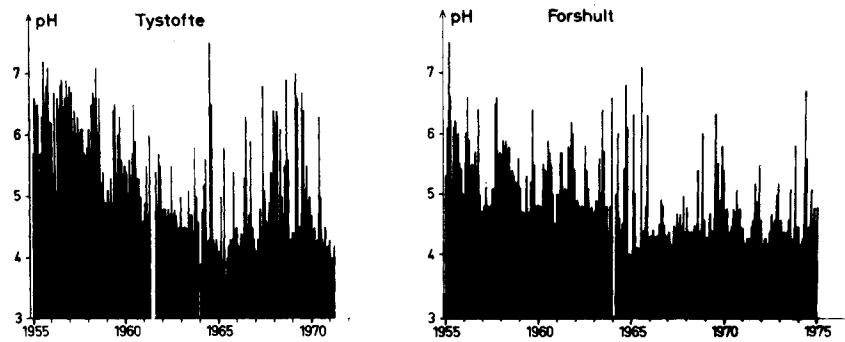


Figure 4. Monthly pH-values from Tystofte in Denmark from 1955 to 1971 and from Forshult in Sweden from 1955 to 1974. See Figure 1 for location of the stations.

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

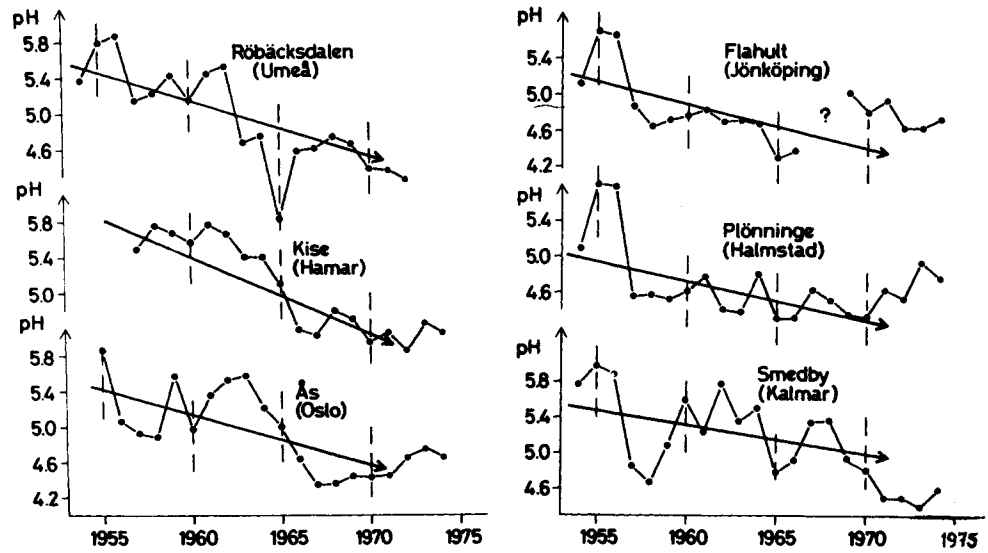


Figure 5. Yearly average pH-values for 2 stations in Norway and 4 in Sweden. The straight trend lines were drawn in 1970. Note the effect of additional data. The station at Flahult was operating only part-time in 1967 and 1968. Stations are localized in Figure 1.

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

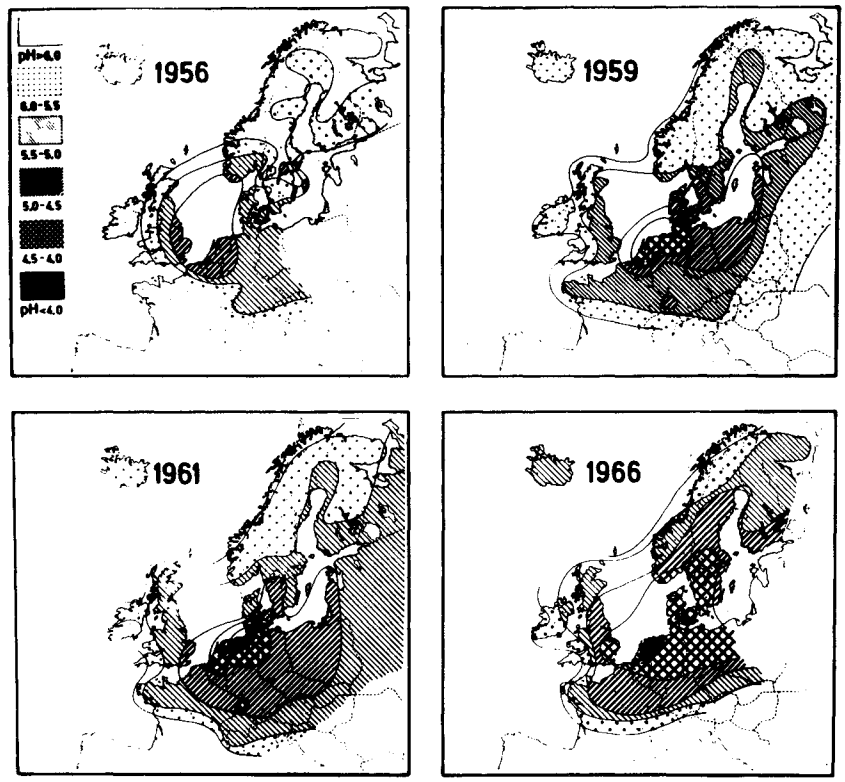


Figure 6. pH-maps for Europe for four years. Isolines differ by 0.5 pH-units. The maps are based on the yearly average of 12 monthly samples.

