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by

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Recent research has resolved many of the controversies which clouded the acid rain problem five years ago. In this presentation I briefly review what I consider to be the key aquatic issues which have been resolved.

The Extent and Severity of the Acid Rain Problem

Surveys have revealed large areas of acid-sensitive waters on all major continents. In such acid-sensitive areas, acid rain has been reported from Brazil, South Africa, China, the U.S.S.R., and most European countries. In North America, parts of the west are also known to be acid sensitive, although acid precipitation is restricted to a few areas downwind from major urban and industrial areas (1).

Most studies of the degree of acidification of lakes and streams have been done in eastern North America, Scandinavia and the northern U.K. Four major approaches have been taken: analysis of long-term trends, 2) comparison of recent and historical data sets, 3) paleoecological studies, and 4) ionic balances.

Trustworthy long-term data sets, using well-calibrated, comparable collection methods, are very scarce. There are a few, nevertheless. The U.S. National Academy of Sciences (2) found two such data sets in acid-sensitive areas of the U.S. collected by the U.S. Geological Survey. Both showed that acidification had occurred.

In addition to the above, there are a few convincing long-term data sets in Canada. The Ontario Ministry of Environment has recorded a decline in the alkalinity of Plastic Lake, in the Muskoka area, for six consecutive years (3). Good records are available for several Nova Scotia rivers (4), and rivers known to have acidified have well-documented declines in the Atlantic salmon fishery (5), very similar to those observed in Scandinavia (6).

The Sudbury and LaCloche areas of Ontario have suffered well known declines in pH and fisheries, with 388 fish populations lost from 50 surveyed lakes. Similar observations have recently been published for the Wawa area of northern Ontario (4).

Several recent studies have shown ways in which older chemical methods can be verified (8) or reproduced (9). In the U.S., these have shown widespread acidification in the Adirondacks, in some cases in New England, and no acidification in Wisconsin (2).

Where paleoecological methods have been used to reproduce historical pH  $th_0 \le e^{-f}$  records from fossil diatoms, results agree very well with the above methods (2).

The ionic ratio method of detecting acidification, best illustrated by Henriksen (10), is based on the assumption that in the absence of acidification, natural waters will have a ratio of  $\frac{\text{alkalinity}}{\text{Ca} + \text{Mg}}$ 

(in equivalents) of approximately 1.0. Several surveys of softwater lakes in the western U.S., Canada, and northern Scandinavia overwhelmingly verify this assumption (11). In areas affected by acid rain, inputs of strong acids would be expected to deplete the alkalinity, and perhaps to increase the Ca + Mg slightly by enhancing geochemical weathering and ion-exchange processes. As a result, the alkalinity/Ca + Mg ratio is expected to decrease in waters damaged by acid rain. A map of eastern North America shows vast tracts where the ratio in acid-sensitive freshwaters averages less than 0.6, and considerable areas where the average is 0.2 or less (Figure 1). It is noteworthy that the shape of affected areas conforms rather nicely to that of sulfate deposition patterns.

Fortunately, lakes are seldom as acid as the precipitation falling into them, or the effects of acid rain would be far more disastrous than they have been. Until recently, it has been assumed that the mechanisms causing this partial neutralization occurred solely in the terrestrial landscape, and that lakes would acidify once geological buffering materials had been depleted (12). However, we now know that in the most sensitive of acid-vulnerable systems, buffering within the lake is likely to exceed that occurring in terrestrial watersheds. Most of the buffering is by biological rather than geochemical reactions, and it is enhanced, not depleted, by acidification (12). Unfortunately, no lakes are 100% efficient at neutralizing incoming acid, so that acidification occurs, but at rates slower than expected in the absence of these internal mechanisms. Very recently, it has been shown that the rate of acidification is predictable using models which are practically identical to those which have allowed the eutrophication problem to be controlled (13).

