Effects of Acid Rain on Freshwater Ecosystems

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Acid-vulnerable areas are more numerous and widespread than believed 7 years ago. Lakes and streams in acid-vulnerable areas of northeastern North America have suffered substantial declines in acid-neutralizing capacity, the worst cases resulting in biological damage. Many invertebrates are very sensitive to acidification, with some disappearing at *p*H values as high as 6.0. However, the recent rate of acidification of lakes is slower than once predicted, in part the result of decreases in sulfur oxide emissions. A discussion of some of the processes that have contributed to the acidification of lakes as well as those that have protected acid-sensitive freshwaters is presented.

When Angus Smith coined the term "acid rain" to refer to the effect that industrial emissions had on the precipitation of the British midlands (*1*), he could scarcely have dreamed that little over a century later the topic would be the subject of research for thousands of environmental scientists that would utilize hundreds of millions of dollars in research funds and would become of international political importance. Although Smith clearly recognized that acid rain caused environmental damage (*2*), the continental scale of acid rain effects was not recognized until the mid-20th century (*3*). It was not until concern was publicly widespread in the late 1970s that governments sponsored large-scale studies of the problem (*4*).

Although much has been learned about the causes, extent, transport, and effects of acid rain, some issues are still debated, which in turn cause polarization among scientists, political parties, states, and countries (*5*). These debates are often based on outdated preconceptions. Many statements of opinion or hypothesis have been misrepresented as "proofs" by later investigators (*6*). Seldom has such a large proportion of ecological science been published in the unrefereed "gray" literature. Research has solved some problems but has also led to the discovery of new ones (*7*). In this article, I attempt to synthesize recent progress made in the understanding of acid rain and its effects on North American aquatic resources.

The Origin and Extent of Acid Rain

A decade ago, most scientists believed that natural unpolluted precipitation would have a *p*H of 5.6, the *p*H of distilled water saturated with CO_2. Despite evidence to the contrary, this simplistic assumption has persisted until recently (*8*). We now know that in remote areas, uncontaminated by either industrial emissions or calcareous dust, precipitation usually has a *p*H value close to 5.0 because it contains small amounts of both weak and strong acids of natural origin (*9*). Unfortunately, in most areas within several hundred kilometers of large centers of human activity, precipitation has much lower *p*H values. Widespread acid rain has been known in northern Europe and eastern North America for some time (*3*). Recent work has led to the discovery of acid rain in western North America, Japan, China, the Soviet Union, and South America (*10*). Globally, anthropogenic emissions of sulfur are comparable in magnitude to emissions from natural sources (*11*), but regionally, in northern Europe and eastern North America, over 90% of sulfur deposited from the atmosphere is anthropogenic (*12, 12a*). About 50% of the sulfates falling in eastern Canada are believed to have originated in the United States, and Canadian emissions contribute substantially to the American acid rain problem, particularly in the Northeast (*12, 12a*). Similarly, much of Scandinavian acid precipitation originates in industrialized areas of central Europe and the United Kingdom (*13*). Earlier claims that acids from volcanoes, trees, salt marshes, or other natural sources cause the acid rain problem have largely ceased (*14*). Polluted air masses have been convincingly tracked across the Atlantic (*15*) and over the North Pole from Eurasia to North America, by using the unique trace metal content of polluted air masses (*15, 16*). Broad regional to global pollution of the atmosphere with acid rain and many other pollutants is clearly a result of human activities (*7*).

The Extent of Acid-Sensitive Areas

The extent of areas that are geologically vulnerable to acid precipitation is much larger than was believed a decade ago. In the United States, large acid-sensitive areas are now known to occur in Minnesota, Wisconsin, upper Michigan, several southeastern states, and many of the mountainous areas of the West, in addition to the well-known northeastern sector of the country (*17*). It is estimated that half of the 700,000 lakes in the six eastern provinces of Canada and south of 52°N have alkalinity values below 50 μeq liter^{-1}, that is, they are extremely acid-sensitive (*18*). Large acid-sensitive areas are known to exist in all western provinces, the Yukon, the Northwest Territories, and Labrador. In Europe, acid-sensitive areas of the Netherlands, Belgium, Denmark, Switzerland, Italy, West Germany, and Ireland have been added to the better known areas of Scandinavia and the United Kingdom. Vast areas of Precambrian and Cambrian geology in Asia, Africa, and South America are also acid-sensitive (*19, 19a*).

Rates of Increase in Acid Rain

Precipitation chemistry data from before the mid-1950s are of questionable reliability, causing considerable controversy over the timing of increases in acid rain (*20*). As a result, the onset of the

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ecological effects of acid precipitation can be deduced only from the timing of changes in lake chemistry or acid-sensitive microfossils and metallic pollutants in sediments, as discussed below. The earliest records of lakes acidified by atmospheric emissions come from Scotland, where analyses of diatoms in sediments showed that lakes were becoming acid in the mid-19th century. Widespread damage to ecosystems of Scandinavia and North America did not begin until the 1930s to 1950s (*21*). This has puzzled many, because sulfur emissions in North America increased most rapidly before 1920, followed by alternating periods of decline and increase (*22*). There are a number of possible reasons for the damage occurring later. The increasing construction of large power plants and smelters with tall smokestacks in the middle of the 20th century was coupled to a decline in the use of coal for home heating, so that a local air pollution problem was transformed into a long-range, transboundary one. Whereas peak fuel combustion once occurred in winter for heating, it now occurs typically in summer, when emissions are directed into a warmer, moister, and thus more reactive atmosphere where oxidation of sulfur compounds is more efficient (*23*). Alkaline materials such as fly ash have been removed from emissions to control particulate pollutants (*24*). Emission of nitrogen oxides and of other pollutants that catalyze the oxidation of sulfur and nitrogen oxides has also increased (*25*). Finally, it probably took years to decades to deplete the acid-neutralizing capacity of lakes, streams, and their catchments, so that *p*H depressions were not noticeable for some time after precipitation became acidic. Better recent chemical records have revealed that the acidity of precipitation has recently increased in the southeastern United States (*26, 26a*). Sulfate concentrations in precipitation are currently from 4 to 16 times as high east of the Mississippi River as they are in regions farther away from anthropogenic sources of sulfur (*27*).

The Extent and Rate of Surface Water Acidification

It is now clear that acid rain has already caused widespread acidification of many aquatic ecosystems in the northeastern United States, Canada, Norway, Sweden, and the United Kingdom. Evidence comes from four sources: geochemical theory, analysis of long-term trends, comparison of older with more recent chemical records, and paleoecological analyses. On the other hand, the rate of change has increased less rapidly in recent years than was feared a decade ago.

Any broad-scale assessment of acidification must be based on geochemical concepts because no historical data are required (*28*). Such studies show that the alkalinity of lakes has been replaced with sulfate over broad areas of Scandinavia, the northeastern United States, and eastern Canada. This causes greatly decreased ratios of alkalinity to Ca^{2+} + Mg^{2+} (Fig. 1) and increased ratios of SO_4^{2-} to Ca^{2+} + Mg^{2+}. Results show that in large areas of geologically sensitive terrain in eastern North America, average lakes have lost over 40% of their original alkalinity. The most sensitive waters of such areas are now entirely devoid of alkalinity, so that inputs of strong acids cause considerable decreases in *p*H (*29*).

Further evidence for lake acidification has been supplied by paleoecological *p*H reconstructions from diatom remains in lake sediments. These reconstructions have shown the rapid acidification of many poorly buffered lakes in the Adirondacks, southern Norway and Sweden, West Germany, Scotland, Wales, central Ontario and Quebec, and Nova Scotia. Rates of acidification have ranged from slow to undetectable for several New England lakes and at a few sites in eastern Canada and in Finland. No paleoecological evidence of acidification has yet been found in midwestern or western North America or in northern Scandinavia (*30*). Although paleoecological investigations are still too few to allow broad-scale regional conclusions to be drawn, in general, more recently acidified lakes and higher rates of acidification have been found in acid-sensitive areas where acid deposition is the highest. This strongly implicates acid precipitation as the cause.

Comparisons of chemical data from lakes that were sampled on two or more occasions many years apart have usually been hampered by the poor documentation of older records, or the unreliability of older chemical methods. Recently, various investigators have developed methods for correcting older data, reproducing older analyses, or both (*31*). This has allowed comparisons of recent and older *p*H or alkalinity records for three areas. These data show that the lakes of the Adirondacks have suffered substantial losses of alkalinity (*32*). The lakes in New Hampshire have not changed detectably in alkalinity, and some lakes in Wisconsin appear to have increased slightly, apparently as a result of modifications in the watersheds. In general, there is a strong tendency for declines in alkalinity to correspond to increases in sulfate, and vice versa (*33*).

A few studies have applied consistent chemical methods over long time periods. Significant increases in SO_4^{2-} and decreases in alkalinity have been recorded for low-alkalinity streams gauged by the U.S. Geological Survey between the mid-1960s and 1983, except in the northeastern United States, where decreased SO_4^{2-}

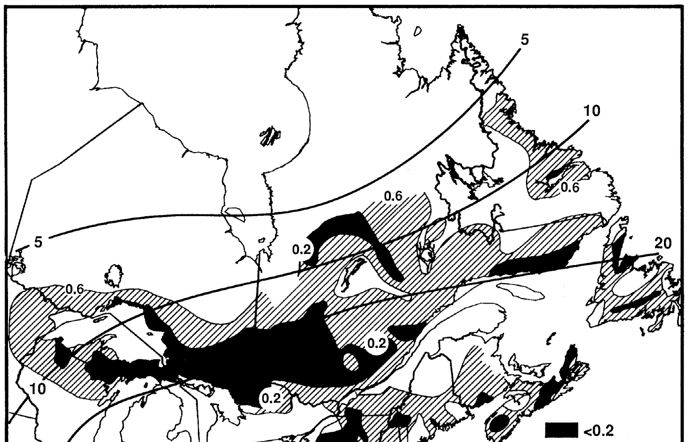

Fig. 1. The average ratio of alkalinity (acid neutralizing capacity) to Ca^{2+} and Mg^{2+} in freshwater lakes of northeastern North America. Average ratios in lakes of pristine areas usually range from 0.6 to 1.1. Inputs of acid, such as acid rain, cause alkalinity to decline and Ca^{2+} and Mg^{2+} to increase. Average values for sensitive lakes in areas with highly acidic deposition are less than 0.2. In individual lakes, zero or even negative values can occur. Only lakes with Ca^{2+} + Mg^{2+} less than 200 μeq $liter^{-1}$ are included. Values were sea-salt corrected where appropriate. The map was compiled by D. S. Jeffries, National Water Research Institute, Burlington, Ontario. Canadian data of roughly 8000 lakes; U.S. data from Linthurst *et al.* and Kanciruk *et al.* (*32*). Heavy lines numbered 5, 10, and 20 indicate sulfate deposition in kilograms per hectare per year and were added by the author.