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

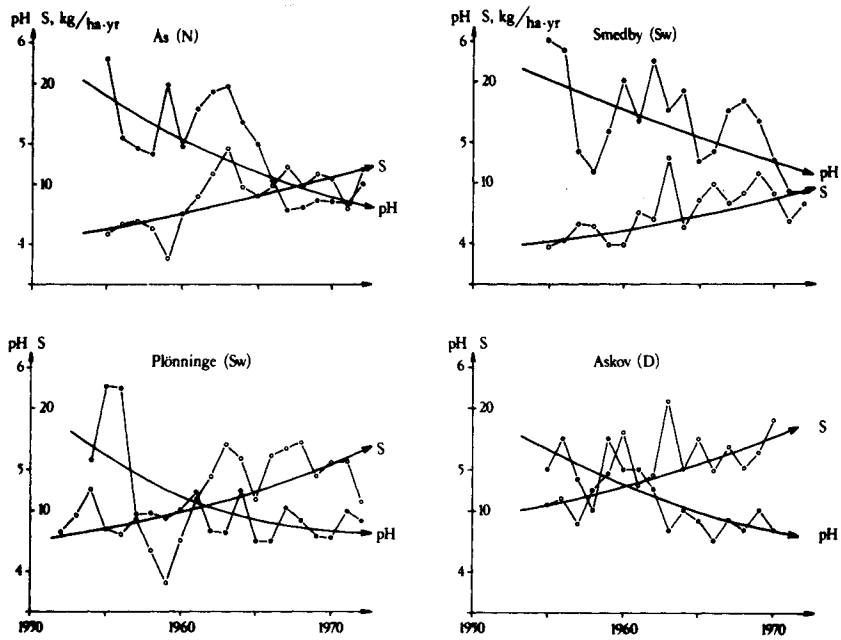


Figure 7. Sulfur and pH as yearly average figures at four stations in Scandinavia. For location, see Figure 1.

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).

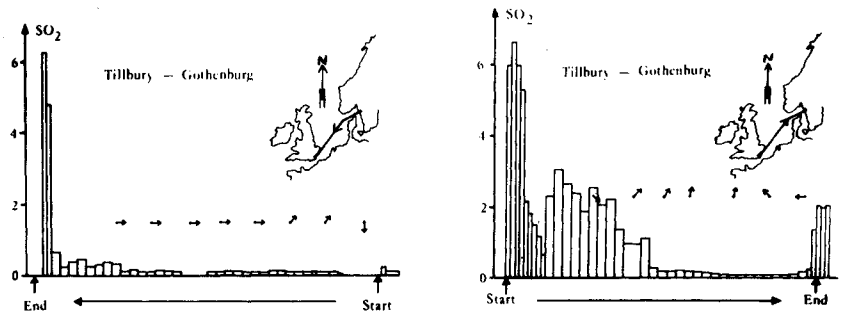


Figure 8. SO_2-data at "sea level" from a cruise by M/S Saga. The route is shown on the small map. The arrows indicate the wind direction. Measurements made by C. Brosset.

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.

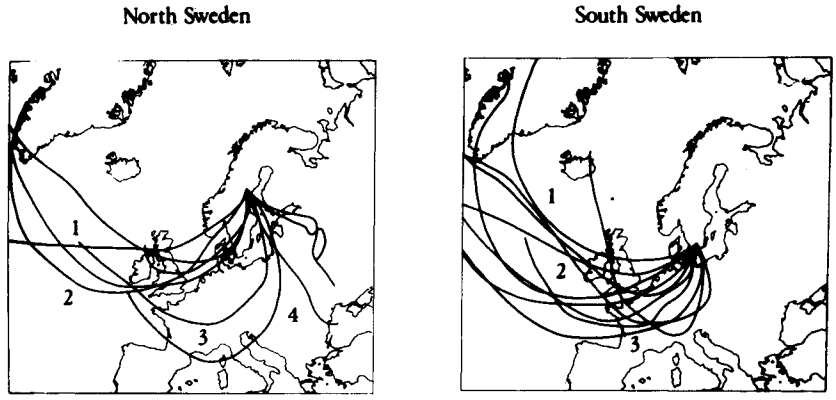
The emission of sulfur varies considerably between different countries in Europe. The figures below are computed from the Swedish Case Study: *Air pollution across national boundaries. The impact on the environment of sulfur in air and precipitation,* (13), which was presented at the UN Conference on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

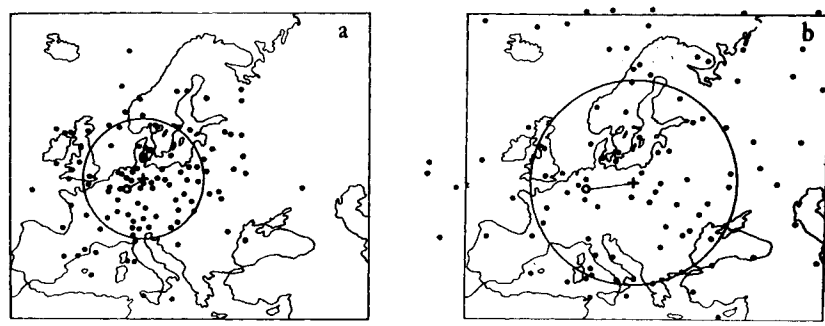


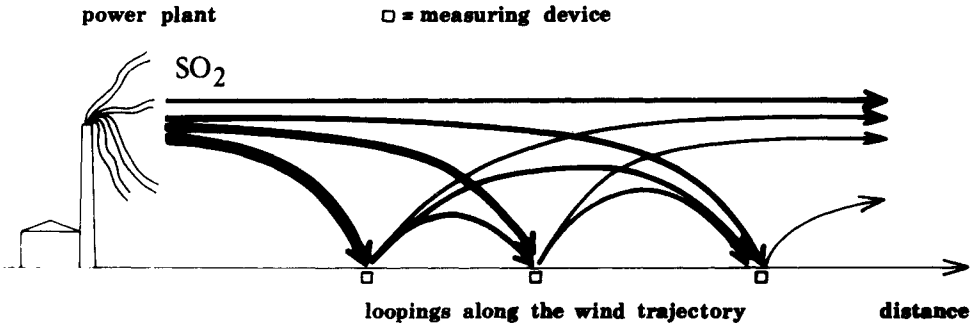
Figure 10. End points of trajectories at a height of 1.5 km from a point (marked by a circle) in northern central Europe for a) 24 hours and b) 60 hours calculated every third day for a period of about one year. 50% of the points are to be found within the circle which are centred around the mean position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

