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ACID PRECIPITATION AND ITS INFLUENCE UPON AQUATIC ECOSYSTEMS—AN OVERVIEW

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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 H ions as H₂SO₄, HNO₃, and HCl can alter and impoverish the species composition of biotic communities, and lead to severe leaching of beneficial metal cations such as Ca 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, K, Ca, and S; 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 Ca.

Basic materials in air pollution, biogenic NH₃ 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.

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 1940s and through the 1950s 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 CO_2 would exhibit a pH of about 5.7, well below the neutral point of 7.0. Added to that primary solution of H_2CO_3 are three strong mineral acids. For example, at Hubbard Brook, New Hampshire (Likens and Bormann, 1974), where H ions account for 69% of cations in precipitation, the anion proportions are sulfate 62%, nitrate 23%, and chloride 14%.

Among these strong acids H_2SO_4 predominates, with a strong correlation evident between H ions and sulfate ions (Gorham, 1955, 1958a), or between H ions and sulfate minus Ca ions (Fisher, 1968; Pearson and Fisher, 1971; cf. however Likens, 1972). The H_2SO_4 originates chiefly from the oxidation of S in fossil fuels (Table I), which is

TABLE I

Estimated rates of sulfur mobilization from biogenic sulfur emissions, fossil fuel combustion, industrial sources, and volcanoes

| Source | Sulfur (10^6 metric t yr^{-1}) | |
|---|---|------------------------------|
| | Friend (1973) | Kellogg <i>et al.</i> (1972) |
| <i>Natural</i> | | |
| Sea spray ^a | 44 | 43 |
| Biogenic (sea) ^a | 48 | 89 |
| Biogenic (land) | 58 | |
| Volcanoes ^b | 2 | 0.7 |
| Total | 152 | 133 |
| <i>Anthropogenic</i> | | |
| Fossil fuel combustion | 51 | 50 |
| Non-fuel sources | 14 | |
| Total | 65 | |
| <i>Examples of individual anthropogenic sources</i> | | |
| 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) | |

^a Most marine emissions return directly to the sea.

^b Stoiber and Jepsen (1973) estimate 5×10^6 metric t yr^{-1} .

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 S. Lesser and more local S sources are sulfide-ore smelters and volcanoes. Locally, gas processing plants can emit sufficient S to have an appreciable impact upon S and acidity in precipitation (Summers and Hitchon, 1973; Summers and Whelpdale, 1976). Whether the catalytic converters

designed to reduce auto emissions will increase concentrations of H_2SO_4 near the ground in urban areas is currently a vexing question (Holden, 1975). Although natural biogenic emissions of S 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 N 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 N_2 also occurs during the process of high-temperature combustion in air. Approximately 5 to 40% of the N in coal and 20 to 100% of the N in oil is oxidized by combustion, and becomes oxidized further to HNO_3 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 indicates coal and petroleum as the

TABLE II
Wide-world emissions of nitrogen oxides by combustion processes and natural sources (Anon., 1975)

| Source | N_{ox} emissions as N (10^6 t yr ⁻¹) |
|-------------------------------|--|
| 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 |

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, H ions exceed sulfate ions in precipitation, and more recently Likens *et al.* (1976) have demonstrated a high degree of correlation between the increase of H-ion input and the increase of nitrate input over the past 10 yr, with no correlation between inputs of H 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 Cl content of coal averages one-fifth the S content (Meetham, 1950), and may reach 1%

by weight as compared with an upper limit of 0.65% in U.S. coals (Abernethy and Gibson, 1963; Perry, 1975). In urban Britain during the decade 1944–1954 the deposit of chloride has been estimated as 400 mg m^{-2} in summer and 670 mg m^{-2} in winter, as compared with 290 and 370 mg m^{-2} of sulfate-S respectively (Parker, 1955). The summer and winter concentrations of chloride in precipitation were 6.7 and 10.3 mg l^{-1} , as compared with 4.8 and 5.6 mg l^{-1} of sulfate-S. 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 to 75 ppm of HCl have been reported in flue gases from coals burned by the Tennessee Valley Authority (Anon., 1975). Small amounts of HCl acid may also come from the interaction of atmospheric NaCl particles with droplets of H_2SO_4 (Gorham, 1958a; Eriksson, 1960), 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 H ions in Bottini's samples below pH 5.7, and no correlation with sulfate. Total solids average 44 mg l^{-1} in the samples below pH 5.7, and 76 mg l^{-1} 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 SO_2 .