and increased alkalinity reflect the decreased emissions and deposition of sulfur during the period (*34*). The alkalinity of Plastic Lake, in the Muskoka region of Ontario, has decreased by an average of 2 μeq liter^{-1} year^{-1} for a period of six consecutive years in the late 1970s and early 1980s (*35*). Substantial alkalinity decreases in four other lakes in eastern Ontario were also recorded in the 1960s and 1970s, where consistent chemical methods were applied (*36*). The acidification of lakes in the LaCloche Mountains, in the Sudbury areas of Ontario, and in Nova Scotian rivers in the 1960s and 1970s is also well documented (*37, 38*). However, alkalinity losses greater than 100 μeq liter^{-1} are unlikely to be caused entirely by acid precipitation (*27, 37*), except perhaps in a few areas of extremely high dry deposition. In such cases land-use changes, disruptions in the internal sources of alkalinity, climatic factors, or analytical errors must be suspected. Records of from 4 to 19 years have shown no decrease in alkalinity or *p*H in lakes of extreme northwestern Ontario, an area where precipitation still has an average *p*H of 4.9 to 5.0 (*39*).

Together, the four lines of evidence demonstrate convincingly that acidification of lakes and streams has occurred in geologically sensitive areas of North America that receive precipitation polluted with strong acids, but not in sensitive areas where atmospheric pollution is still relatively low. Changes in the chemistry of precipitation have occurred so frequently that steady state between atmospheric inputs and lake chemistry cannot have been reached for lakes with long water-residence times (*40*).

Evidence for Biological Change

Most early records of biological damage were confined to adult fishes of species valued for sport. Most of these can tolerate *p*H values of less than 5.5 (*41*). Lakes with higher *p*H values were assumed to be free from biological effects. More recently, juvenile fishes and many organisms lower in the aquatic food web have been shown to be intolerant of much higher *p*H values (*42*). The early disappearance of organisms at lower trophic levels may cause starvation to stress large predatory fishes well before direct toxic action of the hydrogen ion is evident. Several recent studies support this hypothesis (*43*).

Because spawning beds are difficult to locate and young fish are usually difficult to catch, populations may have experienced several years of successive recruitment failure before damage is detected (*44*). In summary, because assessments of biological effects have focused on adult game fish instead of more sensitive juveniles or organisms lower in the food web, our current estimates of biological damage to aquatic communities caused by acid rain are unquestionably too low.

Among larger game fishes, most autumn-spawning species are usually more sensitive to acidification than spring spawners, because the very sensitive hatchlings are present in shallow nearshore waters in early spring when snowmelt can produce a strong acid and aluminum pulse (*45*).

The oligotrophication of acidified lakes, one of the key earlier concerns of ecologists (*46*), does not occur in most cases. While there is some evidence for reduced phosphorus inputs (*47*) or changed forms of phosphorus (*48*) in acidified lakes, most field investigations have found that significant changes in photosynthetic production, biomass, and nutrient concentrations in acidified lakes did not occur (*49*). Indeed, in some cases, phosphorus was mobilized from lake sediments and stream beds during acid pulses (*50*). Likewise, although several investigators have observed an increased abundance of coarse organic matter on surface sediments of acidified lakes (*51*), this has not always caused decreased microbial decomposition, as had been hypothesized (*52*). In contrast to the lack of effect on lake metabolism, changes in species of phytoplankton are dramatic and remarkably similar in most acidified lakes (*51*). The formation of mats of benthic algae or bryophytes in littoral regions of acidified lakes is also widespread (*53*).

Although the number of zooplankton species is usually lower in acidic lakes, the lower biomass once thought to be caused by acidification has recently been shown to be due to lower availability of nutrients (*54*). The few thorough case studies of streams indicate that their biota may be even more sensitive to acidification than that of lakes. The benthic fauna of acidic streams has long been known to be less diverse than in circumneutral ones (*55*). Several species of mayflies and stoneflies disappeared from acidified reaches of streams in the Algonquin Highlands of Ontario between 1937–42 and 1984–85 (*56*). The impoverishment was attributed largely to a decrease in *p*H of up to 1.5 units during spring snowmelt (*57*). Similar conclusions were reached from surveys of stream benthos in Sweden (*58*). In Norway, the stream invertebrate fauna has been severely impoverished by acidification (*59*). Fish kills that have been observed in streams and rivers during acid pulses and the decline in trout or salmon fisheries in acidified waters are good evidence for ecological damage that results from acid rain (*60*).

The Role of Aluminum in Biological Damage

Aluminum is released to lakes and streams from acidified terrestrial soils and lake sediments. Only ionic aluminum and aluminum hydroxide appear to be highly toxic to fishes, and only the former is important at low *p*H (*61*). Other organisms appear to be much less susceptible (*62*). The importance of aluminum seems to vary greatly between ecosystems and with the stage of acidification, as a result of differences in watersheds, aquatic chemical complexes, the presence of refugia, and the behavioral responses of fish species (*63*). Many of the early effects of acidification mentioned above, at *p*H values approaching 6, cannot be attributed to aluminum toxicity (*64*).

The Resistance of Lakes to Acidification

Until recently, scientists believed that the entire resistance of lakes to acidification was supplied by the weathering of geological substrates or the exchange of hydrogen ions for base cations in terrestrial soils of watersheds. As a result, until recently, published models of acidification have focused exclusively on terrestrial processes (*65*).

However, historical studies and whole-lake experiments have revealed that there is an additional resistance to acidification within lakes, and budgets for natural lakes revealed that in some cases terrestrial sources could only account for a part of the observed buffering (*66*). These processes are not 100% efficient at neutralizing incoming acids. Therefore, they have not prevented lakes from acidifying. Yet without them, the acidification of lakes would be much more severe (*67*). These processes involve first-order reactions at sediment surfaces, so that their efficiency is higher in shallower, more slowly flushing lakes and lower in deeper, rapidly flushing lakes (*68*).

Recovery from Acidification

The recovery of lakes and streams after the acidity of precipitation has been reduced is documented in case history studies from areas of eastern Canada where sulfate deposition has decreased substantially in the past 10 to 15 years. In the Sudbury area, a combination of smelter closures and SO_2 controls have reduced emissions to about one-third of their value in the early 1970s (*69*). The concomitant decreases in the acidity of local deposition have been accompanied by rapid increases in alkalinity and *p*H in nearby lakes, and decreased concentrations of SO_4^{2-}, aluminum, and toxic trace metals (*70*). The recoveries have occurred at rates more or less predictable from the water renewal rates of the lakes (*71*). The acidity of at least some of the lakes decreased enough to prevent the extinction or to allow the reintroduction of lake trout or brook trout (*69*). Crustacean zooplankton communities of the lakes have not recovered (*72*), but rotifer populations are returning to those typical of less acidic conditions (*73*). Decreased acidity of the spring melt pulses in streams was also attributed to the decrease in emissions (*74*). Similar increases in *p*H were observed in 54 lakes of the Algoma region in north-central Ontario. In two of the lakes, white sucker (*Catostomus commersoni*) were able to reinvade and survive (*75*).

The reduction of U.S. and Canadian SO_2 emissions has also allowed some recovery of freshwaters in maritime Canada. Sulfate runoff from 12 river watersheds in Nova Scotia and 8 watersheds in Newfoundland has decreased dramatically, accompanied by increases in river *p*H (*76*).

However, it is not clear whether lakes will be able to recover completely. Base cations in soils can be depleted by acidification, and their recovery may take many years (*35*). Also, experimental whole-lake studies show that the reversal of acidification allows only some components of the biota to recover rapidly. Acidification of Lake 223 to *p*H 5.0 eliminated several key species of fishes and invertebrates (*77*). Recovery of the lake to a *p*H of 5.4 to 5.6 by reducing inputs of sulfuric acid allowed two of the remaining species of fishes to resume reproduction. Some species of phytoplankton that had been eliminated by acidification also returned. To date, lake trout have not resumed reproduction. Other species eliminated from the lake have not returned (*71*).

Although it is now clear that reducing emissions of SO_2 will allow the rapid chemical recovery of lakes, it is unlikely that original *p*H values will be reached for many years. Unassisted biological recovery of all original species also appears to be unlikely. Widespread stocking of game fishes and key prey species will be necessary. Even then, the reconstructed food chains may not resemble the original ones. It therefore seems prudent to prevent as much additional ecological damage as we can.

Land Use and Acidification

In some circumstances, land-use changes may have a greater acidifying effect on soils than acid deposition (*78*). Some investigators have argued that deforestation several decades ago resulted in decreases in the acidity of runoff waters that caused the *p*H of lakes to increase. They believe that the regrowth of forests has been responsible for the recent increase in acidification of lakes (*79*). In heavily populated areas, it has been difficult to separate the two causes of acidification. In individual watersheds, studies have shown that acidification results from land use when large deposits of reduced sulfur are exposed to oxygen in the atmosphere by human disturbance, such as in acid mine drainage (*80*) and in areas where ancient marine or wetland sediments have been exposed by drainage and cultivation (*81*).

However, acidification has occurred in remote parts of the North American Precambrian Shield where land use has not changed (Fig. 1). Moreover, where land-use changes have been intensively studied, the evidence does not support the land-management hypothesis. For example, deforestation at Hubbard Brook and the Experimental Lakes Area caused higher losses of H^+ and strong acid anions than under aggrading conditions, as a result of higher nitrification and reoxidation of reduced sulfur compounds (*82*). This is the reverse of what was hypothesized by proponents of the land-use hypothesis. Sulfate is usually the predominant anion in runoff from anthropogenically acidified areas, rather than the organic anions expected if forest regrowth were responsible for acidification (*83*). In Norway, lakes with pristine watersheds and those where land-use changes had occurred were found to acidify at identical rates (*84*). In Scotland and Wales, paleoecological studies have shown that the timing of recent lake acidification is consistent with changes in the strong acid content of precipitation and not with the timing of land-use changes (*85*). Similarly, the rapid acidification of Big Moose Lake in the Adirondacks since 1950 correlates to increases in fossil fuel combustion, not watershed changes (*86*). In summary, terrestrial processes clearly contribute to the acidity of soils and natural waters, but changes in land use cannot explain the widespread acidification of fresh waters in the 20th century.