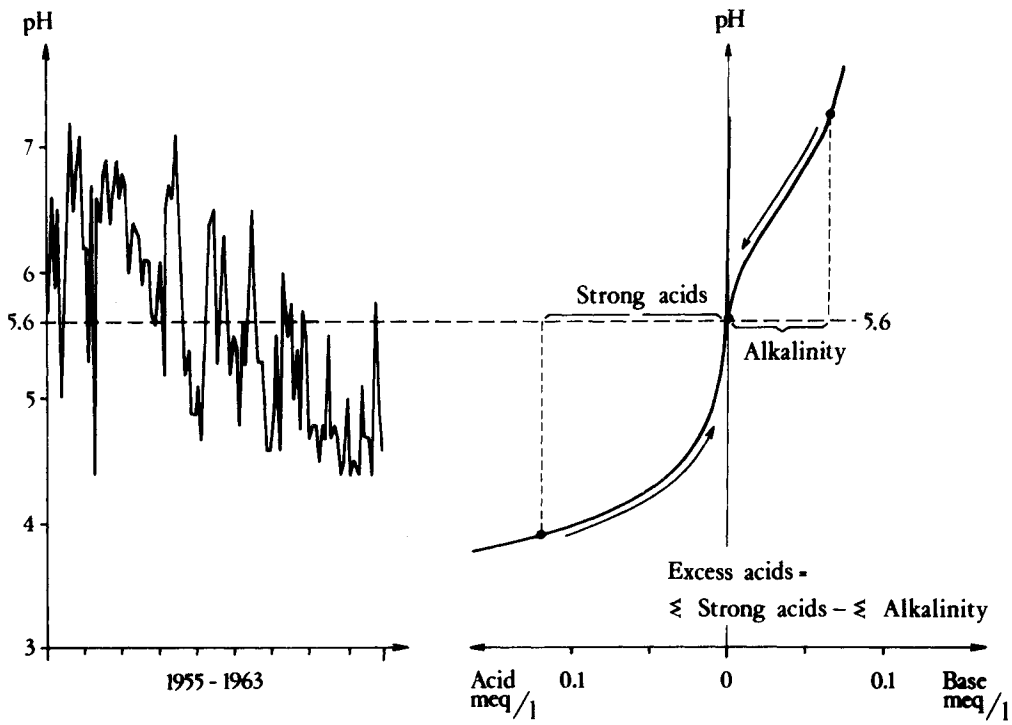


Figure 12. Left: Actual record of monthly pH-values. Right: Analytical and computational procedure of "excess acids".

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

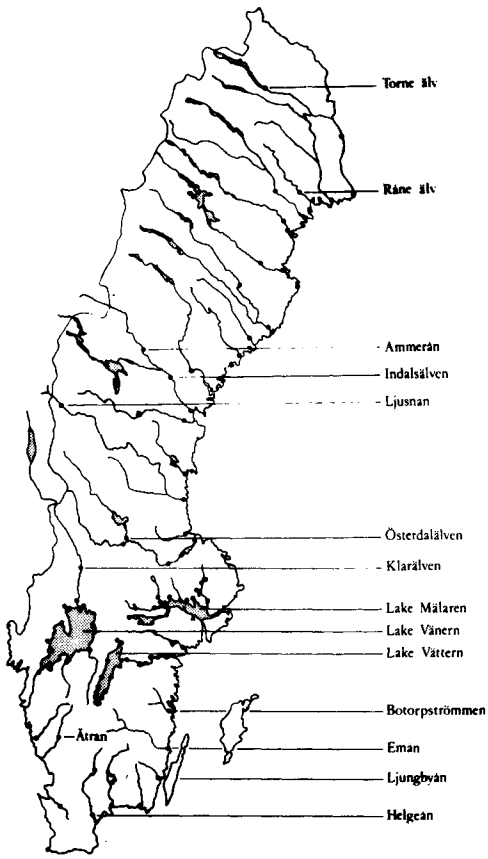


Figure 13. The major lakes and rivers in Sweden. The dots denote the location of the sampling stations. The network is administrated by the Limnological Laboratory, Uppsala, Environmental Protection Board of Sweden.

