

ACID PRECIPITATION AND ITS INFLUENCE UPON AQUATIC ECOSYSTEMS--AN OVERVIEW¹

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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. 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 <u>et al.</u> (1972)
<u>Natural</u>		
Sea spray*	44	43
Biogenic (sea)*	48	} 89
Biogenic (land)	58	
Volcanoes**	<u>2</u>	<u>0.7</u>
Total	152	133
<u>Anthropogenic</u>		
Fossil fuel combustion	51	} 50
Non-fuel sources	<u>14</u>	
Total	65	
<u>Examples of individual anthropogenic sources</u>		
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 5×10^6 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/m² in summer and 670 mg/m² in winter, as compared with 290 and 370 mg/m² 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 combustion. 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

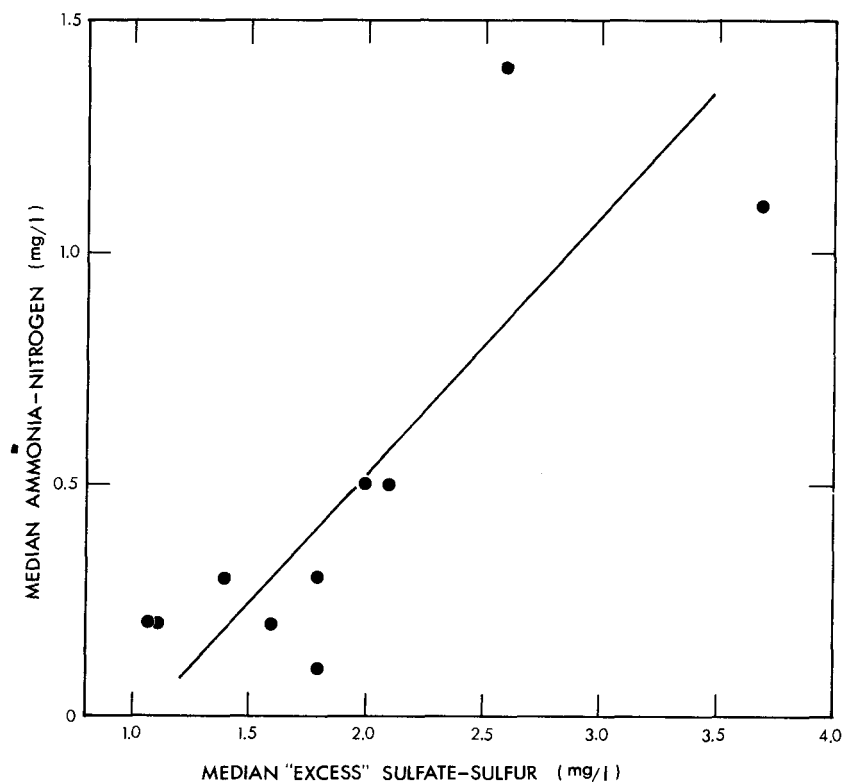


Figure 1. The relationship between ammonia-nitrogen and "excess sulfate-sulfur" (subtracting sulfur from sea salt) in British precipitation. Data of Stevenson (1968), fitted by reduced major axis (Imbrie, 1956) because neither variable is dependent.

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

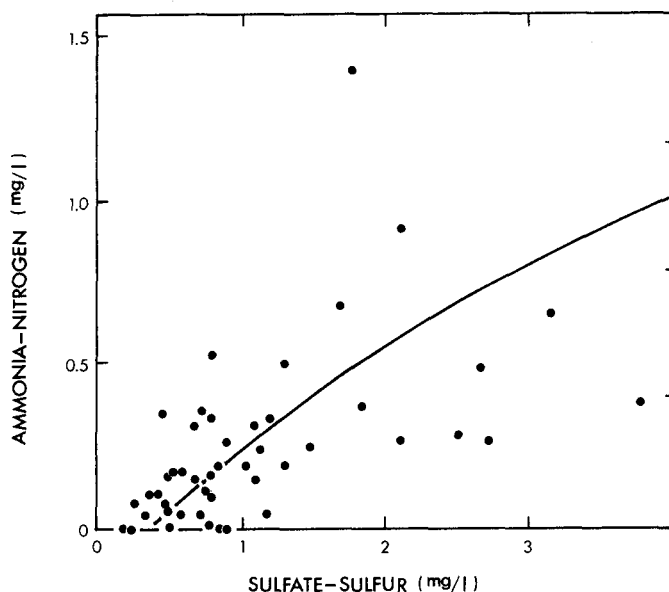


Figure 2. The relationship between ammonia-nitrogen and sulfate-sulfur in Illinois rainwater. Data of Larson and Hettick (1956), fitted by reduced major axis (Imbrie, 1956).