It is noteworthy in view of Dr. Rosenquist's paper that even in pristine acid-sensitive areas of northern and western Canada, where lakes have suffered no detectable increases in acidity, the soils are acid podzols and the runoff from such podzols is typically acidic. In brief, in pristine areas, most clearwater

lakes have circumneutral pH values, even though terrestrial basins have acidic soils, while in acidified areas of Canada there are acid lakes in basins with acidic soils. The relative role of natural organic acids and strong acids from the atmosphere in acidifying lakes was compared in Nova Scotia by Gorham et al. (14). Their conclusions were as follows: In agreement with Prof. Rosenquist, they found that organic acids from watersheds strongly influenced the acidity of lakes in base-poor geological substrates. The maximum predicted effect of organic acids was a decrease of 1 pH unit - a large amount when without organic acids the pH would be only about 6.0, as I shall discuss later.

However, in addition to the natural background of organic acids, strong acids from atmospheric deposition had an extremely clear effect, causing further acidification of Nova Scotia lakes. In brief, it is clear that organic acids do play a role in natural lake acidification. But strong acids from the atmosphere have a very large additional effect. For 234 Nova Scotian lakes, organic anions averaged 49  $\mu$ eq L<sup>-1</sup> and SO<sub>4</sub> 60  $\mu$ eq L<sup>-1</sup>, giving an idea of the average importance of these organic and strong acids. Near large power plants, the relative importance of SO<sub>4</sub> increased even more, reaching values over 150  $\mu$ eq L<sup>-1</sup> (Figure 2).

Data from several other types of studies are inconsistent with the hypothesis that land-use plays a major role in the acidification of freshwaters. Firstly, the vast region of eastern Canada where low ratios of alkalinity/Ca + Mg indicate extreme acidification contains many thousands of lake basins where there have been no land-use changes. Secondly, many paleoecological studies have shown that the timing of acidification is consistent with an increase in acid rain, but not with changes in land use (15). Thirdly, studies in Norway have shown that lakes in watersheds

subjected to land-use had acidified at rates similar to those observed in unmodified watersheds (16). Fourthly, studies of clearcutting and forest fire have shown that nitrification and oxidation of reduced sulfur in watersheds more than balance the expected increase in alkalinity from these perturbations, i.e. the effect is the opposite of that hypothesized (17). Finally, an error in calculation caused some early proponents of the land use hypothesis to overestimate its effect, by assuming that the change in pH per unit strong acid would be linear, rather than the known sigmoid shape of an alkalinity titration curve (18).

This is not to say that land use has no effect. Draining of peatlands or other areas where reduced sulfur has been stored in organic deposits, or mining of sulfide deposits, clearly acidify receiving waters (19). However, such areas are a small proportion of the regions where lake acidification problems have occurred.

We now know that the biological damage due to acid rain has been greatly underestimated. Until recently, it was assumed that freshwaters were not biologically damaged until their pH values decreased below 5.0 to 5.3

We new know that softwater lakes with lower pH support fewer species of organisms than those with higher pH values, regardless of whether the low pH is natural or caused by acid precipitation (Figure 3). It follows that there is no threshold for biological damage; any increase in acidity will cause some degree of biotic impoverishment.

Among the most sensitive groups are Molluscs and benthic crustaceans, mayflies (Ephemeroptera), stoneflies (Plecoptera), and many minnows (cyprinids). Dramatic decreases in the species of these and some other groups begin to occur at pH values of 6.0 or greater (20). Whereas five years ago the destruction of these species was not believed to have a great effect upon

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the sport fishes which are the primary concern of most fishermen, several recent studies have shown that the starvation caused elimination of organisms from the food chain may be an important factor in depleting populations of sport fish (21, Figure 4). We also know that recruitment failure occurs much earlier in the acidification process than harm to adult fish, yet most surveys of fisheries damage have not assessed juvenile stages. The net result of these findings is that it is clear that lakes are harmed far earlier in the acidification process than we believed five years ago.