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

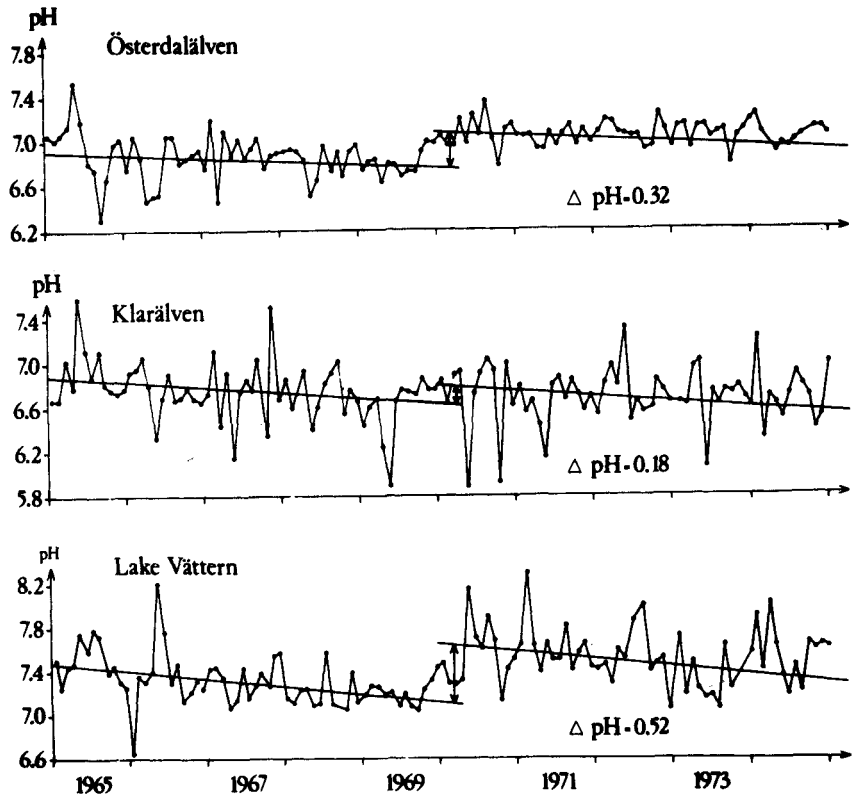


Figure 14. pH-records from 3 sampling stations of the Swedish water quality network during 1965 to 1974. ΔpH refers to the discontinuity denoted by an arrow in the beginning of 1970.

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

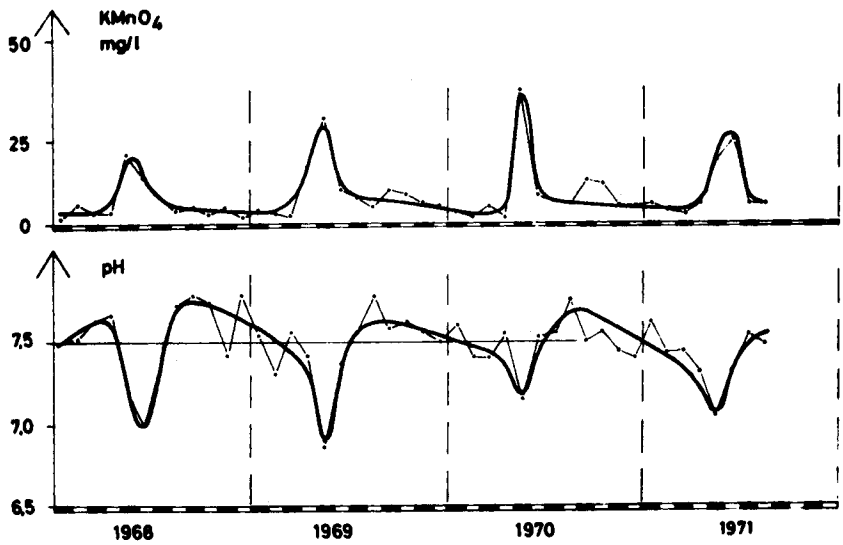


Figure 15. Records of pH and the consumption of $KMnO_4$ from the sampling station at river Ljusnan. See Figure 13 for location of this river.

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

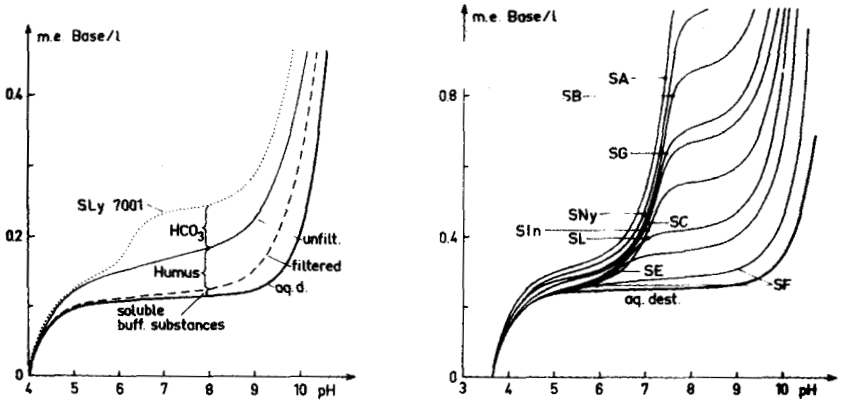


Figure 16. Left: The total buffering capacity of surface water (SLy 7001) is made up by HCO_3, humus and soluble substances. Right: Buffering curves of river waters from the Swedish water quality network. The dot on each curve denotes the pH-value at the time of sampling.