How Much Must We Reduce Sulfur Deposition?

Most scientists now agree that reducing deposition of sulfuric acid will benefit aquatic ecosystems (*86*). As we have seen, data from areas whose acid deposition has decreased confirm this view. The remaining questions are, what degree of reduction is necessary to protect our aquatic resources, and what is the link to emissions of sulfur oxides? A few aquatic ecosystems are naturally acidic enough to have an impoverished biota, even when the *p*H of precipitation is 5.0 or greater, implying that any anthropogenic additions to the acidity of deposition would add to the number of acidic lakes (*87*). Furthermore, if decades of exposure to high inputs of acid have depleted the base cations in watershed soils, even a return of precipitation to natural levels of acidity would not allow waters to recover fully for many years (*35*). Some realistic compromise between ecosystem damage and anthropogenic activity must obviously be struck. This problem may be approached in several ways:

First, almost all areas where the average ratio of alkalinity to $Ca^{2+} + Mg^{2+}$ in acid-sensitive lakes has been reduced by acidification to values of 0.6 or less are bounded by the 10 kg ha^{-1} $year^{-1}$ isopleth for wet SO_4^{2-} deposition (Fig. 1). In lakes where original alkalinity was 50 μeq $liter^{-1}$ or less, even declines in the ratio to 0.6 would usually be accompanied by decreases in *p*H of several tenths of a unit. Given the sensitivity of aquatic food chains to any decrease in *p*H (*43*), deposition of over 10 kg ha^{-1} $year^{-1}$ can be expected to cause some biological impoverishment in our most sensitive fresh waters.

Second, all lakes that are claimed to have been acidified are located in areas receiving precipitation with *p*H values less than 4.6 to 4.7 (*88*). Statistical analysis of precipitation data from the eastern United States reveals that such *p*H values in precipitation usually occur where SO_4^{2-} deposition is less than 14 kg ha^{-1} $year^{-1}$ (*89*). Because of the short time intervals considered and other shortcomings of the historical data sets on which these conclusions are based, these observations are probably less sensitive than the ratio of alkalinity to $Ca^{2+} + Mg^{2+}$.

Third, in Sweden, a maximum allowable SO_4^{2-} deposition of 9 kg ha^{-1} $year^{-1}$ has been deduced from a comparison of the current *p*H values observed in extremely sensitive lakes in areas with different sulfur deposition values (*90*). Finally, some acidification has been recorded in very sensitive lakes receiving SO_4^{2-} depositions of 16 to 25 kg ha^{-1} $year^{-1}$ (*91*).

In summary, it appears that the limit to SO_4^{2-} deposition must be somewhere between 9 to 14 kg ha^{-1} year^{-1} to protect our most sensitive aquatic ecosystems (*92*). These values are far below the values of 20 to 50 kg ha^{-1} year^{-1} currently measured in most of eastern North America and most of western Europe, and would only be attained by substantial reductions in anthropogenic emissions of SO_2.

Interaction of Acid Rain with Other Pollutants and Terrestrial Ecosystems

Clearly, we know enough about the effects of acid rain on aquatic ecosystems to make a strong case for regulating emissions of sulfur oxides. However, while the debate about controlling acidifying emissions has focused almost entirely on SO_2, emissions of nitrogen oxides have received little attention and have increased much more rapidly than SO_2 in recent decades (*7, 93*). The resulting nitric acid plays an increasing role in the acidification process and is particularly important during the spring, when melting of polluted snow normally causes a strong acid pulse (*93*). In addition, nitrogen oxides are known to react in the atmosphere to form ozone, which is highly toxic to terrestrial plants (*94*).

Metals are also known to exacerbate the acidification problem. The case of aluminum leached from soils and sediments was discussed earlier. In addition, many toxic trace metals are emitted from the same sources that release oxides of sulfur and nitrogen. These are distributed almost as widely as acid rain (*95*). As precipitation becomes more acid, a higher proportion of these will be soluble in rain, mist, and fog. Prior to the industrial revolution, the trace metal inputs to ecosystems were small. In the past 100 to 200 years inputs have increased rapidly, and many of the trace metal biogeochemical cycles are dominated by anthropogenic inputs, even at very remote locations (*96, 97*).

At circumneutral *p*H values, most trace metals are quite insoluble in water, sorbing quickly to particles in lake water, which sink rapidly (*98*). Even many fold increases in metal inputs may result in concentrations that are below the limits of detection of standard chemical methods for analyzing lake water (*97*). It is therefore much easier to detect increases in lake sediments. However, some of the sedimented trace metals may be remobilized or remain in solution longer as lakes acidify (*99*), increasing the exposure to aquatic organisms (*100*). The acidification of ground water may also mobilize trace metals, and acidic water supplies are known to dissolve metals from plumbing, possibly constituting a drinking water hazard in some areas (*101*). Although there have been few studies, a number of cases have documented ecological effects that result from interactions between acid rain and metals (*61–64, 102*).

Interactions between oxides of sulfur, oxides of nitrogen, ozone, carbon monoxide, hydrocarbons, and methane are known or suspected to contribute to a variety of adverse environmental effects, ranging from acidification of ecosystems to crop damage, depletion of the ozone layer, and climatic change (*103*).

In forests, agricultural lands, and wetlands, the causes of observed damage appear to be more complicated than in lakes and streams, with many air pollutants acting in concert, in some cases exacerbating the effects of natural stresses such as cold and drought (*104*). Acid rain appears to play some role in the observed damage. It is clearly instrumental in mobilizing the soil aluminum which causes root damage in forests, and in leaching plant nutrients from foliage (*104*). Polluted fogs and mists also expose terrestrial plants to concentrations of acid much higher than in rain, causing direct foliar damage in some cases (*105*). Long-range transport of sulfur in the atmosphere has caused increased haze in both Arctic and temperate regions (*106*). In summary, reducing emissions of sulfur and nitrogen oxides would be beneficial to softwater aquatic ecosystems and probably to terrestrial ecosystems as well. Regional air pollution is much more severe than we believed in the past, and more comprehensive measures to control it are necessary to preserve the integrity of the biosphere (*107*).

REFERENCES AND NOTES

1. R. A. Smith, *Mem. Lit. Philos. Soc. Manchester, Ser. 2* **10**, 207 (1852). More recently, researchers have used the terms "acid precipitation," "acid deposition," or even "acidifying deposition" as more precise descriptors of the problem. Here I retain the term "acid rain" as originally described by Smith and as understood by the general public.
2. E. Gorham, *R. Soc. London Notes Records* **36**, 267 (1982).
3. S. Odén, *Dagens Nyheter* (*Stockholm*), 24 October 1967; "The acidification of air and precipitation and its consequences in the natural environment," *Ecology Committee Bulletin No. 1* (National Science Research Council, Stockholm, 1968); G. E. Likens, F. H. Bormann, N. M. Johnson, *Environment* **14**, 33 (1972); G. E. Likens and F. H. Bormann, *Science* **184**, 1176 (1974).
4. The history of acid-precipitation research has been documented by E. B. Cowling, *Environ. Sci. Technol.* **16**, 110A (1982). The ACIDOC database listed 6000 publications on acid rain from 1967 to March 1986.
5. I. J. Wilk, *Sci. Total Environ.* **44**, 293 (1985). A good part of the controversy has resulted from doubt and confusion deliberately fostered by vested-interest groups.
6. M. Havas, T. Hutchinson, G. E. Likens, *Environ. Sci. Technol.* **18**, 1976A (1984).
7. In particular, the long-range transport and environmental toxicity of a wide variety of substances in addition to acids have been revealed, which has led to recent references by the media to "toxic rain." The subject was reviewed in *Atmosphere-Biosphere Interactions: Toward a Better Understanding of the Ecological Consequences of Fossil Fuel Combustion* (National Academy Press, Washington, DC, 1981) and in G. J. MacDonald, *Climate Change and Acid Rain* (Mitre Corporation, McLean, VA, 1986).
8. Evidence that strong acids were present in natural rain has existed for 30 years. E. Gorham, *Geochim. Cosmochim. Acta* 7, 231 (1955); *Ir. Nat. J.* **12**, 1 (1957); *Philos. Trans. R. Soc. Lond. Ser. B.* **247**, 147 (1958); *Geol. Soc. Am. Bull.* **72**, 795 (1961); E. Barrett and G. Brodin, *Tellus* 7, 251 (1955); L. Granat, *ibid.* **24**, 550 (1972). Strangely, this work was ignored in the acid-rain literature before 1982.
9. R. J. Charlson and H. Rodhe, *Nature (London)* **295**, 683 (1982); J. N. Galloway, G. E. Likens, W. C. Keene, J. M. Miller, *J. Geophys. Res.* **87**, 8771 (1982).
10. W. M. Lewis, Jr., and M. C. Grant, *Science* **207**, 176 (1980); ———, J. F. Saunders III, *Water Resour. Res.* **20**, 1691 (1984); D. Zhao and B. Sun, *Ambio* **15**, 2 (1986); J. N. Galloway, Z. Dianwu, X. Jiling, G. E. Likens, *Science* **236**, 1559 (1987); E. E. Breslav *et al.*, *Meteorol. Gidrol.* **5**, 108 (1985); B. Wells, *Scientiae* (*Milan*) **26**, 24 (1985).
11. M. V. Ivanov, "The global biogeochemical sulfur cycle," in *Some Perspectives of the Major Biogeochemical Cycles* (SCOPE Report 17), G. E. Likens, Ed. (Wiley, New York, 1981), pp. 61–78.
12. L. N. Overrein in (*12a*), pp. 43–52; J. N. Galloway and D. M. Whelpdale, *Atmos. Environ.* **14**, 409 (1980); A. J. S. Tang, A. Ahmed, M. A. Lusis, *Ontario Ministry of Environment, Toronto, Report ARB-110-86* (1986); J. A. Fay, S. Kumar, D. Golom, *Atmos. Environ.* **20**, 1487 (1986).

12a. "Ecological effects of acid deposition," National Swedish Environment Protection Board Report PM 1636 (1983).