We have also confirmed that once acidifying inputs are decreased, lakes become less acid very quickly. Emissions of  $\mathrm{SO}_2$  in the Sudbury area have decreased to about 30% of values in the early 1970's. The acidity and sulfate of lakes has decreased correspondingly, at rates predictable from water renewal (22, Figure 5). In some cases, the recovery of lakes has been enough to allow reproduction of fish to resume, or at least for them to be successfully restocked (23). Concentrations of toxic trace metals have also decreased.

However, it seems unlikely that complete biological recoveries can occur without restocking. Some of the most sensitive species, such as molluscs and benthic crustaceans, have poor powers of dispersal, and it is unlikely that they can reinvade most of the waters from which they have been eliminated. In experimentally-acidified Lake 223, lake trout have not resumed recruitment, even though the pH of the lake has been raised to 5.6, a value at which reproduction took place prior to acidification (22). It thus appears that partial, but not complete biological recovery of lakes may result from decreased emission of SO<sub>2</sub>.

Several recent studies have directly addressed the problem of setting limits which will protect aquatic ecosystems to acid deposition . Obviously,

the only way to protect all aquatic ecosystems would be to eliminate anthropogenic sulfur emissions completely, for many lakes have biotas restricted to some degree by pH, even under pristine conditions. It is unlikely that society would accept this alternative.

Several studies suggest that deposition, measured as wet sulfate, of 9 to  $14 \text{ kg ha}^{-1} \text{ yr}^{-1}$  would protect most aquatic ecosystems. For example, note that on Figure 1, the area of decreased bicarbonate is almost totally in regions where deposition exceeds  $10 \text{ kg ha}^{-1} \text{ yr}^{-1}$ . Gorham et al. (24) deduced from the chemistry of precipitation that a standard of  $14 \text{ kg ha}^{-1} \text{ yr}^{-1}$  is likely to protect most lakes in the eastern U.S. Our studies of a lake which receives an artificial input of  $11 \text{ kg ha}^{-1} \text{ yr}^{-1}$  show that the only detectable biological effects are changes in phytoplankton species and gill damage in fathead minnows (25). In Scandinavia, no detectable acidification of lakes occurs where deposition (corrected for sea salts) is less than  $9 \text{ kg ha}^{-1} \text{ yr}^{-1}$  (26). These studies have already inspired the State of Minnesota to set a deposition standard of  $11 \text{ kg } \text{SO}_4 \text{ ha}^{-1} \text{ yr}^{-1}$  to protect its acid-sensitive ecosystems.

We have often heard the argument that we do not know enough to regulate acid precipitation. Certainly, we do not know all facets of the acid rain problem, for scientific knowledge is never complete. Still, there is consensus among at least 95% of scientists on major acid rain issues (27). In the past, we have regulated most pollutants based on far less evidence - for example, the regulation of phosphorus, based on relatively few field studies, allowed the rapid recovery of lakes from eutrophication (28), and the control of pesticides allowed the rapid recovery of fish-eating birds (29). While most recent environmental legislation has been based on little more than intelligent guesses, the proportion of successes is far higher than that of failures.

The lack of controls on acid rain is thus clearly for political, and not scientific reasons. Perhaps the recently illustrated success of reducing  $\rm SO_2$  emissions in Ontario will cause politicians to develop some spine, for substantial improvements in many ecosystems should occur within a couple of terms in office!