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 Loss (%)
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 ₂ O	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 $\mu\text{mho/cm}$, 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 (peroxyacetyl 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
		$\mu\text{g}/1000 \text{ m}^3$											
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 air-borne 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

$$\frac{\text{air concentration of lead}}{\text{air concentration of scandium}} \bigg/ \frac{\text{average soil concentration of lead}}{\text{average soil concentration of scandium}},$$

TABLE IX

Minor metallic elements in precipitation and surface waters ($\mu\text{g/l}$)

	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

¹Kramer (1973), total, sites include Sudbury²Kramer (1975)³Shiomi and Kuntz (1973)⁴Lazrus *et al.* (1970)⁵Stokes *et al.* (1973)⁶Chawla and Chau (1969)⁷Biesinger and Christensen (1972)⁸Turekian (1969)

* not detected

** two samples, 7 and 20 $\mu\text{g/l}$

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 ($\mu\text{g/l}$)	9	6	5	5	5	9	6
Ni ($\mu\text{g/l}$)	4	4	3	3	4	5	6
Pb ($\mu\text{g/l}$)	7	7	7	17	39	28	40
Zn ($\mu\text{g/l}$)	114	60	52	120	66	104	65
Fe ($\mu\text{g/l}$)	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 μm) than those originating by condensation during or after the combustion processes which give rise to air pollution (diameter range approximately 0.1-1 μm). 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 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

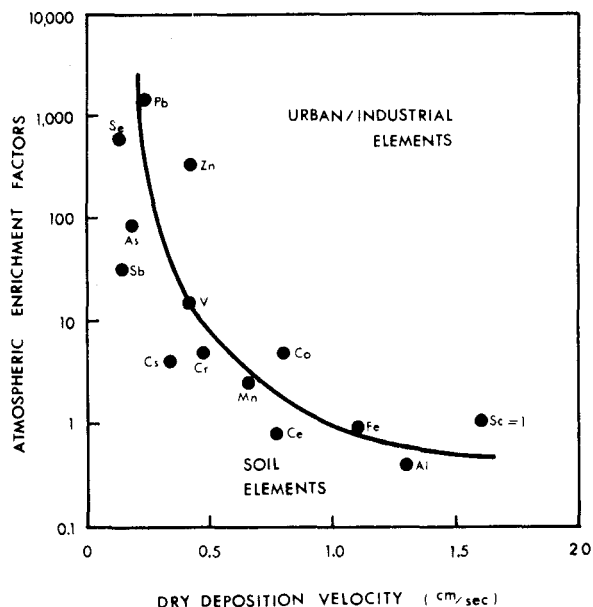


Figure 3. The relationship between atmospheric enrichment factors and dry deposition velocities for atmospheric elements at Chilton, England, after Peirson et al. (1974). Enrichment factors are normalized to the element scandium, which is derived predominantly from the soil, as follows:

$$\frac{\text{air concentration of element}}{\text{air concentration of Sc}}$$

$$\frac{\text{average soil concentration of element}}{\text{average soil concentration of Sc}}$$

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 facilitating 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 m³ or less in rural and coastal areas to about 50 mg/100 m³ in densely populated industrial sites. Mean daily concentrations occasionally reached 400 mg/100 m³, usually during severe fogs. Similarly, the deposit of total combustible matter ranged from about 44 g/100 m²/month (about 8 mg/l of rain) in little-polluted areas to 540 g/100 m²/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 m²/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 $\mu\text{g}/\text{l}$ in the forests of western Ontario to 82 and 130 $\mu\text{g}/\text{l}$ 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 ($\mu\text{g/l}$)	
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 <i>et al.</i> (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.