13. Originally proposed by S. Odén [see (*3*)]. Summarized by Overrein [see (*12*)].
14. Most of these claims had been made in the popular, rather than the scientific, literature and seem designed by vested-interest groups to create the illusion of controversy. However, the recent hypothesis by W. M. Brown [*Fortune* **113** (no. 3), 125 (1986)] that bird droppings cause acid rain, while probably done in jest, has attracted renewed concern by bureaucrats and politicians.
15. L. A. Barrie, *Atmos. Environ.* **20**, 643 (1986).
16. K. A. Rahn, *ibid.* **15**, 1457 (1981); ——— and D. H. Lowenthal, *Science* **228**, 275 (1985); *ibid.* **223**, 132 (1984); D. E. Patterson and R. B. Husar, *Atmos. Environ.* **15**, 1479 (1981).
17. Detailed U.S. maps of sensitivity to acidification may be obtained from the National Clean Air Fund, Washington, DC 20003, and from J. M. Omernik, Corvallis Environmental Research Laboratory, U.S. Environmental Protection Agency, Corvallis, OR 97333. See J. M. Omernik and C. F. Powers, *Ann. Assoc. Am. Geog.* **73**, 133 (1983).
18. Most scientists consider lakes with alkalinities less than 200 μeq liter^{-1} to be acid-sensitive. J. R. M. Kelso *et al.*, *Can. Spec. Publ. Fish. Aquat. Sci.* **89** (1986).
19. A number of characteristics of lakes and their watersheds can render them acid-sensitive. These include thin, noncalcareous soils, small drainage areas, short water-residence times, high elevation, and low biological productivity. See also the section on "Resistance of Lakes to Acidification." Summaries of both acid-sensitive areas and acid-precipitation problems for European and North American countries are given in (*19a*) and in papers in *Water, Air, and Soil Pollution*, volumes 30 and 31 (1986). Ecological problems occur when acidic precipitation falls in such acid-sensitive areas. There is evidence that such problems are currently increasing in developing countries. See also J. J. San Jose *et al.*, *Tellus* **37B**, 304 (1985); H. Rodhe and R. Herrera, Eds., *Proceedings of Workshop on Acidification in the Tropics* (Wiley, New York, in press). Acid-sensitive lake districts in the U.S.S.R. were described by I. V. Baranov, *Limnological Lake Types—U.S.S.R.* (Hydrometeorological Institute, Leningrad, 1962).

19a. D. Drablos and A. Tollan, Eds., *Ecological Impact of Acid Precipitation* (SNSF Project, Oslo, Norway, 1980).

20. Measurements of *p*H and alkalinity were usually made with colorimetric indicators. These often changed the alkalinities and *p*H of the poorly buffered samples from acid-sensitive lakes. Older data sets were seldom complete enough to allow calculation of ionic balances, the method now used as a standard check on chemical accuracy. As an example, the increase in extent of acid rain in North America, described by C. V. Cogbill and G. E. Likens [*Water Resour. Res.* **10**, 1133 (1974)] and G. E. Likens and T. J. Butler [*Atmos. Environ.* **15**, 1103 (1981)] was disputed by G. J. Stensland and R. G. Semonin [*Bull. Am. Meteorol. Soc.* **63**, 1277 (1982)]. See also C. V. Cogbill, G. E. Likens, T. J. Butler, *Atmos. Environ.* **18**, 2261 (1984). Recent analyses of SO_4^{2-} and NO_3^- in ice cores from South Greenland show increases in deposition of SO_4^{2-} and NO_3^- from 1900 onward, generally supporting the claims of Likens and colleagues.

21. The history of acid rain as determined from diatom fossils is reviewed by R. W. Battarbee and D. F. Charles, *Water Air Soil Pollut.* **30**, 347 (1986). A recently documented example of early acidification in North America is Hannah Lake, near Sudbury, Ontario, which began acidifying soon after the opening of the nearby Copper Cliff smelter in 1880 [S. S. Dixit, A. S. Dixit, R. D. Evans, *Sci. Total Environ.* **67**, 53 (1987)].

22. R. Husar and J. M. Holloway in (*12a*), pp. 95–115. Emissions of SO_2 in Europe increased little from 1900 to 1950, then more than doubled by the late 1970s [H. Dovland and S. Semb in (*19a*), pp. 14–21].

23. J. G. Calvert *et al.*, *Nature (London)* **317**, 27 (1985).

24. A. P. Altshuller, *Environ. Sci. Technol.* **14**, 1337 (1980); see also R. Patrick, V. P. Binetti, S. G. Halterman, *Science* **211**, 446 (1981).

25. See G. J. MacDonald in (*7*). Recently, L. O. Hedin, G. E. Likens, and F. H. Bormann [*Nature (London)* **325**, 244 (1987)] have shown that while SO_4^{2-} has declined in precipitation in the northeastern United States as a result of sulfur emission controls in the early 1960s, NO_3^- has increased and base cations have decreased. The net result has been little change in the acidity of precipitation. H. Rodhe and M. J. Rood [*ibid.* **321**, 762 (1986)] recorded similar replacements of sulfuric acid with nitric acid at European sites.

26. P. L. Brezonik, E. S. Edgerton, C. D. Hendry, *Science* **208**, 1027 (1980); G. J. Stensland, D. M. Whelpdale, G. Oehlert in (*26*a), chap. 5.

26a. *Acid Deposition: Long-Term Trends* (National Academy Press, Washington, DC, 1986).

27. J. N. Galloway, G. E. Likens, M. E. Hawley, *Science* **226**, 829 (1984).

28. Analyses are based on normal geochemical ratios expected from the weathering of rocks and soils. In acid-vulnerable areas unaffected by acid rain, the average ratio of alkalinity to $Ca^{2+} + Mg^{2+}$ in surface waters averages from 0.8 to 1.1. Although the oxidation of minerals containing reduced sulfur or the presence of large concentrations of organic acids can cause naturally low values, in surveys of several thousand lakes, such cases have never been found to reduce average values of the ratio outside the above range in pristine areas of Europe and North America. Acid precipitation depletes the alkalinity of lakes by replacing HCO_3^- with SO_4^{2-}, and may cause $Ca^{2+} + Mg^{2+}$ to increase as a result of increased weathering of soils and lake sediments. Consequently, the ratio of alkalinity to $Ca^{2+} + Mg^{2+}$ in lakes has decreased in regions receiving acid precipitation. The subject is reviewed by A. Henriksen, in *Acid Rain/Fisheries*, T. A. Haines, Ed. (American Fisheries Society, Bethesda, MD, 1982), pp. 103–121. See also R. F. Wright, "Predicting acidification of North American lakes," *Report 4/1983* (Norwegian Institute for Water Research, Oslo, Norway, 1983); D. H. Landers *et al.*, *Characteristics of Lakes in the Western United States*, vol. 1 of *Population Descriptions and Physicochemical Relationships* (EPA-600/3-86/054a, Environmental Protection Agency, Washington, DC, 1986). While soils based on weathering of gypsum or other minerals high in sulfate can cause the ratio of alkalinity to $Ca^{2+} + Mg^{2+}$ to be low even in the absence of acid rain, broad surveys of pristine areas have seldom revealed these exceptions to cause average ratios less than 0.6.

29. D. S. Jeffries, *Proceedings CEC* [Commission of European Communities, Brussels, Belgium] *Workshop on Acidification of Rivers and Lakes*, (Grafenau, Federal Republic of Germany, 28 to 30 April 1986).

30. General reviews are given in J. P. Smol, R. W. Battarbee, R. B. Davis, J. Merilainen, Eds., *Diatoms and Lake Acidity* (Junk, Dordrecht, Netherlands, 1986); D. F. Charles and S. A. Norton in (*26a*), chap. 9; and Battarbee and Charles in (*21*). See also D. F. Charles *et al.*, *Biogeochemistry* **3**, 267 (1987). Recent evidence for severe acidification in central Ontario and Quebec is given by S. S. Dixit, *Can. J. Bot.* **64**, 1129 (1986); S. S. Dixit *et al.* in (*21*); and S. S. Dixit, A. S. Dixit, R. D. Evans, *Water Air Soil Pollut.*, in press. Lakes analyzed were near smelters at Wawa and Sudbury, or in areas of Muskoka and Haliburton, where atmospheric trajectories implicate emissions from both the U.S. coal belt and Canadian smelters. In Nova Scotia, large *p*H decreases have occurred in the most sensitive lakes, while better buffered ones are not badly damaged. See J. K. Elner and S. Roy, *Water Air Soil Pollut.* **32**, 17 (1987). Relatively few lakes have been investigated by paleoecological analyses. Techniques are improving rapidly and the method is our most powerful tool for deducing the history of lake acidification. In particular, inclusion of both chrysophyceans and diatoms seems to have increased the resolution of the method. For example, see K. N. Gibson, J. P. Smol, J. Ford, *Can. J. Fish. Aquat. Sci.*, in press, and papers by Dixit *et al.* (*21, 30*). Estimates of acidification from paleoecological analyses must be regarded as minima, for only *p*H decreases greater than 0.2 to 0.3 *p*H unit can be detected. Such decreases occur only after substantial alkalinity losses have taken place.

31. Reviewed by J. R. Kramer *et al.* in (*26a*), chap. 7. See also A. W. Andren and B. Bischoff, *Int. J. Environ. Anal. Chem.* **22**, 259 (1985) and C. Asbury, F. Vertucci, M. Mattson, G. E. Likens, M. Best, unpublished data.

32. Kramer *et al.* (*31*) found that the degree of loss of alkalinity from Adirondack lakes depended on the assumptions made in correcting older data. However, Asbury *et al.* (*31*) reproduced older methods and conducted empirical tests with 20 analysts, using modern samples to obtain corrections for older data. Furthermore, they showed that many errors were made in earlier treatments of historical data, for example, the inclusion of limed lakes in the analyses. They concluded that the median alkalinity loss for Adirondack lakes was 50 μeq liter^{-1}. Alkalinity had decreased in 257 of the 318 lakes examined. Similar declines in alkalinity and increases in acidity for Norway were reported by R. F. Wright *et al.*, *Water Air Soil Pollut.* **6**, 483 (1976).