In addition to strong acids, weak acids may also be found in precipitation (Krupa *et al.*, 1976), but appear not to contribute appreciably to free H ions in rural precipitation (Galloway *et al.*, 1976).

A point that arises here is how to refer free H ions to the various anions in precipitation. Cogbill and Likens (1974), after subtracting other sea-salt ions in proportion to Na, have assumed a straightforward stoichiometry by which H 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 H 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 H 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 HCl prevailing in cities, whereas H_2SO_4 predominates in rural Britain, is believed to be the greater solubility of gaseous hydrogen chloride as compared to SO_2 , 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 HNO_3 ought also to fall out nearer to source than H_2SO_4 , because NO is oxidized more rapidly than SO_2 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 S 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), have resulted in a broader dispersion of gaseous SO_2 and its oxidation product H_2SO_4 , 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.*, 1976).

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 SO_2 , 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 S-scavenging process (Nisbet, 1975). Other mechanisms of atmospheric cleansing which may have deleterious effects deserve greatly increased study. A good deal of the SO_2 emitted into the air is absorbed directly upon the moist surfaces of plants, soils, etc., where it may subsequently be oxidized to H_2SO_4 . According to Nisbet (1975; cf. Eriksson, 1960), deposition of sulfates in precipitation accounts for 40 to 80% of the S deposited on land, with direct absorption of SO_2 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 SO_2 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 Na, Mg, Ca, and chloride, and release from leaf cells appreciable amounts of Mn, K, and in the case of spruce forest, H 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 S, one-third as much NH_3 , and one-half as much nitrate. Snow in central Alberta also contained much less S and chloride than rain (Summers and Hitchon, 1973), and Beamish (1974) has reported a similar situation for S 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 Na 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, 1976), 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 NH_3 from dairy farms as a factor reducing the acidity of precipitation in Denmark and parts of south Sweden. Where $(\text{NH}_4)_2 \text{SO}_4$ is an important component of precipitation, it is 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 Ca minus sulfate ions; and an equally distinct correlation between H ions and sulfate minus Ca ions. The clear inference is that in some cases acid, S-bearing aerosols predominate, and in other cases alkaline calcareous dust.

Junge and Werby (1958) noted a pronounced maximum for Ca in precipitation (excluding dry fallout between rainfalls) in the southwestern U.S.A., 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 Ca to the ground, Eriksson