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

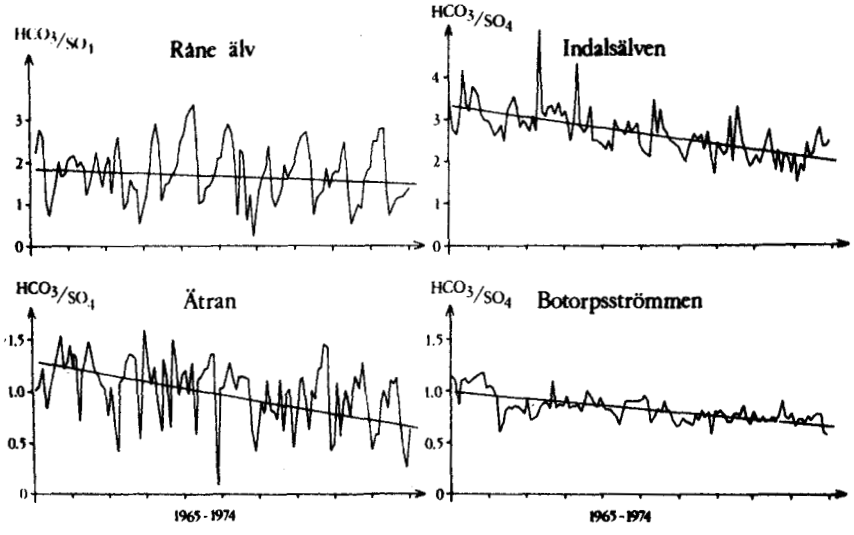


Figure 17. The ratio of bicarbonate to sulfate on an equivalent basis for four rivers of the Swedish water quality network. For location of the sampling stations, see Figure 13.

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

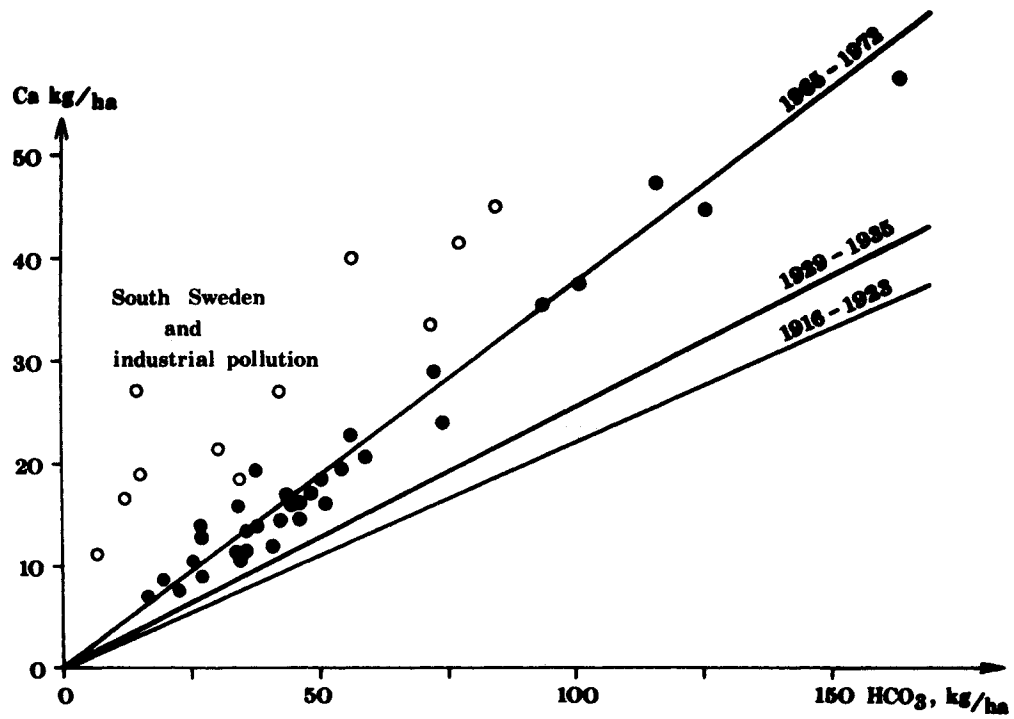


Figure 18. The discharge of Ca and HCO_3 by Swedish rivers at different time intervals. The circles refer to rivers in south Sweden and those polluted by calcium sulfate.

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

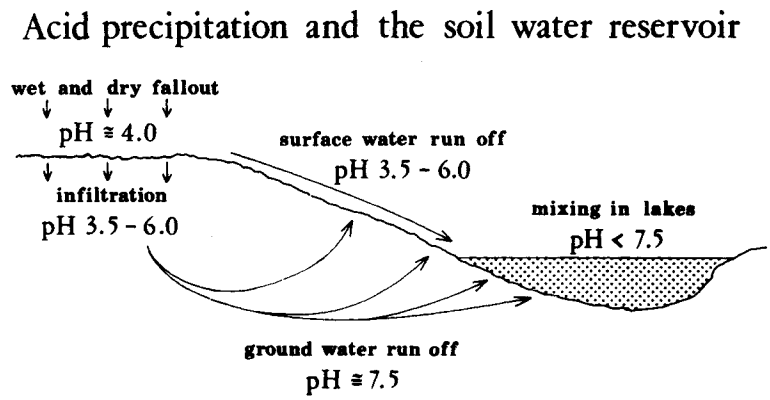


Figure 19. Part of the hydrological cycle related to soils and surface waters with respect to pH-changes along different pathways.

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.