33. See Kramer *et al.* (*31*) and J. A. Rogalla, P. L. Brezonik, G. E. Glass, *Water Air Soil Pollut.* **31**, 93 (1986). Increases in alkalinity such as those seen in Wisconsin may be due to human disturbances in the watershed such as road building and cottage construction, which generally increase inputs of base cations to lakes. See also P. Kilham, *Limnol. Oceanogr.* **27**, 856 (1982). A general correlation between ($Ca^{2+} + Mg^{2+}$ − alkalinity) and sulfate is evident for lakes in northeastern North America (see R. A. Linthurst *et al.*, *Characteristics of Lakes of the Eastern United States*, vol. 1 (USEPA/600/4-86/007a, Washington, DC, 1986) and P. Kanciruk *et al.*, vol. 3 (USEPA/600/4-86/007c, Washington, DC, 1986).

34. J. T. Turk, *U.S. Geol. Surv. Water Supply Pap. 2249* (1983). See also (*31*). Once again, conclusions for individual regions generally agree with those of paleoecological and geochemical methods.

35. P. J. Dillon, R. A. Reid, E. de Grosbois, *Nature (London)* **329**, 45 (1987). The increase in acidity occurred even though deposition of SO_4^{2-} and H^+ had recently decreased. Such data have caused some people to conclude that emissions of sulfur do not cause lake acidification. However, Dillon *et al.* showed that the continued acidification was due to exhaustion of base cations in the watershed by years of acid rain. See also B. J. Cosby, G. N. Hornberger, J. N. Galloway, R. F. Wright, *Water Resour. Res.* **21**, 51 (1985).

36. P. J. Dillon *et al.*, *J. Fish. Res. Board Can.* **35**, 809 (1978).

37. Rates of up to 0.1 *p*H unit per year were recorded in some cases. See N. Conroy, K. Hawley, W. Keller, *Extensive Monitoring of Lakes in the Greater Sudbury Area* (Ontario Ministry of Environment, Rexdale, Ontario, 1978).

38. H. Harvey and C. Lee, in *Acid Rain/Fisheries*, R. Johnson, Ed. (American Fisheries Society, Bethesda, MD, 1982), pp. 45–55; W. Watt, C. Scott, W. White, *Can. J. Fish. Aquat. Sci.* **40**, 462 (1983).

39. D. W. Schindler and T. Ruszczynski, *Can. Fish. Mar. Serv. Tech. Rep. 1147* (1983); G. A. Linsey and D. W. Schindler, unpublished data.

40. See (*25*) and Dillon *et al.* [in (*35*)]. In general, lakes must be flushed three times with input waters of a new chemical composition before approaching steady state.

41. The extensive, careful sport fishing records kept in Norway, Sweden, the United Kingdom, and eastern Canada were the earliest indicators of changes that resulted from acidification, and early scientific surveys concentrated on the same species. Recent general reviews of *p*H tolerance of organisms are given by J. M. Eilers, G. J. Lien, R. G. Berg, *Tech. Bull. Dep. Nat. Resour. Madison, Wisconsin* **150** (1984); J. J. Magnuson, J. P. Baker, E. J. Rahel, *Philos. Trans. R. Soc. London Ser. B* **305**, 501 (1984); T. A. Haines, in (*26a*), chap. 8; K. H. Mills and D. W. Schindler, *Water Air Soil Pollut.* **30**, 779 (1986).

42. Reviewed by J. Økland and K. A. Økland, *Experientia* **42**, 471 (1986); Mills and Schindler in (*41*); G. Mierle, K. Clark, R. France, *Water Air Soil Pollut.* **31**, 593 (1986).

43. D. W. Schindler *et al.* [*Science* **228**, 1395 (1985)] showed that several key food organisms for lake trout were eliminated in Lake 223, an experimentally acidified lake. As a result, trout became very thin. Trout mortality increased, and reproduction ceased at *p*H values below 5.4 [K. H. Mills, S. M. Chalanchuk, L. C. Mohr, I. J. Davies, *Can. J. Fish. Aquat. Sci. Suppl. 1* **44**, 114 (1987)]. Overall, the number of species identified in Lake 223 decreased by 30% as the *p*H was decreased from 6.5 to 5.1. Recently, similar observations have been made in Plastic Lake in a food chain leading to sunfish (P. J. Dillon, Ontario Ministry of Environment, personal communication). Other experiments have shown that starvation increases the vulnerability of smallmouth bass to acidification [W. Kwain, R. W. McCauley, J. A. MacLean, *J. Fish Biol.* **25**, 501 (1984); G. L. Cunningham and B. J. Shuter, *Can. J. Fish. Aquat. Sci.* **43**, 869 (1986)]. In the past, it has been assumed that food-chain effects were secondary in importance to direct toxic action on fish [B. D. Rosseland, *Water Air Soil Pollut.* **30**, 451 (1986)]. However, the references usually quoted as proof for this offer scanty evidence. In fact, Rosseland found that predatory fishes in acidified lakes usually became thinner.

44. Reviewed by Rosseland in (*43*). See also Schindler *et al.* in (*43*) and Mills and Schindler in (*41*); J. M. Gunn, *Environ. Biol. Fishes* **17**, 241 (1986); Mills *et al.* in (*43*).

45. For example, lake trout (*Salvelinus namaycush*) usually spawn in late September to November, in less than 2 m of water, close to shore. Egg envelopes protect developing embryos, so that they tolerate low *p*H quite well. Embryos hatch in February or March, after which hatchlings hide in redds (spawning beds) in nearshore rocky rubble until after ice-out. Hatching greatly increases the vulnerability of embryos to acidification, and acid and aluminum pulses associated with spring snowmelt are toxic to the hatchling trout. See Gunn in (*44*) and J. M. Gunn and W. Keller, *Water Air Soil Pollut.* **30**, 545 (1986). It is estimated that acidification has caused lake trout to become extinct in 3% of the Ontario lakes. A further 16% of lake trout lakes are currently acidified or extremely sensitive. The problem is confined to the eastern half of the province. When eliminated by acidification, lake trout are not replaced by an alternate predator [G. L. Beggs, J. M. Gunn, C. H. Olver, *Ontario Fish. Tech. Rep. No. 17* (1985); Gunn in (*44*); J. M. Gunn and D. L. G. Noakes, *Can. J. Fish. Aquat. Sci.*, in press]. Other salmonids have life cycles somewhat similar to those of lake trout, but the effects of acidification are not as well documented. Rosseland (*43*) provides information on European species. Walleye, which spawn during snowmelt at the mouths of streams, are an exception to the fall spawning generalization. Their eggs develop very rapidly, and hatching may occur early enough for juveniles to be affected by the spring acid pulse. Where studies have been done, juvenile invertebrates have also proven to be more sensitive than adults. Because of their short life expectancies, a few successive recruitment failures can cause them to be eliminated from a water body. For examples, see M. Berrill, L. Hollett, A. Margosian, J.

Hudson, *Can. J. Zool.* **63**, 2586 (1985); J. B. Rooke and G. L. Mackie, *ibid.* **62**, 1474 (1984); R. W. Nero and D. W. Schindler, *Can. J. Fish. Aquat. Sci.* **40**, 1905 (1983); and Mierle *et al.* in (*42*).