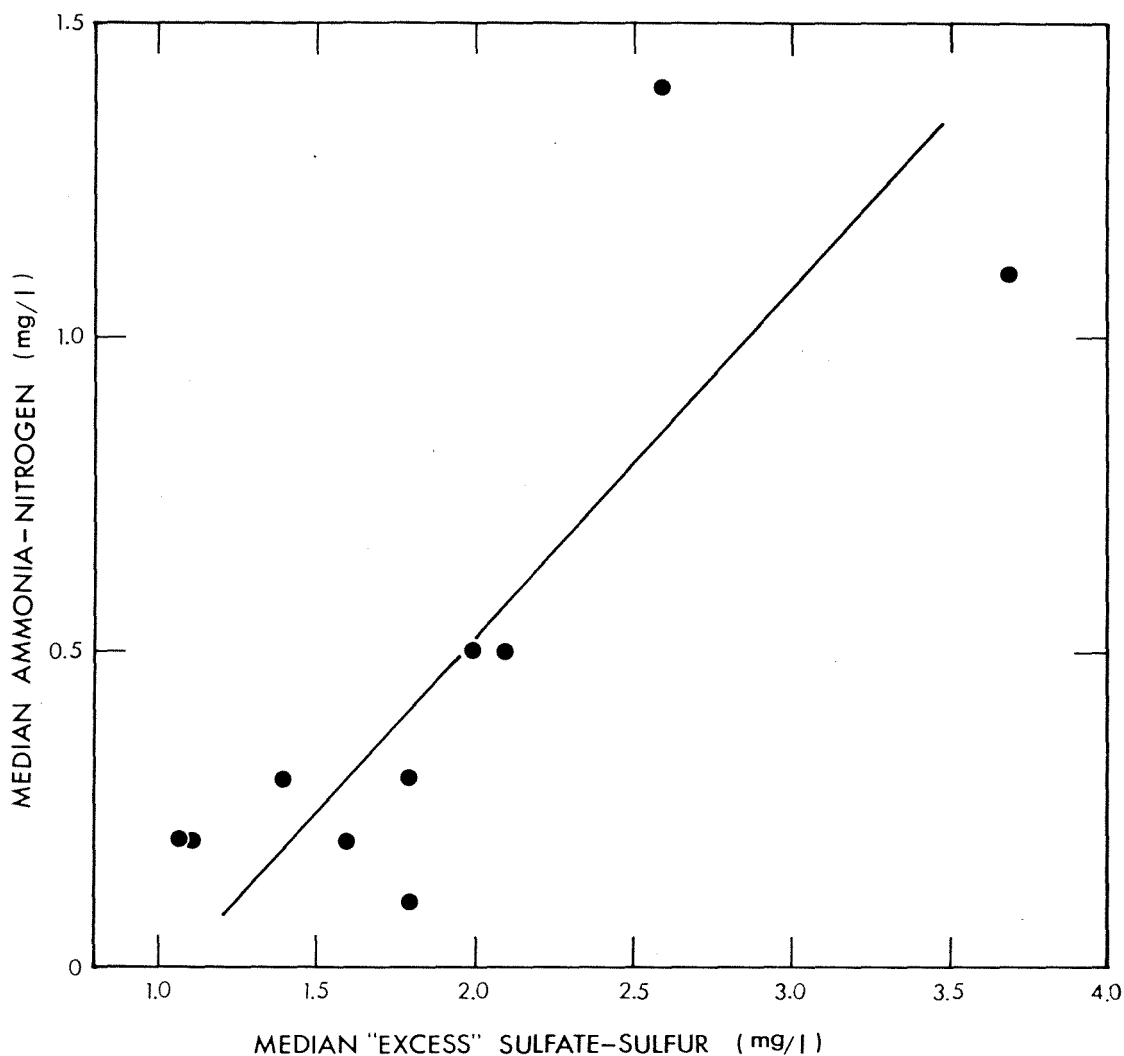


Fig. 1. The relationship between ammonia-nitrogen and "excess sulfate-sulfur" (subtracting sulfur from sea salt) in British precipitation. Date of Stevenson (1968), fitted by reduced major axis (Imbrie, 1956) because neither variable is dependent.

(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 CO_2 (Nisbet, 1975). Smith *et al.* (1970) provide extensive data on dust deposition in the U.S.A. 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 to 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 to 8). The eastern dusts are usually faintly acid (pH 6 to 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