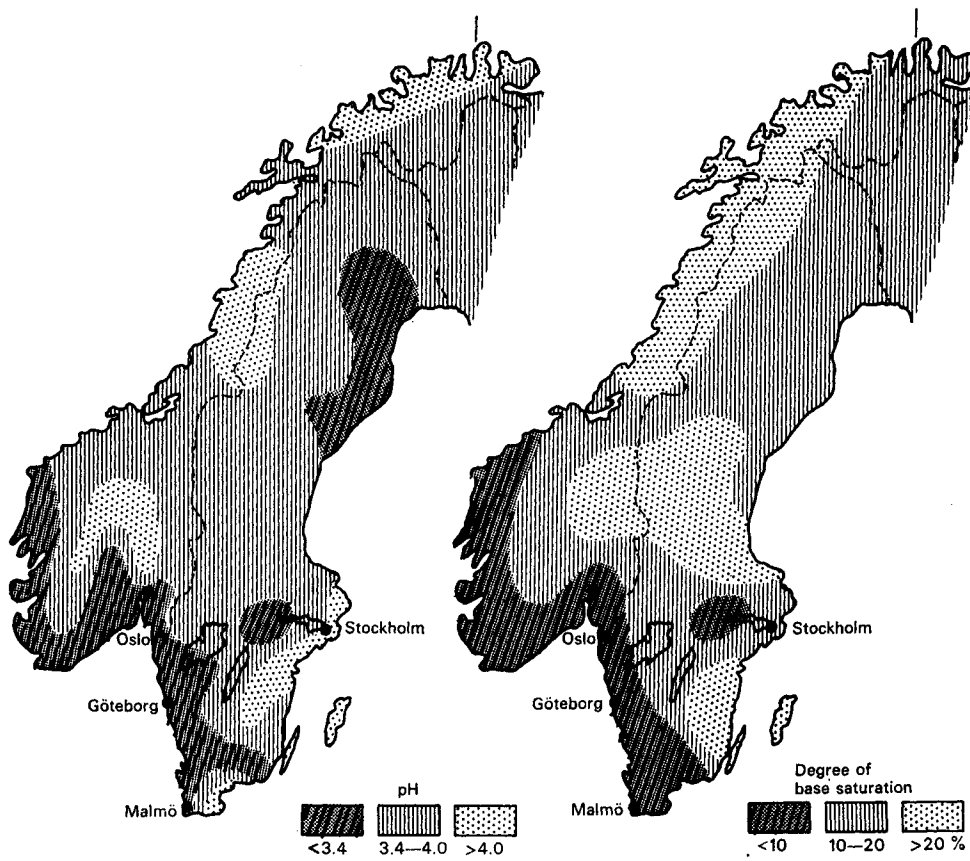


Figure 20. pH and the degree of base saturation in the upper 5 cm of podsolized forest soils in Scandinavia.

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.

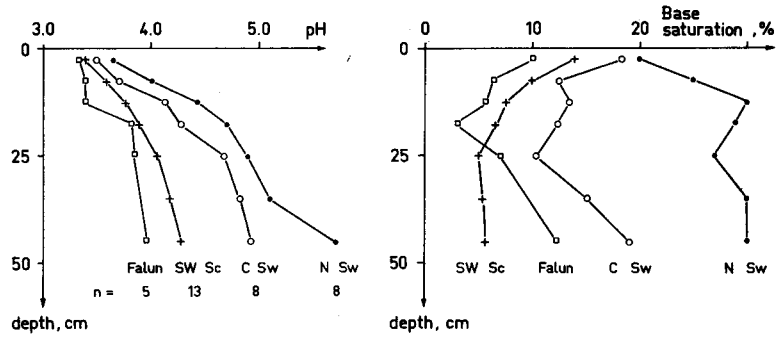


Figure 21. Profile data on pH and the degree of base saturation from the following parts of Scandinavia: South-West part of Scandinavia, Central Sweden and North Sweden. The Falu-area is also included. Data are averaged for the indicated number of profiles.

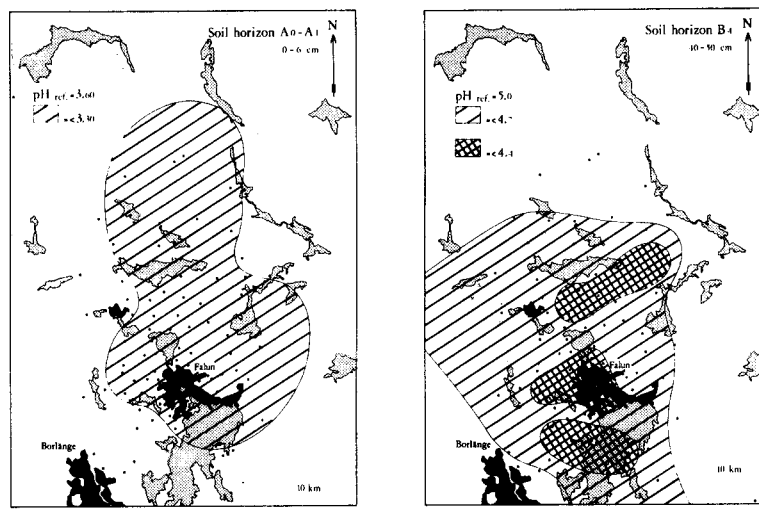


Figure 22. The maps show the pH-depression at horizon A_0-A_1 and B_4 in the Falu area. Reference values refer to sites outside the map.

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.

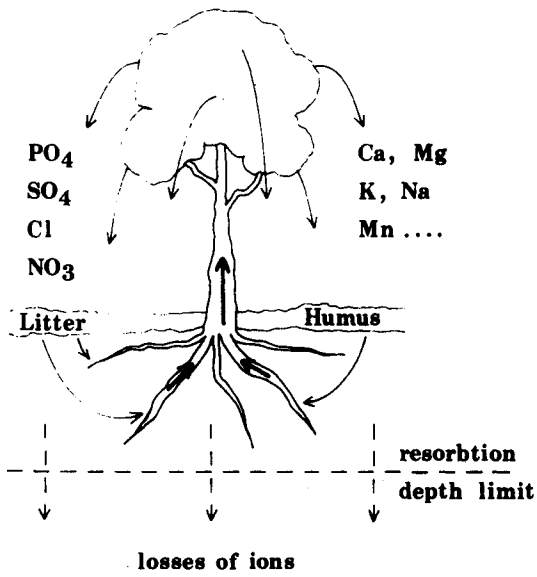
Biological acidification will be considerably enhanced when the production of organic matter is larger than the decomposition. This takes place in nature when peat bogs or forest peats are formed, and these systems are also very acid. However, the same applies to systems influenced by man. The harvest 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