46. O. Grahn, H. Hultberg, L. Landner, *Ambio* **3**, 93 (1974). G. Hendrey, K. Baalsrud, T. S. Traaen, M. Laake, G. Raddum, *ibid.* **5**, 224 (1976).
47. H. Hultberg [*Ecol. Bull. (Stockholm)* **37**, 64 (1985)], G. Persson and O. Broberg [*ibid.* **37**, 10 (1985)] and O. Broberg [*Acta Univ. Ups.* **92**, 16 pp. (1987)] have shown that phosphorus yields from terrestrial watersheds decrease as a result of acidification. These authors hypothesize that the mechanism involves the binding of phosphorus to aluminum released from acidified soils.
48. R. W. Ogburn III, D. Breedlove and Associates, P. L. Brezonik, *Water Air Soil Pollut.* **30**, 1001 (1986).
49. P. J. Dillon, N. D. Yan, W. A. Scheider, N. Conroy [*Ergeb. Limnol.* **13**, 317 (1979)] found that the phosphorus-chlorophyll and phosphorus productivity relations in acidified lakes did not differ from those in circumneutral ones and that the relations did not change after lakes were limed. Schindler *et al.* (*43*), J. A. Shearer, E. J. Fee, E. DeBruyn and D. R. DeClercq [*Can. J. Fish. Aquat. Sci. Suppl. 1* **44**, 83 (1987)], and J. A. Shearer and E. R. DeBruyn [*Water Air Soil Pollut.* **30**, 695 (1986)] found no decreases in phytoplankton production or standing crops during the experimental acidification of two lakes with sulfuric acid and a third with nitric acid. B. Almer, W. Dickson, C. Ekström and E. Hörnström [in *Sulfur in the Environment*, J. Nriagu, Ed., Part II, *Ecological Impacts* (Wiley, New York, 1978)] reported similar observations. The higher transparency of acidified lakes, which early investigators assumed to be caused by reduced standing crops of phytoplankton, is instead due to decreased organic staining caused by precipitation of dissolved organic compounds with aluminum or to changes in the properties of dissolved organic matter [N. D. Yan, *Can. J. Fish. Aquat. Sci.* **40**, 621 (1983); S. W. Effler, G. C. Schafran, C. T. Driscoll, *ibid.* **42**, 1797 (1985); R. B. Davis, D. S. Anderson, F. Berge, *Nature (London)* **316**, 436 (1985); Shearer *et al.* (see above) and Shearer and DeBruyn (see above)]. The resulting increase in light penetration may affect thermal stratification enough to decrease habitat for cold-water species in summer [S. W. Effler and E. M. Owens, *J. Environ. Eng.* **111**, 822 (1985)]. However, M. A. Turner *et al.* [*Can. J. Fish. Aquat. Sci. Suppl. 1* **44**, 135 (1987)] found a slight decrease in net production of algae attached to rock substrates in three artificially acidified lakes. The decrease was attributed to limiting concentrations of dissolved inorganic carbon at low *p*H. The species composition of aquatic macrophytes is unaffected by acidification, but their biomass may increase [N. D. Yan, G. E. Miller, I. Wile, G. G. Hitchin, *Aquat. Bot.* **23**, 27 (1985); I. Wile, G. E. Miller, G. G. Hitchin, N. D. Yan, *Can. Field Nat.* **99**, 308 (1983)].
50. R. J. Hall, C. T. Driscoll, G. E. Likens, *Freshwater Biol.*, **18**, 17 (1987); P. J. Curtis, personal communication.
51. Reviewed in P. J. Dillon, N. D. Yan, H. H. Harvey, *CRS Crit. Rev. Environ. Control* **13**, 167 (1984); A. P. Altshuller and R. A. Linthurst, Eds., *The Acidic Deposition Phenomenon and Its Effects*, vol. 2, *Effects Sciences* (USEPA/600/8-83-016B, Washington, DC, 1984); P. M. Stokes, *Water Air Soil Pollut.* **30**, 421 (1986). See also Schindler *et al.* in (*43*) and D. L. Findlay and S. E. M. Kasian [*Water Air Soil Pollut.* **30**, 719 (1986)].
52. C. A. Kelly, J. W. M. Rudd, A. Furutani, and D. W. Schindler [*Limnol. Oceanogr.* **29**, 687 (1984)] found no decreases in oxygen or carbon metabolism in an experimentally acidified lake. S. S. Rao, A. A. Jarkovic, and J. O. Nriagu [*Environ. Pollut. Ser. A* **36**, 195 (1984)] found no differences in bacterial numbers between acid and circumneutral lakes, although the former exhibited an accumulation of organic material in sediments, suggesting lower decomposition rates. S. S. Rao and B. J. Dutka [*Hydrobiologia* **98**, 153 (1983)] found that acid-stressed softwater lakes north of Lake Superior contained fewer bacteria than nearby unstressed lakes. In some cases the accumulation of coarse organic matter on lake sediments may reflect the disappearance of macroinvertebrates which "shred" large particles, while overall carbon metabolism, which is dominated by microorganisms, is unimpeded. See discussion by Dillon *et al.* (*51*). Indeed, the increased temperatures observed in the depths of acidifying lakes caused by increased lake clarity [Yan in (*49*) and Effler and Owens in (*49*)] would be expected to enhance microbial decomposition. The increases in sulfate and nitrate which accompany acidification also enhance the activity of sulfate-reducing and denitrifying bacteria [R. B. Cook and D. W. Schindler, *Ecol. Bull. (Stockholm)* **35**, 115 (1983); J. W. M. Rudd *et al.*, *Limnol. Oceanogr.* **31**, 1267 (1986)].
53. P. M. Stokes, in *Effects of Acidic Precipitation on Benthos*, R. Singer, Ed. (Canterbury Press, New York, 1981), p. 119; see Stokes in (*51*); see Yan *et al.* in (*49*).
54. N. D. Yan, *Can. J. Fish. Aquat. Sci.* **43**, 788 (1986).
55. D. W. Sutcliffe and T. R. Carrick, *Freshwater Biol.* **3**, 437 (1973).
56. R. J. Hall and F. P. Ide, *Can. J. Fish. Aquat. Sci.*, in press. Streams that did not have severe spring *p*H depressions had no changes in species in the same time interval.
57. Such large *p*H depressions were not recorded in the earlier study reported in (*56*). Experimental additions of acid, or acid and aluminum, to streams show that the effects on insects include increased downstream drift and reduced ability of some species to move on water surfaces resulting from changes in surface tension caused by complexes of aluminum and dissolved organic carbon. The most sensitive reaches of streams are often headwaters where recolonization of invertebrates from upstream areas cannot occur. See R. J. Hall and G. E. Likens, *Can. J. Fish. Aquat. Sci.* **41**, 1132 (1985); R. J. Hall, C. T. Driscoll, G. E. Likens, J. M. Pratt, *Limnol. Oceanogr.* **30**, 212 (1985); Hall *et al.* in (*50*).
58. E. Engblom and P.-E. Lingdell, *Inst. Freshwater Res., Drottningholm Rep.* **61**, 60 (1984).
59. G. G. Raddum and A. Fjellheim, *Verh. Internat. Verein Limnol.* **22**, 1973 (1984).
60. Acid pulses commonly accompany the melting of acid snow, which has accumulated air pollutants all winter, or follow periods of prolonged drought, when acidic aerosols are solubilized and washed into lakes and streams. Records of the resulting fish kills go back to the first two decades of the century in Norway [I. Muniz in (*12a*), p. 299; Rosseland in (*43*)].
61. Concentrations as low as 0.1 to 0.2 mg liter^{-1} may be toxic in these forms. Reviewed by J. P. Baker, in R. G. Johnson, Ed., *Acid Rain/Fisheries* (American Fisheries Society, Bethesda, MD, 1982), p. 165; in Dillon *et al.* and USEPA in (*51*).
62. R. Playle, thesis, University of Manitoba (1985); M. Havas and G. E. Likens, *Can. J. Zool.* **63**, 1114 (1985); D. F. Malley and P. S. S. Chang, *Arch. Environ. Contam. Toxicol.* **14**, 739 (1985).
63. The terrestrial reactions which release aluminum are still not completely understood. See C. T. Driscoll, N. van Breeman, J. Mulder, *Soil Sci. Soc. Am. J.* **49**, 437 (1985) and D. K. Nordstrom and J. W. Ball, *Science* **232**, 54 (1986). The speciation of aluminum depends on both *p*H and concentrations of dissolved organic matter. See C. Driscoll, J. P. Baker, J. J. Bisogni, Jr., C. L. Schofield, *Nature (London)* **284**, 161 (1980). Both the form of aluminum present and its toxicity are dependent on concentrations of hydrogen ion, base cations, and duration of exposure [N. J. Hutchinson, K. E. Holtze, J. R. Munro, T. W. Pawson, *Ann. Soc. R. Zool. Belg. Suppl. 1* **117**, 201 (1987)]. The most devastating effect on fishes appears to be asphyxiation when polymeric and colloidal aluminum compounds physically obstruct gill function. In most waters this effect will be maximal at *p*H values of 5.2 to 5.4 [C. T. Driscoll *et al.* (see above)]; C. M. Neville, *Can. J. Fish. Aquat. Sci.* **42**, 2004 (1985)]. Aluminum appears to be an important factor in the mortality of brook trout during episodic events in Adirondack streams. Playle [in (*62*)] found that while exposure of caged *Pimephales* to aluminum and acid in situ resulted in 100% mortality, uncaged fish were able to avoid high-aluminum waters. Gunn and Noakes [in (*45*)] and R. J. Hall, G. E. Likens, S. B. Fiance, and G. R. Hendrey [*Ecology* **61**, 1976 (1980)] reported similar avoidance of high aluminum by brook trout.
64. Aluminum is sparingly soluble at such high *p*H values. Its effects are typically associated with episodic acid pulses such as those mentioned above. See Rosseland (*43*), Gunn (*44*), and Gunn and Keller (*45*).
65. In large watersheds with well-developed soils, terrestrial watersheds supply most of the acid-neutralizing capacity (ANC) of lakes. The degree of soil development has been shown to control the extent of acidification of Adirondack lakes [R. April and R. M. Newton, *Water Air Soil Pollut.* **26**, 373 (1985); C. T. Driscoll and R. M. Newton, *Environ. Sci. Technol.* **19**, 1018 (1985)]. The Integrated Lake-Watershed Acidification Study model of S. A. Gherini *et al.* [*Water Air Soil Pollut.* **26**, 425 (1985)] contains a module for in-lake processes; however, these processes are not measured directly.
66. In-lake generation of alkalinity has been observed for over half a century, so that its omission from acidification models is peculiar. For example, see S. Yoshimura, *Jpn. J. Geol. Geogr.* **9**, 61 (1931); C. H. Mortimer, *J. Ecol.* **29**, 280 (1941); *ibid.* **30**, 147 (1942); G. E. Hutchinson, *Ecol. Monogr.* **11**, 21 (1941). In particular, drainage lakes with small watersheds and thin, undeveloped acid soils or seepage lakes in unreactive geological settings receive little buffering from their watersheds, and much of their ANC is generated in situ. Most of the ANC is generated by microbial reduction of sulfate and nitrate [D. W. Schindler, R. Wagemann, R. B. Cook, T. Ruszczynski, J. Propkopwich, *Can. J. Fish. Aquat. Sci.* **37**, 342 (1980)], although some is also produced by exchange for base cations in surface sediments [R. B. Cook, C. A. Kelly, D. W. Schindler, M. A. Turner, *Limnol. Oceanogr.* **31**, 134 (1986); D. W. Schindler, M. A. Turner, M. P. Stainton, G. A. Linsey, *Science* **232**, 844 (1986); S. L. Schiff and R. F. Anderson, *Water Air Soil Pollut.* **31**, 941 (1986)]. The generation of ANC increases as the input of strong acid anion increases. See Cook and Schindler in (*52*); D. W. Schindler, in *Chemical Processes in Lakes*, W. Stumm, Ed. (Wiley, New York, 1985), pp. 225–250. Earlier, it was believed that sulfate reduction could only occur in lakes with anoxic hypolimnia. Recent work has shown that most ANC-generating activity occurs in the epilimnions of lakes [D. W. Schindler and M. A. Turner, *Water Air Soil Pollut.* **18**, 259 (1982); C. A. Kelly and J. W. M. Rudd, *Biogeochemistry* **1**, 63 (1984); Cook *et al.* (see above)].
67. The rates of sulfate and nitrate reduction are similar for lakes in several areas of the world [see Rudd *et al.* (*52*)]. Terrestrial and aquatic rates of alkalinity generation for a number of sites were reviewed by D. W. Schindler, *Water Air Soil Pollut.* **30**, 931 (1986).
68. Models based on sulfate and nitrate inputs, removal of these inputs to sediments, and water renewal allow the degree of buffering that results from retention of these two ions to be predicted rather precisely. L. A. Baker, P. L. Brezonik, C. D. Pollman, *Water Air Soil Pollut.* **31**, 89 (1986); C. A. Kelly *et al.*, *Biogeochemistry* **3**, 129 (1987). Models are nearly identical to those that have provided a successful basis for controlling eutrophication [R. A. Vollenweider, *Schweiz. Z. Hydrol.* **37**, 53 (1975)]. In-lake buffering processes are reviewed by D. W. Schindler [in (*66*)] and P. L. Brezonik, L. A. Baker, and T. E. Perry in *Sources and Fates of Aquatic Pollutants*, R. A. Hites and S. J. Eisenreich, Eds., *Adv. Chem. Ser.*; no. 216 (American Chemical Society, Washington, DC, 1987), pp. 229–260.
69. W. Keller and J. R. Pitblado, *Water Air Soil Pollut.* **29**, 285 (1986). In the 1960s and early 1970s, smelters in the Sudbury area emitted from 4000 to 7000 metric tons of SO_2 daily. From 1978 onward, values ranged from 1000 to slightly over 2000 tons per day.
70. T. C. Hutchinson and M. Havas, *Water Air Soil Pollut.* **28**, 319 (1986); W. Keller, J. R. Pitblado, N. I. Conroy, *ibid.* **31**, 765 (1986); P. J. Dillon, R. A. Reid, R. Girard, *ibid.*, p. 59. It will be several years before these systems reach a new steady state so that the total extent of recovery can be assessed.
71. D. W. Schindler, *Proceedings, CEC Conference on Reversibility of Acidification*, Grimstad, Norway, 9 to 11 June 1986. As of 1987, at a *p*H of 5.5, there has been no return of the two fish species eliminated from the lake. Chironomid communities still resemble those found at *p*H 5.0 (I. Davies, personal communication). The lake has been invaded by brook stickleback *Culaea inconstans* (K. Mills, personal communication).