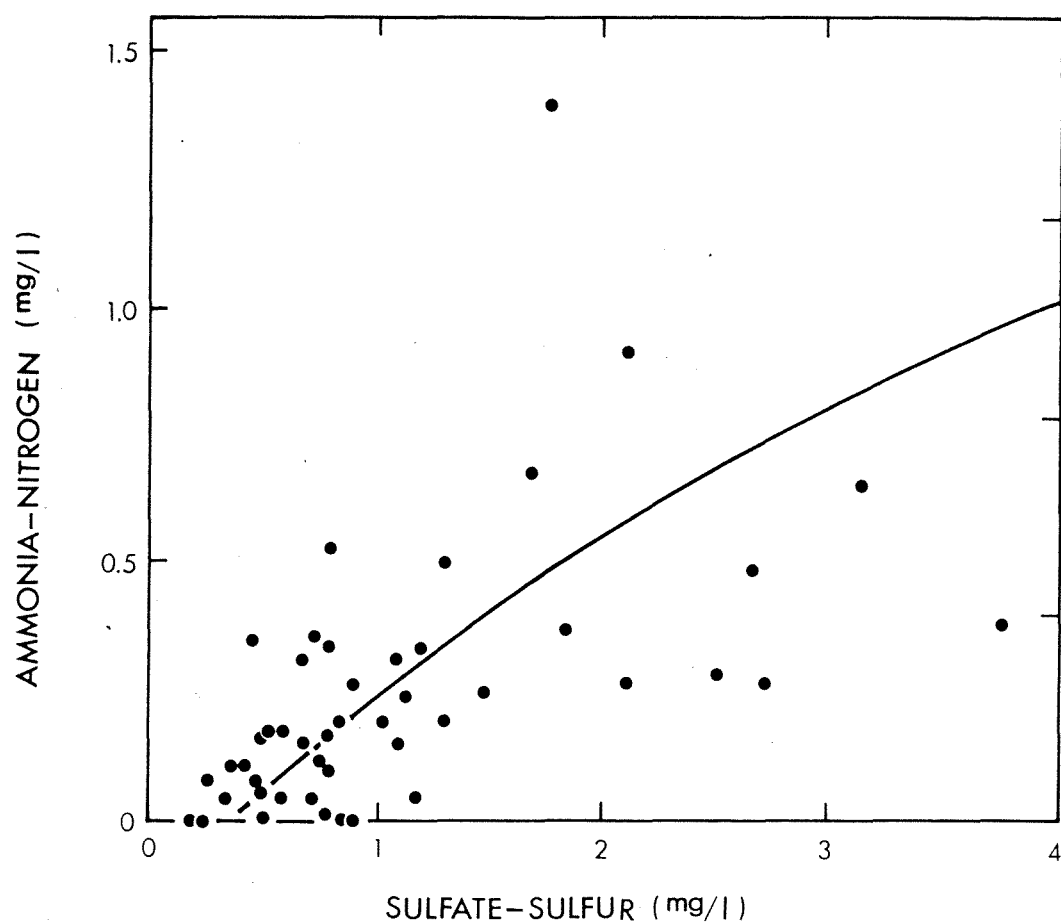


Fig. 2. The relationship between ammonia-nitrogen and sulfate-sulfur in Illinois rainwater. Data of Larson and Hettick (1956), fitted by reduced major axis (Imbrie, 1956).

TABLE III
Dustfall in the U.S.A. (data of Smith *et al.*, 1970)

| Location | Site | State | Oxidized dust (kg ha ⁻¹ mo ⁻¹) | Dust pH | Oxidation loss (%) |
|------------------|--------------|-------------|--|------------|-----------------------|
| North Central | Sidney | Montana | 70 | 7.9 | 11 |
| | 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 |
| South | McCredie | Missouri | 48 | 6.7 | 11 |
| | 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.

(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 Ca content of precipitation in that region. Table IV (Gorham, 1961) provides an analysis of dust from Greenland ice, which may be representative of long-distance fallout.

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 |

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.A., 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 noncalcareous 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 of *Sphagnum* bogs on deep peat near the northwestern forest border exhibit Ca concentrations averaging 4.4 mg l⁻¹ and pH values of 4.0 in their waters (Hofstetter, 1969), whereas about 100 km to the east Ca concentrations are only 1.7 mg l⁻¹ and pH values 3.5 (Heinselmann, 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 Ca. 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 (1976), 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

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 PO ₄ -P (µg l ⁻¹) |
|--------------|-------------------------------------|-----|---------|------------------|------------------|--------------------|--|
| | | | Ca | SiO ₂ | SO ₄ | NO ₃ -N | |
| 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 ^a | 1.2 ^a | 0.2 | 6 |

^a In four samples from a single lake at different times.

the forests of western Ontario (Barica and Armstrong, 1971). The melted Ontario snow is very dilute (specific conductivity 11 µmho cm⁻¹, 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 windstorms in the last several decades, which blew large amounts of dust into the state from the west. Table VI shows various aspects of 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 P, 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.

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^{-1}) | Total $\text{PO}_4\text{-P}$ ($\mu\text{g l}^{-1}$) |
|---|------------------|--|--|---|
| 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) |

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, 1976), 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 CO_2 . 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 Cu/Ni 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,

TABLE VII
Emissions of sulfur oxides in Minnesota and neighboring states
(from Anon., 1974)

| State | Category | Sulfur oxide emissions, 1972 (10 ³ t yr ⁻¹) |
|-------------------------------|--------------------------------------|---|
| 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 ^a | 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 |

^aFrom Hutchinson and Whitby, 1975

precipitation which is not already strongly acidified may become so by throughfall, and especially by stem flow (Nihlgård, 1970). Soils, of course, have a neutralizing capability which varies greatly with differences in their degree of saturation by metal cations such as Ca and Mg, 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 H₂SO₄ (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 SO₂, O₃, nitrogen oxides, and compounds

such as PAN (peroxyacyl nitrate), etc., which affect terrestrial ecosystems (cf. papers reviewed by Webster, 1967; Hindawi, 1970; Tamm and Aronsson, 1972; Ferry *et al.*, 1973; Anon., 1973; Smith, 1974; Missouri Botanical Garden, 1975). Other pollutants are of far greater significance for aquatic ecosystems, chief among them H 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