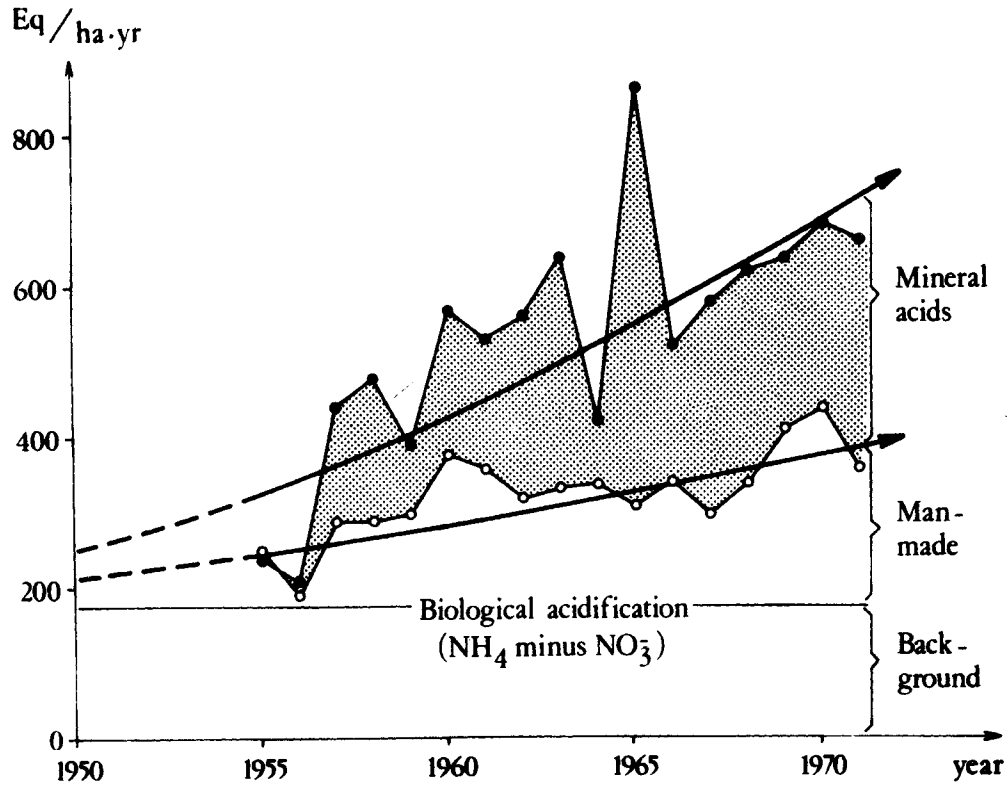


Figure 24. The curves show the time sequence of acidification due to mineral acids (= excess acids) and to biological processes. The background figure is computed from data in Figure 2. The computation is relevant for the southwestern part of Scandinavia and is based on data from the International Meteorological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

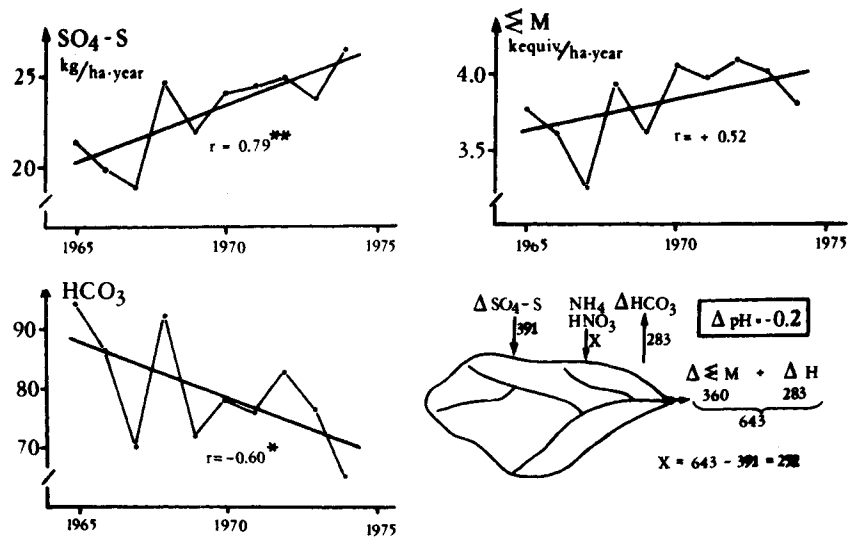


Figure 25. Discharge of SO_4-S, HCO_3 and the sum of cations (ΣM) from the drainage area of river Ätran. Changes of these quantities during the last ten years are given in eq/ha. X denotes the magnitude of processes due to biological acidification. Original data are recomputed to cancel the variations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

REFERENCES

Odén, S. THE ACIDIFICATION OF AIR AND PRECIPITATION AND ITS CONSEQUENCES ON THE NATURAL ENVIRONMENT. Swedish Nat. Sci. Res. Council, Ecology Committee, Bul. 1, pp 68, 1968. (In Swedish.) Also: Tr - 1172, Translation Consultants, Ltd., Arlington, Va., US.

Gorham, E. On the acidity and salinity of rain. GEOCHIM. ET COSMOCHIM. ACTA, 7, 231 - 239, 1955.

Gorham, E. Atmospheric pollution by hydrochloric acid. QUART. J. ROY. MET. SOC., 84, 273 - 276, 1958.

Gorham, E. Free acid in british soils. NATURE, 181, 106, 1958.

Gorham, E. Free acid in Minnesota podzols. ECOLOGY, 39, , 1958.

Environmental Research. Statens offentliga utredningar, 1967:43 (In Swedish).