72. N. D. Yan, personal communication.

73. H. J. MacIsaac, W. Keller, T. C. Hutchinson, N. D. Yan, *Water Air Soil Pollut.* **31**, 791 (1986).

74. W. Keller *et al.* [in (*70*)].

75. J. R. M. Kelso and D. S. Jeffries, *Can. J. Fish. Aquat. Sci.*, in press.

76. M. E. Thompson, *Water Air Soil Pollut.* **31**, 17 (1986).

77. See D. W. Schindler *et al.* in (*43*).

78. D. W. Johnson and D. D. Richter, Proceedings of the *Technical Association of Pulp and Paper Industry Research and Development Conference*, D. H. Alban, *Soil Sci. Soc. Am.* **46**, 853 (1982); S. I. Nilsson, H. G. Miller, J. D. Miller, *Oikos* **39**, 40 (1982). Soils are acidified naturally as plants grow, because they take up more base cations than strong acid anions. This would cause a charge imbalance in the plant if it did not export H^+ through the roots. Soluble, colored organic acids (humic and fulvic) are also formed as plants decompose in soil humic layers. These are generally precipitated in less acid, deeper soil horizons [W. H. McDowell and T. E. Wood, *Soil Sci.* **137**, 23 (1984)]. B. D. LaZerte and P. J. Dillon [Appleton, WI, 30 September to 3 October 1984. (Tappi Press, Atlanta, 1984), pp. 149–156. *Can. J. Fish. Aquat. Sci.* **41**, 1664 (1984)] showed that sulfate dominates the acidic anions in runoff from forested catchments on an annual basis, while organic acidity was of minor importance. However, where *Sphagnum* bogs predominate in the drainage basins of lakes or streams, organic acids alone can cause water to be acid. In such cases, deposition of inorganic acids causes further acidification [E. Gorham, J. K. Underwood, F. B. Martin, J. G. Ogden III, *Nature (London)* **324**, 451 (1986)].

79. I. T. Rosenquist, in *Advances in Environmental Science and Engineering*, J. R. Pfafflin and E. N. Ziegler, Eds. (Gordon & Breach, New York, 1980), vol. 3, pp. 56–79. However, Rosenquist erroneously assumed that the change in *p*H per unit acid received by an ecosystem would be linear, greatly underestimating the effect of strong acids on ecosystems, which are buffered by bicarbonate and other anions that are not linearly related to *p*H values. D. J. A. Brown and K. Sadler [*J. Appl. Ecol.* **18**, 433 (1981)] made the same error. These errors were illustrated by H. M. Seip and S. Rustad [*Water Air Soil Pollut.* **21**, 217 (1984)]. E. C. Krug and C. R. Frink [*Science* **221**, 520 (1983)] hypothesized that the sulfate falling with acid rain replaced natural organic acids exported from watersheds. If their hypothesis was correct, as anthropogenic inputs of sulfate are reduced soils should have produced a compensating amount of organic acid, thereby maintaining the *p*H of lakes. This did not happen. See also LaZerte and Dillon (*78*) and Dillon *et al.* (*35*).

80. R. B. Brugam and M. Lusk, in *Diatoms and Lake Acidity*, J. P. Smol, R. W. Battarbee, R. B. Davis, J. Merilainsen, Eds. (Junk, Dordrecht, Netherlands, 1986), pp. 115–129.

81. I. Renberg, *ibid.*, pp. 213–219.

82. G. E. Likens, F. H. Bormann, N. M. Johnson, D. W. Fisher, R. S. Pierce, *Ecol. Monogr.* **40**, 23 (1970); R. D. Fuller, C. T. Driscoll, G. B. Lawrence, S. C. Nodvin, *Nature (London)* **325**, 707 (1987); S. E. Bayley and D. W. Schindler, in (*82a*), pp. 531–548.

82a. T. C. Hutchinson and K. Meema, Eds., *Effects of Acidic Deposition on Forests, Wetlands, and Agricultural Ecosystems*, NATO ASI Series, vol. G16 (Springer-Verlag, New York, 1987).

83. See Gorham *et al.* in (*78*). E. Gorham, J. A. Janssens, G. W. Wheeler, P. H. Glaser, (*82a*), pp. 493–512. Reviewed by M. L. Jones, D. R. Marmorek, B. S. Reuber, P. J. McNamee, L. P. Rattie, *"Brown Waters"; Relative Importance of External and Internal Sources of Acidification on Catchment Biota* (Environmental Social Systems Analysts, Ltd., Toronto, 1986); B. D. LaZerte and P. J. Dillon in (*78*).

84. D. Drablos, I. Sevaldrud, J. A. Timberlid in (*19a*), pp. 354 and 367.

85. R. J. Flower and R. W. Battarbee, *Nature (London)* **305**, 130 (1983); R. W. Battarbee, R. J. Flower, A. C. Stevenson, B. Ripley, *ibid.* **314**, 350 (1985); S. Fritz *et al.*, in *Working Paper 16*, A. C. Stevenson and S. T. Patrick, Eds. (Geography Department, University College, London, 1987).

86. Six summary reports were commissioned between 1981 and 1984 by the U.S. Environmental Protection Agency, the National Academy of Sciences, the Office of Science and Technology Policy, and the Office of Technology Assessment. A recent comparison of these reports revealed that they agreed on almost all aspects of the acid precipitation problem. See Ad Hoc Committee on Acid Rain: "Science and policy, is there scientific consensus on acid rain?" (excerpts from six governmental reports) (Institute for Ecosystem Studies, Mary Flagler Cary Arboretum, Millbrook, NY, 1985).

87. Of several hundred small lakes surveyed by the author and his colleagues in northwestern Ontario, northern Manitoba, and Northwest Territories, less than 1% had *p*H values less than 5.5. Without exception, these were brown-water lakes with natural acidity caused by organic acids. Similarly, studies in the central and western United States and Canada [for example, Linthurst *et al.* in (*33*); Landers *et al.* in (*28*); J. M. Melack, J. L. Stoddard, C. A. Ochs, *Wat. Resour. Res.* **21**, 27 (1985)] have shown few lakes with low *p*H or low ratios of alkalinity to Ca^{2+} + Mg^{2+}. However, the proportion of naturally acidic waters in the maritime Canadian provinces is much higher. Most of these are strongly colored, implying that organic acids were responsible. They are exceptionally vulnerable to further acidification by acid rain [see Gorham *et al.* in (*78*)].

88. Reviewed by V. A. Mohnen and J. W. Wilson [in *Acid Deposition: Environmental, Economic and Policy Issues*, D. D. Adams and W. P. Page, Eds. (Plenum, New York, 1985), pp. 439–452]; E. B. Cowling in (*12a*), pp. 53–73. J. L. Schnoor, N. P. Nikolaidis, and G. E. Glass, [*J. Water Pollut. Contr. Fed.* **58**, 139 (1986)] proposed that a *p*H of 4.6 in precipitation is necessary to protect the most acid-sensitive lakes in the midwestern United States.

89. E. Gorham, F. B. Martin, J. T. Litzau, *Science* **225**, 407 (1985).

90. W. Dickson in (*12a*), pp. 267–273. A variety of unpublished estimates, all in the range from 9 to 20 kg ha^{-1} were summarized in "Proposed acid deposition standard and control plan: Statement of need and reasonableness" (Minnesota Pollution Control Agency, Minneapolis, 1985).

91. Summarized by the Minnesota Pollution Control Agency in (*90*). In one recent case, the gills of the minnow *Pimephales promelas* were shown to suffer damage in a lake experimentally acidified with 11 to 12 kg of SO_4^{2-} per hectare per year as H_2SO_4 [R. L. Leino, P. W. Wilkinson, J. G. Anderson, *Can. J. Fish. Aquat. Sci. Suppl. 1* **44**, 126 (1987)].

92. To date, the only standard that is similarly strict in North America was imposed by the State of Minnesota in 1986, after extensive hearings in a court of administrative law. See "Report of the administrative law judge." *Report PCA-85-002-AK, 6-2200-34-1* (Minnesota Pollution Control Agency, Minneapolis, 1986). At higher deposition values, we must be prepared for some loss of resources.

93. On a year-to-year basis, much of the acidifying effect of nitric acid is neutralized when NO_3^- is assimilated by plants or denitrified to N_2 (D. W. Schindler *et al.*, unpublished data). However, nitric acid is often quantitatively more important than sulfuric acid in causing acid pulses during snowmelt, when organisms are inactive as a result of low temperatures (J. N. Galloway and P. J. Dillon (*12a*), pp. 145–160. The molar ratio of NO_3 to SO_4^{2-} in snowpacks is often 2:1 in eastern North America [reviewed by P. W. Summers and L. A. Barrie, *Water Air Soil Pollut.* **30**, 275 (1986), and P. W. Summers, V. C. Bowersox, G. J. Stensland, *ibid.* **31**, 523 (1986)].

94. Ozone is currently estimated to cause losses of several billion dollars annually to U.S. agriculture and forestry. Reviewed by R. M. Adams, *Am. J. Agric. Econ.* **68**, 464 (May 1986).

95. Reviewed by National Academy Press (*7*); J. O. Nriagu, *Nature (London)* **279**, 409 (1979); P. G. Campbell, P. M. Stokes, J. N. Galloway, *Acid Deposition: Effects on Geochemical Cycling and Biological Availability of Trace Metals.* (National Academy Press, Washington, DC, 1985).