TABLE VIII
Annual averages for trace elements in British air (from Stocks *et al.*, 1961)

| Site | | Cu | Ni | Pb | Zn | As | Mn | Sb | V | Cr | Mo | Co | Be |
|-----------------|------|------------------------|-----|------|-----|-----|-----|----|----|----|-----|-----|------|
| | | μg/1000 m ³ | | | | | | | | | | | |
| Rural (n=3) | Min. | 7 | 1 | 80 | 48 | 5 | 5 | 1 | 1 | 1 | 0.3 | 0.3 | 0.06 |
| | Max | 38 | 75 | 470 | 205 | 27 | 13 | 5 | 2 | 3 | 1.3 | 0.9 | 0.15 |
| Urban (n=12) | Min | 44 | 2 | 260 | 130 | 31 | 12 | 4 | 1 | 2 | 1.3 | 1.0 | 0.19 |
| | Max | 252 | 205 | 1430 | 490 | 130 | 130 | 20 | 54 | 22 | 6.1 | 4.3 | 1.00 |

normal precipitation in Ontario). Organic toxins also accompany acid precipitation. A factor 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, 1976) 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 phytoplankton (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, 1976). 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 Cu, Ni, Pb, Zn, Fe, Mn, 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 Zn, Cu, and Pb are in the order of several micrograms per liter of

TABLE IX
Minor metallic elements in precipitation and surface waters ($\mu\text{g l}^{-1}$)

| | Precipitation | | | | Surface waters | | | | | | | | |
|----|-----------------------|------------------------|-------------------------------|---------------------|------------------------------|------------------------------------|------------------------|----------------------------|----------------------------|---------------------------------|------------------------------------|-----|------|
| | Ontario ^{ab} | | Southern Ontario ^c | U.S.A. ^d | Sudbury 9 lakes ^e | Water supplies U.S.A. ^d | Lake Erie ^f | Lake Superior ^g | Streams (est) ^h | Minnesota 33 lakes ⁱ | High Sierra 114 lakes ^f | | |
| | (max ^a) | (median ^a) | (min ^a) | (mean) | (max) | (mean) | | | (mean) | | | | |
| Cu | 700 | 9 | nd ⁱ | 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 ^j | 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 |

^a Kramer (1973), total, sites include Sudbury.

^b Kramer (1974).

^c Shiomi and Kuntz (1973).

^d Lazrus *et al.* (1970).

^e Stokes *et al.* (1973).

^f Chawla and Chau (1969).

^g Biesinger and Christensen (1972).

^h Turekian (1969).

ⁱ Not detected.

^j Two samples, 7 and 20 $\mu\text{g/l}$.

precipitation; and mosses dependent for their mineral supply largely upon atmospheric sources are known to be strongly contaminated with these elements and with Cd, Ni, Cr and Hg (Rühling and Tyler, 1973). Precipitation in southern Ontario (Table X) does not show a clear increase in trace elements, except for Pb, 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.

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 ($\mu\text{g l}^{-1}$) | 9 | 6 | 5 | 5 | 5 | 9 | 6 |
| Ni ($\mu\text{g l}^{-1}$) | 4 | 4 | 3 | 3 | 4 | 5 | 6 |
| Pb ($\mu\text{g l}^{-1}$) | 7 | 7 | 7 | 17 | 39 | 28 | 40 |
| Zn ($\mu\text{g l}^{-1}$) | 114 | 60 | 52 | 120 | 66 | 104 | 65 |
| Fe ($\mu\text{g l}^{-1}$) | 27 | 10 | 17 | 35 | 29 | 32 | 48 |
| SO ₄ (mg l^{-1}) | 6.6 | 8.0 | 6.6 | 10 | 8.8 | 12 | 12 |
| Ca (mg l^{-1}) | 3.5 | 4.4 | 3.8 | 4.5 | 4.3 | 7.0 | 6.5 |

Open lake \longleftarrow \longrightarrow Strongly urban

According to Peirson *et al.* (1974), from studies in widely separated non-urban regions of the British Isles, a fairly uniform airborne particulate material may be widespread in northern latitudes, varying considerably in concentration but rather little in elemental composition except very close to major industrial sources. For example, in 1972 the average concentration of Pb in British air ranged from 29 to 330 ng kg⁻¹ at seven sites, and Sc ranged from 0.014 to 0.180 ng kg⁻¹. However, if Pb is normalized to Sc, an element largely derived from the soil, by calculating

$$\frac{\text{air concentration of Pb}}{\text{air concentration of Sc}} \bigg/ \frac{\text{average soil concentration of Pb}}{\text{average soil concentration of Sc}}$$