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## List of Figures

- Figure 1. A map of the ratio ANC/Ca + Mg, where ANC is acid neutralizing capacity (= alkalinity). Values less tha 0.6 indicate moderate depletion of alkalinity by acidification, while values less than 0.2 indicate extreme depletion. From Schindler (Science, in press).
- Figure 2. Decline of lakewater  $SO_4^{2-}$  outward from the Halifax-Dartmouth power plant in Nova Scotia. After Gorham et al. (14).
- Figure 3. The relative frequency of various freshwater taxa as a function of pH. From Mills and Schindler ( $10^{20}$ ).
- Figure 4. Changes in several parameters in Lake 223 during acidification, including comparisons with pristine reference lakes in the area when this was possible. (A) Changes in the relative abundance of major phytoplankton groups and in small phytoplankton (species less than 30 µm in maximum dimension; roughly the size edible by zooplankton) in the epilimnion prior to and during acidification. Data shown are averages for the ice-free season. More detailed seasonal information on species composition and actual abundance is given in the test. (B) Phytoplankton production in the euphotic zone compared to several control lakes. Values in this and several subsequent panels are normalized to both control lakes and long-term means as described in (1861). Vertical bars represent single standard deviations for the normalized annual means of all reference lakes. (C) Epilimnion phytoplankton biomass, normalized as in panel B. (D) Epilimnion chlorophyll a compared to control lakes as in panel C. (E) Emerging dipterans caught by transparent submerged funnel traps in Lake 223 and in unacidified Lake 226S.

Values are morphometrically corrected averages calculated annually from catches of 8 to 27 emergence traps per lake, monitored weekly during the ice-free season. (F) Changes in relative biomass of zooplankton groups in the whole water column during the study period (except 1975 and 1976). Note the increases in Rotifera and Cladocera, and the steady or declining contribution of Cyclopoida and Calanoida. Mean ice-free season zooplankton biomass was 261  ${\rm mg~m}^{-2}$  in 1974, 413  ${\rm mg~m}^{-2}$  in 1980, and 250-384  ${\rm mg~m}^{-2}$  in the 1981-1983 period. (G) The condition index for lake trout in Lake 233 and unmodified Lake 224, illustrating an initial increase in condition, followed by a dramatic decline during acidification. Condition =  $10^5$  w/l  $^3$ m where w is weight and l is fork length. A similar increase was observed in condition of Lake 223 white sucker in the first few years, but the decline after that date was not as pronounced as for lake trout. Vertical bars are 95 percent confidence limits. (H) The populations of crayfish (Orconectes virilis) and slimy sculpin (Cottus cognatus) during acidification, derived from areal counts done by scuba divers at night. Counts were made along eight transects and were stratified by depth and habitat type. Dashed lines indicate 95 percent confidence limits for population estimates. (I) Relative population size structure of fathead minnow (Pimephales promelas) during acidification. Numbers are from trapnet catches. The scarcity of new recruits in 1979 led to a total population collapse 2 years later. Note the difference in scale for the 2 years. Crosshatched bars represent 1978; and open bars represent 1979. (J) The concentration of soluble silicate in Lake 223,

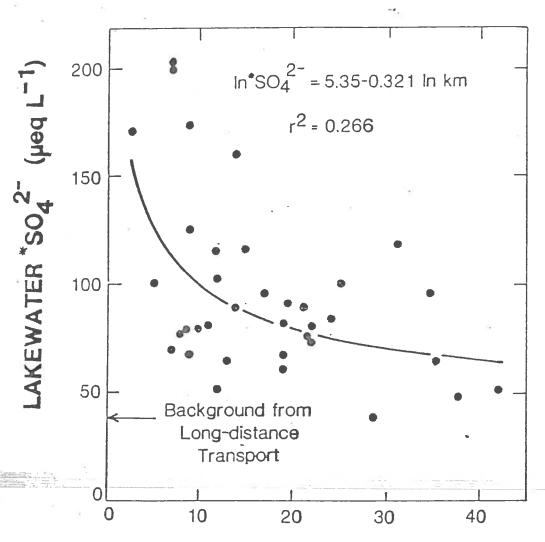
normalized as described in (44). (K) Relative population size structure of pearl dace (Semotilus margarita). Numbers are from trapnet catches. Note the high recruitment in 1980 as Pimephales declined, followed by recruitment failure in Semotilus by 1982, at lower pH. Crosshatched bars represent 1980: clear bars 1982. (L) Simpson's diversity index calculated over time for phytoplankton species in Lake 223 Samples were taken every 2 to 3 weeks.