Likens, G. E. and F. H. Bormann. Acid Rain: A serious regional environmental problem. SCIENCE, 184, 1176 - 1179, 1974.

Brosset, C. Air-Born Acid. AMBIO, 2, 2 - 9, 1973.

Charlson, R. J. et al. $H_2SO_4/(NH_4)_2SO_4$ background aerosol: Optical detection in St. Louis region. ATMOSPHERIC ENVIRONMENT, 8, 1257 - 1267, 1974.

Granat, L. On the relationship between pH and the chemical composition in atmospheric precipitation. TELLUS, 24, 550 - 560, 1972.

Cogbill, C. V. and G. E. Likens. Precipitation in the northeastern United States. WATER RESOURCES RESEARCH, 10(6), 1133 - 1137, 1974.

Rodhe, H. MEASUREMENTS OF SULFUR IN THE FREE ATMOSPHERE OVER SWEDEN 1969-1970. Int. Met. Inst., Report AC 12, 1971.

Air pollution across national boundaries. The impact on the environment of sulfur in air and precipitation (ed. B. Bolin). Sweden's Case Study for the United Nations conference on the human environment. Stockholm, 1971.

Brosset, C. Pers. Comm. at a seminar in Stockholm, April 17, 1975.

Eriksson, E. Sulfur dioxide and the acidification of precipitation--facts and speculations. IVL's konferenshandlingar, 86 - 95, 1969 (In Swedish).

Odén, S. and T. Ahl. The acidification of Scandinavian Lakes and Rivers. YMER ÅRSBOK, 103 - 122, 1970. (Swedish with English summary).

Odén, S. and J. Bergholm. The chemistry of snow. 1. Ionic separation during melting. MS, pp 9, 1971.

Hagen, A. and A. Langeland. Polluted snow in Southern Norway and the effect of the meltwater on freshwater and aquatic organisms. ENVIRON. POLLUT. 5, 45 - 57, 1973.

Henriksen, A. et al. Melting of polluted snow in a lysimetre at constant temperature. SNSF, Internal Report 1, pp 18, 1974 (In Norwegian).

Hultberg, H. Concentration of acid compounds and some biological effects on surface waters in western Sweden. IVL, Report B 247, 44 - 47, 1975 (In Swedish).

Odén, S. and T. Ahl. The longterm changes in the pH of lakes and rivers in Sweden. Supporting studies to Sweden's Case Study (ref. 13), pp 13, 1972.

Odén, S. and T. Ahl. The sulfur budget of Sweden (in preparation).

Andersson, R. STUDIES OF BASE SATURATION, EXCHANGE CAPACITY AND ADSORBED IONS OF FOREST SOILS IN SCANDINAVIA. Thesis for the degree of Agronomy, pp 33, 1971 (In Swedish).

Bartling, M. STUDIES OF pH AND BUFFER CAPACITY OF FOREST SOILS IN SCANDINAVIA. Thesis for the degree of Agronomy, pp 40, 1971 (In Swedish).

Odén, S. and R. Andersson. THE LONGTERM CHANGES IN THE CHEMISTRY OF SOILS IN SCANDINAVIA DUE TO ACID PRECIPITATION. Supporting studies to Sweden's Case Study (ref. 13), pp 19, 1972.

Odén, S. and R. Andersson. MECHANISMS AND THE INTEGRATED EFFECT OF SOIL ACIDIFICATION (in preparation).

Jonsson, B. and R. Sundberg. HAS THE ACIDIFICATION BY ATMOSPHERIC POLLUTION CAUSED A GROWTH REDUCTION IN SWEDISH FORESTS? Royal College of Forestry, Research Notes 20, pp 46, 1972.

Westman, L. Air pollution indications and growth of spruce and pine near a sulfite plant. AMBIO 3, 189 - 193, 1974.

Dahl, E. and O. Skre. An investigation of the effect of acid precipitation on land productivity. Nordforsk, Miljövårdssekretariatet, Publ. 1971:1, 27 - 39 (In Norwegian).

Lundmark, J. E. SITE FACTORS AND HEIGHT GROWTH OF PINE AND SPRUCE IN SWEDEN.

Odén, S. The acidification of soils due to nitrogen fertilization and the atmospheric fallout of ammonium. SKOGS - OCH LANTBRUKSAKAD. TIDSKR. 113, 45 - 48, 1974 (In Swedish).

Pierre, W. Effect of nitrogenous fertilizers on soil acidity. IND. ENG. CHEM., 23, 1440 - 1443, 1931.

Andersson, R. The acidifying effect of nitrogen fertilizers on Swedish Farm Soils. GRUNDFÖRBÄTTRING 26, 11 - 24, 1973/74 (In Swedish with English summary).

Gran, O. and H. Hultberg and L. Landner. Oligotrophication--a self-accelerating process in lakes subjected to excessive supply of acid substances. AMBIO III, 93 - 94, 1974.

Odén, S. and T. Ahl. MAN-MADE CHANGES OF THE SCNADINAVIAN ENVIRONMENT AND THE BALTIC SEA. 19th Congress of the International Association of Limnology, Sept. 1974, Winnipeg, Canada.

National Academy of Sciences (USA). ATMOSPHERIC CHEMISTRY: PROBLEMS AND SCOPE. Panel on Atmospheric Chemistry, National Academy of Sciences (USA). Washington, D. C. 130 pp.

Frohliger, J. O. and R. Kane. Precipitation: Its acidic nature. SCIENCE 189:455-457, 1975.

Likens, G. E., N. M. Johnson, J. N. Galloway and Bormann. Acid precipitation: Strong and Weak Acids. SCIENCE 190: In Press, 1976.