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 Na, Cl, and Br) 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 (Al, Ce, Fe) to between about 10 and 1000 in another (V, Sb, As, Zn, Se, Pb), with a third group between about 2 and 6 (Mn, Cs, Co, Cr). The first three elements, which are not enriched relative to Sc, are almost certainly derived largely from soil dust, and the second group of highly enriched elements presumably derives 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

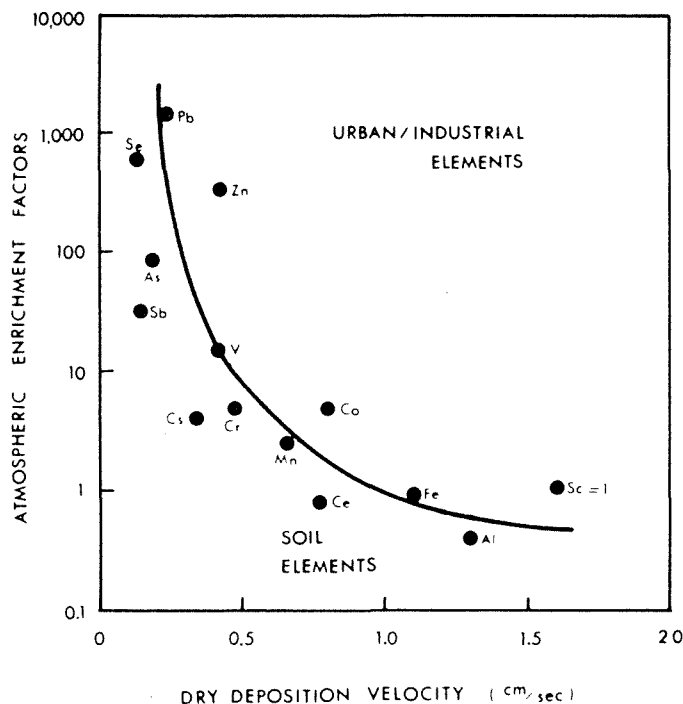


Fig. 3. The relationship between atmospheric enrichment factors and dry deposition velocities for atmospheric elements at Chilton, England, after Peirson *et al.* (1974). Enrichment factors are normalized to the element scandium, which is derived predominantly from the soil, as follows:

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

Dry deposition velocities are calculated as:

$$\text{rate of dry deposition/concentration in air.}$$

rate of dry deposition divided by the air concentration. This calculation shows that the elements of low atmospheric enrichment, and derived chiefly from the soil, exhibit dry deposition velocities above 0.7 cm s^{-1} , 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 s , 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 to $100 \mu\text{m}$) than those originating by condensation during or after the combustion processes which give rise to air pollution (diameter range approximately 0.1 to $1 \mu\text{m}$). 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

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 | Range (six sites) | Gas platform North Sea | Sea water |
|---------|---------|----------------------|---------------------------|--------------------|
| Al | < 503 | < 230-770 | 2400 | 1-10 |
| As | < 8 | 1.3-12 | 45 | 3.0 |
| Br | 446 | 33-1300 | 2300 | 65 000 |
| Ce | < 0.44 | < 0.1-0.55 | < 4 | 0.4 |
| Cl | 50 700 | 3000-105 000 | 210 000 | 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 | 25 400 | 1700-56 000 | 100 000 | 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 |

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 lakes near Sudbury, Ontario. The addition of lime to acid lake waters has apparently been successful in facilitating the restoration of fish populations (Wright, 1975), 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 exhibited 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 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 metals 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 P 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)⁻¹ or less in rural and coastal areas to about 50 mg (100 m³)⁻¹ in densely populated industrial sites. Mean daily concentrations occasionally reached 400 mg (100 m³)⁻¹, usually during severe fogs. Similarly, the deposit of total combustible matter ranged from about 44 g (100 m²)⁻¹ mo⁻¹ (about 8 mg l⁻¹ of rain) in little-polluted areas to 540 g (100 m²)⁻¹ mo⁻¹ (about 98 mg l⁻¹ 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⁻¹ of carbon (Neumann *et al.*, 1959), approximately equivalent to 1.6 to 6.8 mg l⁻¹ 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⁻¹ (Gorham, 1961).