Figure 5. Observed reductions in sulfate in lakes near Sudbury, Ontario following reductions in  ${\rm SO}_2$  emissions. The predicted values are those expected due to flushing of the lakes by water renewal.

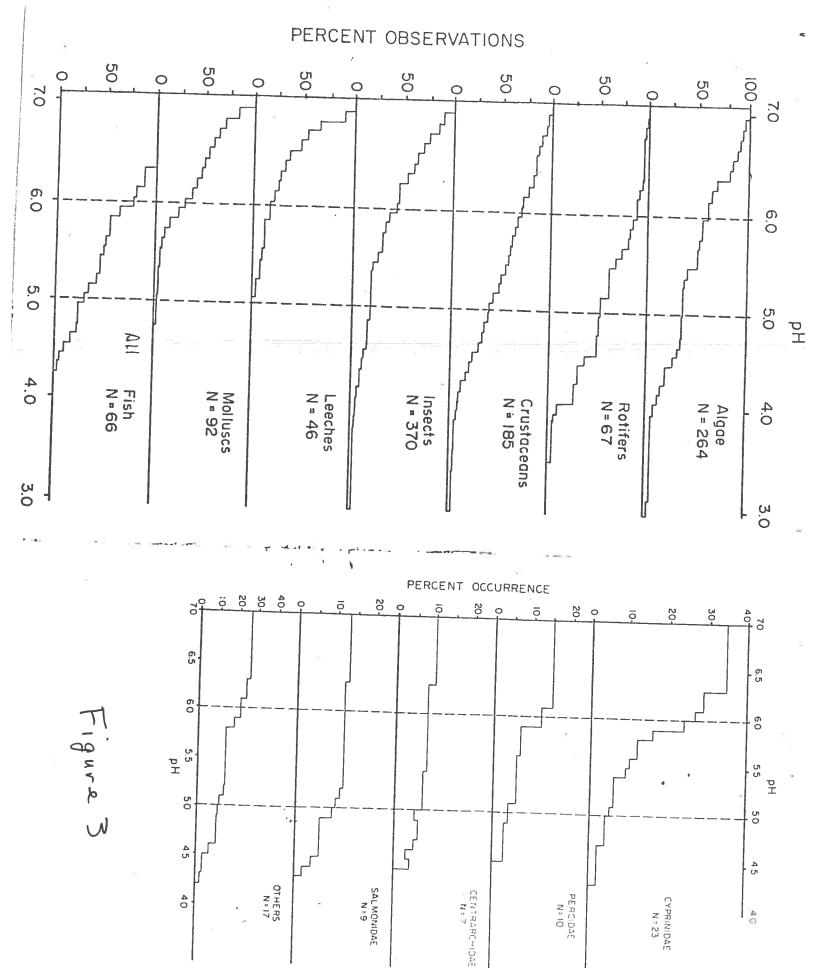


Figur 1



DISTANCE FROM POWER PLANT (km)

Fig. 2. Decline of lakewater  $*SO_4^{2-}$  outward from the Halifax-Dartmouth power plant (n=36, rejecting one outlier).