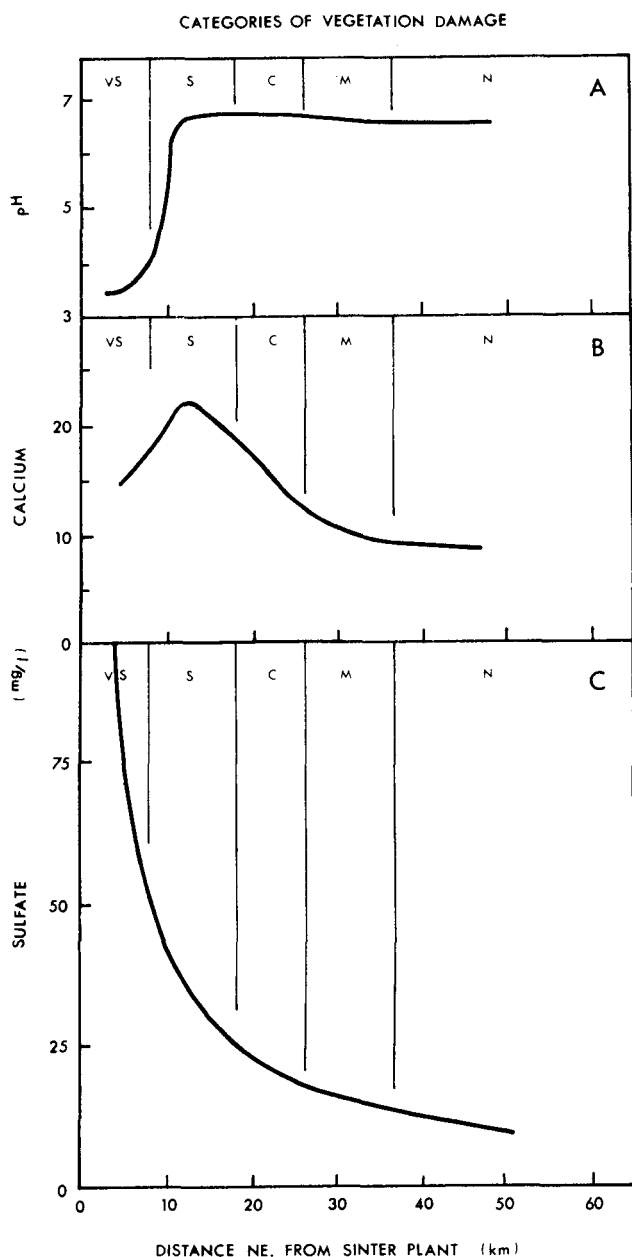


Figure 4. The relationships of sulfate, calcium, and pH in lake and pond waters at Wawa, northwestern Ontario, to distance from an iron-sintering plant, after Gordon and Gorham (1963). Subjective aerial estimates of forest damage are given as very severe (VS), severe (S), considerable (C), moderate (M), 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

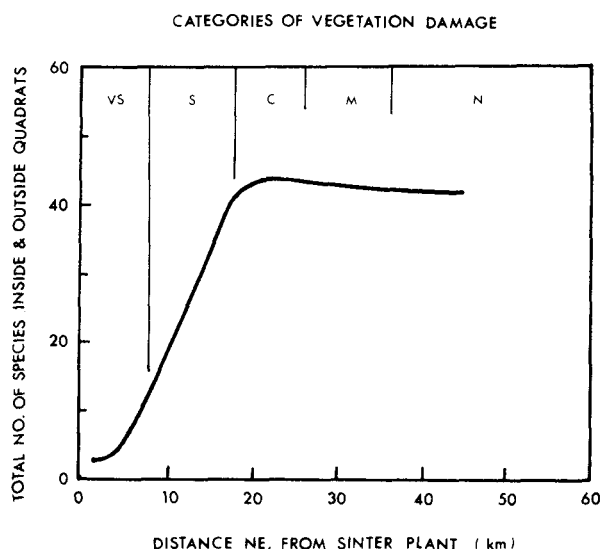


Figure 5. The relationship of the diversity of terrestrial flora at Wawa, northwestern Ontario, to distance from an iron-sintering plant, after Gordon and Gorham (1963). Subjective aerial estimates of forest damage are given as very severe (VS), severe (S), considerable (C), moderate (M), and not obvious (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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