Of the combustible material in British precipitation, tars soluble in carbon disulfide contributed 3 and 18 g (100 m²)⁻¹ mo⁻¹ in little polluted and heavily polluted sites, or 0.5 and 3.2 mg l⁻¹ respectively. A detailed examination of organic (and potentially carcinogenic) components in the smoke of British air has been made by Stocks *et al.*

TABLE XII

Annual averages for polycyclic hydrocarbons in British air (from Stocks *et al.*, 1961)

| | | Total smoke (mg/ 1000 m ³) | 3:4 Benz- pyrene | 1:2 Benz- perylene | Pyrene | Flor- anthene (µg/ 1000 m ³) | 1:2 Benz- pyrene | Coro- nene | Anth- anthrene |
|-----------------|-----|---|---------------------|-----------------------|--------|---|---------------------|---------------|-------------------|
| 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 |

(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.

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 K are also highly correlated with sulfate there (Gorham, 1955, 1958a), and Ca is strongly correlated with sulfate in urban British rain (Gorham, 1958b). Figures 1 and 2 demonstrate a strong correlation of NH_3 with sulfate. Some of the added materials, such as Ca, 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, S 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 P 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, P is if anything rather low.

TABLE XIII
Total phosphorus in precipitation

| | Total P (μl^{-1}) | |
|--------------------|-----------------------------------|--|
| 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 ^a | 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 |
| North England | 14 | Gore (1968) |
| North England | 27 | Carlisle <i>et al.</i> (cited by Gore, 1968) |
| Sweden | 17-34 | Tamm (cited by Gore, 1968) |

^a Median 81 (Kramer, 1974).

However, differences in technique (digestion, filtration, etc.) may be responsible for some of the observed variation. Shiomi and Kuntz (1973) found no increase of P in urban as compared with non-urban sites (but their and Kramer's data are unusually high). According to Odén (1975) 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 Tables V and VI which range from $6 \mu\text{g l}^{-1}$ in the forests of western Ontario to 82 and $130 \mu\text{g l}^{-1}$ 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 P inputs.

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 Fe-sintering plant in Wawa, northwestern Ontario (Gordon and Gorham, 1963), the concentration of Ca in lake waters is sharply elevated in the intermediate pollution range, but decreases again (though not to unpolluted baseline levels) where S 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, Ca and Mg have increased in lakes and rivers under the influence of acid precipitation which has replaced bases adsorbed on the soil exchange complex by H ions (Odén, 1976; Wright, 1976). Severe leaching, however, may acidify the entire soil column below pH 5, in which case Al is mobilized into soil waters and aquatic ecosystems where it can be distinctly toxic (Wright, 1976; Hutchinson and Whitby, 1975). According to Reuss (Missouri Botanical Garden, 1975), anion-adsorbing polymers of hydroxy-Fe and Al 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 Fe/Mn 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.