96. R. J. Lantzy and F. T. Mackenzie, *Geochim. Cosmochim. Acta* **43**, 511 (1979). Recently, increased concentrations of trace metals, sulfates, and nitrates have been found in the most remote areas of the Northern Hemisphere, in glaciers and lake sediments [for example, see P. A. Mayewski *et al.*, *Science* **232**, 975 (1986)]; R. C. Finkel and C. C. Langway, Jr., *J. Geophys. Res.* **91**, 9849 (1986); J. O. Nriagu and H. K. T. Wong, *Water Air Soil Pollut.* **31**, 999 (1986); M. G. Johnson, *Can. J. Fish. Aquat. Sci.* **44**, 3 (1987).

97. B. LaZerte, *Water Air Soil Pollut.* **31**, 569 (1986).

98. P. H. Santschi *et al.* [*Can. J. Fish. Aquat. Sci.* **43**, 60 (1986)] review the role of particles in removing trace metals from the water column. See also N. Arafat and J. O. Nriagu, *Water Air Soil Pollut.* **31**, 991 (1986); J. W. Murray, in *Sources and Fates of Aquatic Pollutants* (Advances in Chemistry Series, 216), R. A. Hites and S. J. Eisenreish, Eds. (American Chemical Society, Washington, DC, 1987), pp. 153–184.

99. D. W. Schindler, R. H. Hesslein, R. Wagemann, W. S. Broecker, *Can. J. Fish. Aquat. Sci.* **37**, 373 (1980); P. J. Dillon, H. R. Evans, P. J. Scholer, *Biogeochemistry*, in press.

100. As the *p*H of water decreases, the concentrations of a number of metals, some of them toxic, increase in fish and other aquatic organisms [S. A. Meger, *Water Air Soil Pollut.* **30**, 411 (1986); H. H. Harvey, G. A. Fraser, J. M. McArdle, *ibid.*, p. 515; R. L. France, *Can. J. Fish. Aquat. Sci.* **44**, 107 (1987)].

101. H. Hultberg and S. Johansson, *Nordic Hydrol.* **12**, 51 (1981); A. Henriksen and L. A. Kirkhusmo, *ibid* **13**, 183 (1982); USEPA in (*51*).

102. For example, concentrations of selenium are known to trigger blooms of foul-smelling *Chrysochromulina brevurrita* in acid lakes [J. D. Wehr and L. M. Brown, *Can. J. Fish. Aquat. Sci.* **42**, 1783 (1985)]. Chrysophycean species composition in acid lakes is also known to be sensitive to trace metals [S. S. Dixit, thesis, Queen's University, Kingston, Ontario (1986)]. The interactive effects of acid and aluminum were described earlier.

103. See MacDonald in (*7*); J. S. Gaffney, G. E. Streit, W. D. Spall, J. H. Hall, *Environ. Sci. Technol.* **21**, 519 (1987).

104. J. N. Woodman and E. B. Cowling, *Environ. Sci. Technol.* **21**, 120 (1987); also "Group Summary Report: Forest Decline" in (*82a*), pp 619–623; G. E. Likens, F. H. Bormann, P. S. Pierce, J. S. Eaton, N. M. Johnson, *Biogeochemistry of a Forested Ecosystem* (Springer-Verlag, New York, 1977); C. T. Driscoll and G. C. Schafran, *Nature (London)* **310**, 308 (1984); R. M. Klein and T. D. Perkens, *Ambio* **16**, 86 (1987).

105. See papers in (*82a*). Fogs polluted by anthropogenic contaminants may be an order of magnitude more acid than precipitation. Widespread occurrence and correlation of acid fogs with high sulfate and high ozone episodes have only recently been noticed. Effects seem to be increased still more by evaporation, and direct damage to plants may occur. K. C. Weathers *et al.*, *Nature (London)* **319**, 657 (1986); M. H. Unsworth, *ibid.* **312**, 262 (1984).

106. One of the most remarkable demonstrations of long-range atmospheric transport has been the discovery that detectable pollution of the North American arctic occurs from pollutants originating in Eurasia. While "arctic haze" has been known for 30 years, it was not until the late 1970s that scientists linked it to man-made air pollutants. The arctic-haze problem is largely confined to winter, when a persistent high-pressure region over Siberia causes strong airflow from populated areas of northern Eurasia into the Arctic. This polluted arctic air mass may extend as far south as the U.S.–Canadian border in midwinter. At the same time, prevailing winds carry North American pollutants over the North Atlantic. Remarkably, the source regions for the aerosols causing arctic haze can be identified by matching the ratios of trace metals in the aerosols to those emitted from burning the fuels of various source regions. Numerous gaseous pollutants and pesticides carried by long-range transport have also been identified in polar regions. Many of these are known to enhance the greenhouse effect [see MacDonald in (*7*)]. They have also more than doubled the ionic strength of ice deposited in the Arctic in the past 30 years. The scattering of light by the aerosols clearly has an important effect on visibility, and the nucleation of ice crystals by aerosols may have an additional effect. Soot-laden aerosols may also increase the blackness of the snowpack, causing decreases in albedo of 1 to 10%. This has considerable potential for climatic effects. Because effects tend to increase with snowmelt, they could intensify any spring-melt acid pulse. Fortunately, so far,

there are no documented cases of dangerously acidic precipitation from the high Arctic, but the effects of air pollutants may be particularly serious in the Arctic in the decades ahead [see the review by L. A. Barrie, *Atmos. Environ.* **20**, 643 (1986)]. The role of sulfate aerosols in reducing visibility at temperate latitudes is reviewed by J. Trijonis, in (*26a*), chap. 4.
107. F. H. Bormann and G. E. Likens, *Bioscience* **37**, 370 (1987).
108. For this review, a number of scientists contributed prepublication copies of their recent work or advice on recent publications. These include C. Asbury, L. A. Barrie, F. H. Bormann, P. Brezonik, D. F. Charles, R. B. Cook, C. S. Cronan, P. J. Dillon, F. Elder, J. N. Galloway, E. Gorham, R. J. Hall, N. J. Hutchinson, D. Jeffries, D. Landers, G. E. Likens, R. A. Linthurst, K. H. Mills, J. Nriagu, J. P. Smol, M. E. Thompson, K. Webster, D. Whelpdale, and R. F. Wright. The manuscript was critically reviewed by L. A. Barrie, P. Brezonik, D. Charles, R. Cook, P. J. Dillon, F. Elder, J. N. Galloway, E. Gorham, R. J. Hall, R. E. Hecky, R. H. Hesslein, K. H. Mills, M. A. Turner, and D. Whelpdale. D. S. Jeffries also provided Fig. 1. E. Marshall provided invaluable assistance with the bibliography and D. Laroque assisted in keeping the manuscript updated. Supported by the Canadian Department of Fisheries and Oceans.

Infrared Laser Spectroscopy of Molecular Ions

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The development of new techniques for infrared laser spectroscopy of molecular ions has resulted in an explosion of high-quality data for important charged molecules. Velocity modulation laser spectroscopy, which exploits the motions of charged particles in electrical plasmas to eliminate interference from neutral absorbers, is rapidly producing a large body of new results for both positive and negative molecular ions. This information will have an important impact on chemistry, biology, and astrophysics.

THE STRUCTURES, PROPERTIES, AND DYNAMICS OF charged molecules are of substantial contemporary interest because of their crucial roles in such diverse and timely contexts as plasma processing of semiconductor devices, electron and proton transfer in biological systems, the formation and evolution of stars and planetary systems from interstellar dust clouds, and the chemistry and physics of planetary atmospheres. Although perhaps not seeming to be qualitatively different from their neutral counterparts, molecular ions do, in fact, present a unique set of difficult challenges to both theoreticians and experimentalists. As a consequence, it is only recently that these species have become amenable to detailed investigations. Technological innovations, such as the development of tunable infrared lasers and the explosion of large-scale computer technology, have certainly been necessary ingredients for this surge of progress, but new intellectual advances have actually been the seminal elements in the "molecular ion revolution."

In his *Science* article (*1*) entitled "Methylene: A paradigm for computational quantum chemistry," H. F. Schaefer described the recent advances made in ab initio quantum chemistry that have resulted in the availability of accurate and reliable theoretical predictions to guide the design and interpretation of molecular ion spectroscopy experiments. The principal impediment to experimental investigations of molecular ion spectra is simply the difficulty of obtaining sufficient concentrations to produce a detectable interaction with electromagnetic radiation. This difficulty is the result of both the inherently high chemical reactivity of charged molecules and the elementary fact that like charges repel each other. The problems associated with producing detectable concentrations of ions have limited the spectroscopic information previously available to either optical emission spectra, which were obtained for a variety of diatomic and a few polyatomic ions, or to infrared spectra measured in highly perturbative condensed-phase environments. High-resolution techniques, such as microwave and infrared laser spectroscopy, which yield far more detailed information for individual unperturbed molecules in the gas phase (the distribution of electrons in a molecule, precise molecular geometries, and barriers to internal motions, for example) were considered inapplicable to this entire class of molecules. Even more serious was the fact that the molecular ions of greatest importance possess closed electron shells, and do not exhibit accessible electronic spectra. Then, nearly 15 years ago, two independent experimental breakthroughs occurred that dramatically changed this situation and began the molecular ion revolution.

One of these experiments, carried out by Wing and co-workers (*2*), combined infrared laser excitation of a velocity-tuned ion beam with sensitive mass spectroscopic detection of the ions themselves to indirectly measure the vibration-rotation spectrum of a few very simple ions (HD^+, HeH^+, and D_3^+) with extreme precision. Because the concentration of ions in such a beam is so small, the effects of the infrared radiation were detected by monitoring changes induced in the ion current that resulted when ions transferring their charge through collisions with a buffer gas underwent vibrational transitions. This indirect (mass spectrometric) approach has since been developed by Carrington, Moseley, and others into a general technique for measuring spectra of molecular ions in the ultraviolet-visible region as well as in the infrared. A considerable body of interesting structural and dynamical information has been obtained as a result of this important development.

Woods and co-workers (*3*) pioneered the other major experimental breakthrough somewhat earlier by directly measuring rotational absorption spectra of a series of simple ions (CO^+, HCO^+, and HNN^+) generated in an electrical discharge. By overcoming the technical problems associated with using such violent means to produce the ions, spectroscopists could take advantage of the high concentrations of ions that exist in electrical discharges because of the mutual shielding effects of electrons and ions. Direct absorption spectroscopy of several kinds of laboratory plasmas has subsequently been used for studies of many molecular ions in the microwave, infrared, and visible regions.

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