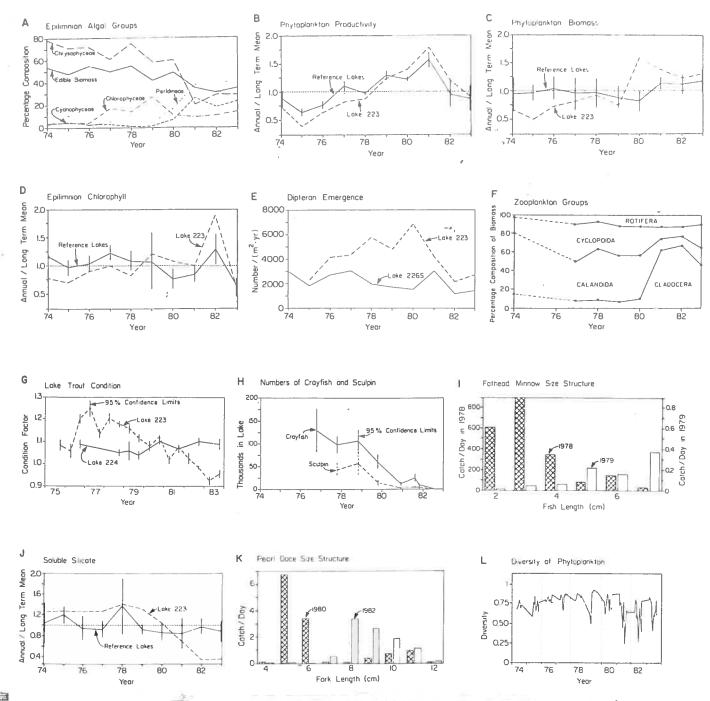


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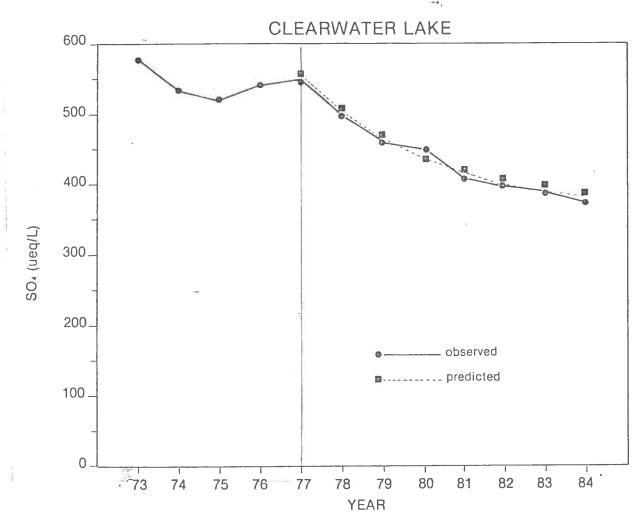
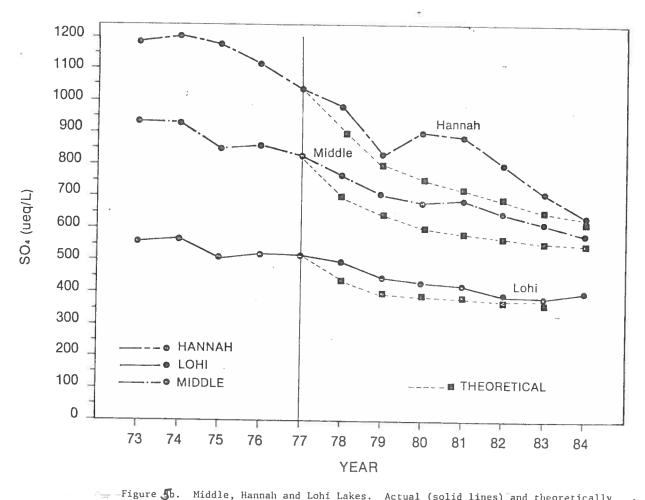


Figure **5**a. Clearwater Lake. Actual (solid lines) and theoretically predicted (dotted lines, equation 1) reductions in sulfate in lakes near Sudbury. Predictions were made from 1976 onward. Figures modified from Dillon et al. (1986). Water renewal times used in equation 1 from Scheider (1984).



Middle, Hannah and Lohi Lakes. Actual (solid lines) and theoretically predicted (dotted lines, equation 1) reductions in sulfate in lakes near Sudbury. Predictions were made from 1976 onward. Figures modified from Dillon et al. (1986). Water renewal times used in equation 1 from Scheider (1984).