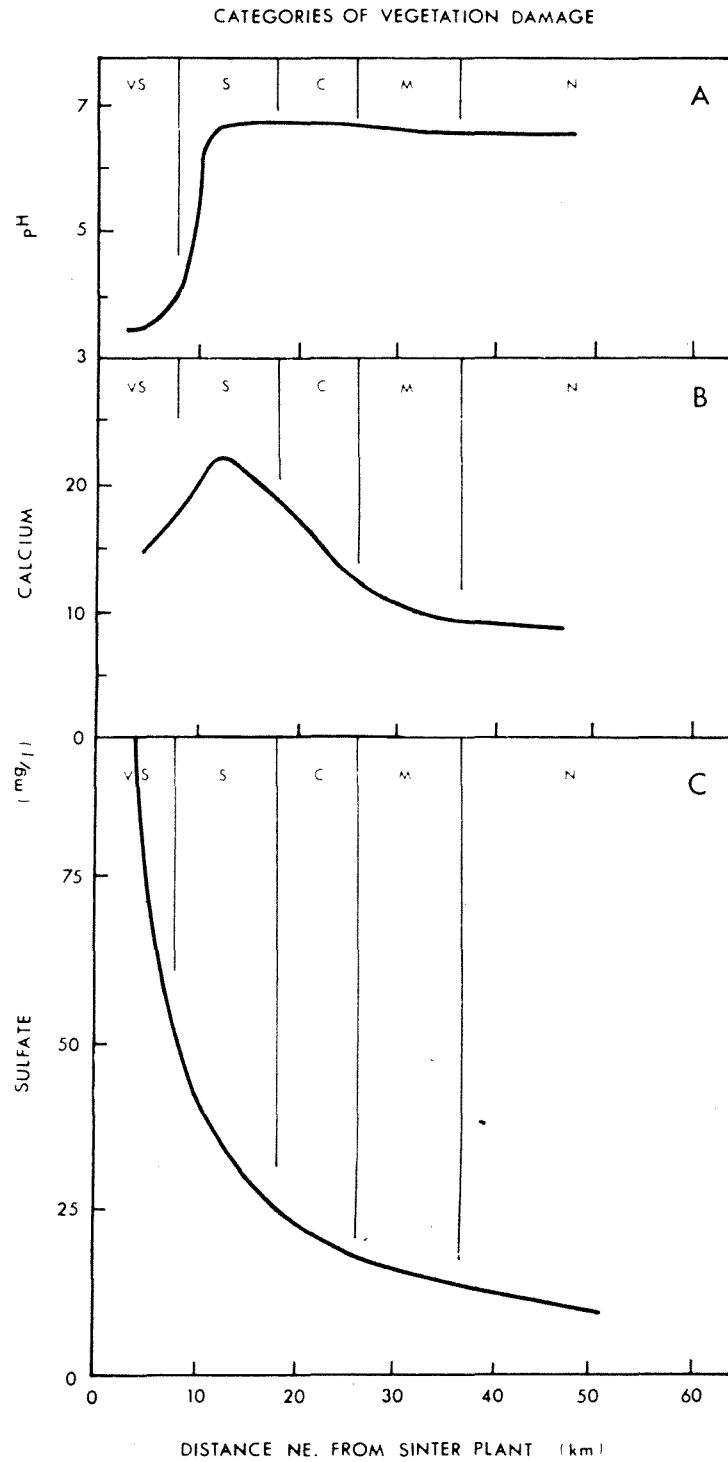


Fig. 4. The relationships of sulfate, Ca and pH in lake and pond waters at Wawa, northwestern Ontario, to distance from an iron-sintering plant, after Gordon and Gorham (1963). Subjective aerial estimates of forest damage are given as very severe (VS), severe (S), considerable (C), moderate (M), and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

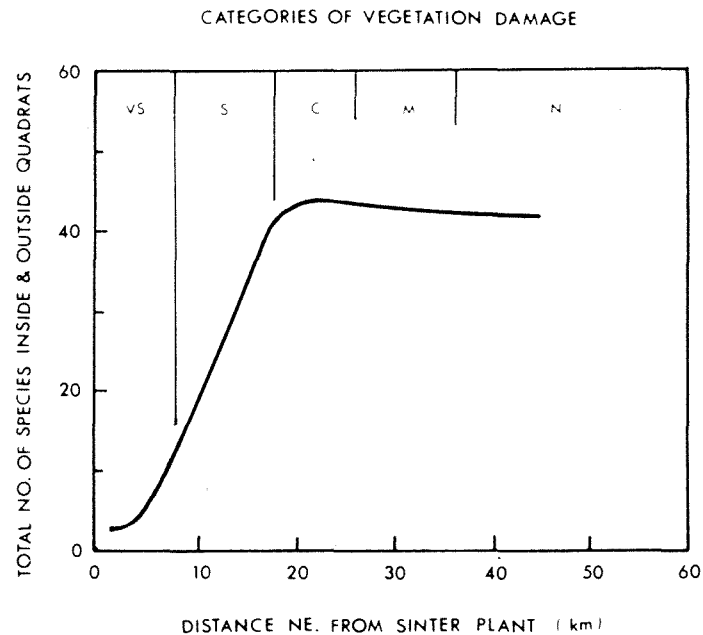


Fig. 5. The relationship of the diversity of terrestrial flora at Wawa, northwestern Ontario, to distance from an iron-sintering plant, after Gordon and Gorham (1963). Subjective aerial estimates of forest damage are given as very severe (VS), severe (S), considerable (C), moderate (M), and not obvious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

unfortunate exception of white pine, *Pinus strobus*) seem able to survive the relatively low levels of S pollution beyond about 20 km from the source. However, once S 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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