OVERVIEW OF HISTORICAL AND PALEOECOLOGICAL STUDIES OF ACIDIC AIR POLLUTION AND ITS EFFECTS

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ABSTRACT. Historical evidence of acid deposition and its effects which was presented at Muskoka, Ontario in September, 1985 is summarized. This evidence consists of written records of the past chemistry and biology of atmospheric, terrestrial, and aquatic systems; it also includes evidence from archived collections which were "revisited", from tree rings, and from the chemical and biological "records" in lake sediment and peat from which histories of airborne contaminants and ecosystem responses to these contaminants were inferred.

1. INTRODUCTION

Historical and paleoecological studies have contributed significantly to our understanding of acidic precipitation and its effects. In this overview, we give selected highlights of the papers that were included in the section on "Historical Perspectives of Acidification" at the International Symposium on Acidic Precipitation in Muskoka, Ontario in 1985.

2. FOREST DAMAGE

Johnson (1986) describes the widespread red spruce decline in northeastern United States since ca. 1960 and analyzes its possible causes. He also presents historical information on red spruce declines in the 1870's and 1880's. Air pollutant concentrations were certainly

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very much lower in 1870-1890 than since 1960, and he argues that pollutants were not the cause of the early declines but that natural causes were. As the causes of the post-1960 decline have not definitely been shown to be anthropogenic, Johnson's finding of earlier, natural declines strengthens the argument that natural factors, if not solely responsible, could at least be having an amplifying effect. By study of affected populations, climatic records, and tree rings, he shows that the recent decline could be a function of anomalously cold winter and spring weather. He argues that while there is a correlation between the recent decline and high concentrations of air pollutants, particularly at high elevation, it is unlikely that pollutants alone are responsible for so widespread a phenomenon.

3. FISHES, OTHER AQUATIC BIOTA, AND WATER CHEMISTRY

Haines and Baker (1986) review historical fisheries and pH data for lakes in certain areas of the United States east of the Great Lakes, and find that the Adirondack Mts., New York, data set remains the strongest for evaluating the role of acidification in decline of fisheries. These authors systematically evaluate alternative explanations for the decline and conclude that acidification is the most likely cause. Fisheries declines associated with acidity have also been found in Pennsylvania and Massachusetts, but the quality and/or quantity of the data are lower than in the Adirondacks. Data from New Hampshire and Vermont suggest limited effects on fisheries, and for Maine no effects have yet been demonstrated.

Losses of fish populations in southern Norway are documented by Sevaldrud and Skogheim (1986), based on interviews. Interview results held up well for reliability when checked by test fishing at a subsample of lakes. These authors report that pre-1978 trends of declining brown trout and perch populations have continued in 1983. Lakes with decreased or exterminated populations of either species had lower Ca concentrations, lower pH, and higher labile Al concentrations than lakes whose populations remained unchanged between 1978 and 1983.

Leuven _et al._ (1986) report that at least 67% of the Netherlands' lentic soft waters (<1 meq L^{-1}) have been acidified. This conclusion is based on historical chemical and biological data, inference from water chemistry models of acidification, and paleoecological studies. These authors report losses of fish stocks in the soft waters, based on historical records and on inference from the present distributions of fishes and water chemistry.

Stewart _et al._ (1986) review the evidence for loss of fisheries in Ontario lakes. The authors demonstrate loss of fisheries that are apparently related to large point sources of acidifying emissions such as Sudbury. Stewart _et al._ (1986) find only one Ontario lake where acidification is not related to such a point source. This lake, located in the south-central part of the province, shows evidence of fishery loss apparently resulting from acidification by regional acid deposition. The authors stress that the finding of only one such site may be due to inadequate data. Evidence for decreased quality of spawning habitat for lake trout, in terms of increased episodic pH depression and increased Al is presented for sites both near to and distant from large point sources.

By a comparison of invertebrates found in 1937-1942 with those found in 1984 in the same Ontario streams, Hall and Findeis (1985) inferred that water acidification had taken place there. Acid sensitive species such as certain mayflies, stoneflies and caddisflies had "disappeared" from streams that in 1984 experienced strong pH depressions (to pH 4.9) but the species were still present in streams whose pH remained $\geq$6.0.

4. CHEMISTRY OF LAKE SEDIMENT AND PEAT

Norton (1986) discusses the chemical record of air contaminants in lake sediments and attempts to link this record to air pollution history and the acidification of lake water. He demonstrates the difficulties in making these linkages. The stratigraphy of airborne contaminants in lake sediments cannot be interpreted simply as a direct quantitative chronologic record of atmospheric deposition on the lake. The sedimentary record reflects, in addition to direct atmospheric loading, effects of the terrestrial watershed in "processing" deposits from the atmosphere (affecting fluxes to the lake), variable distributions of sediment constituents within the lake, and post-depositional modifications of the sediments. Norton shows that it is possible to strengthen the interpretation of the chemical sedimentary record in terms of airborne contaminants and their effect by the analysis of multiple sedimentary components in the same core, and by sorting through multiple working hypotheses to explain correlated changes.

Stratigraphic records of S in lake sediments in the Adirondacks, northern New England, northern Great Lake States, and northern Florida were described by Mitchell et al. (1985). The data were collected as part of the Paleoecological Investigation of Recent Lake Acidification (PIRLA) Project (Charles et al., 1986). Sulfur concentrations and accumulation rates in pre-1900 sediment are similar in all regions. Sulfur enrichment of post-1900 compared to pre-1900 sediment was observed in the four regions. Enrichment factors greater than 2 were most consistently found in the Adirondacks, as would be predicted from patterns of atmospheric deposition (Altwicker and Johannes, 1985). Stratigraphic patterns were most difficult to interpret in the Florida lakes. There and elsewhere, the use of sedimentary stratigraphy of S as a chronologic record of deposition of atmospheric S must be approached with great caution because of confounding factors including diagenesis and mobility of S in sediments. This problem is also discussed by Norton (1986).

The widespread increase of Hg starting in sediment dated at mid- to late- 1800's, such as that reported by Megar (1986) for northern Minnesota, supports the belief that long range atmospheric transport of

Hg has resulted in contamination of sediments and watersheds remote from point sources. Megar also proposes that acidic precipitation could enhance the transport of Hg from lake watersheds. Increases since 1800 of several other elements associated with acidic precipitation and other air pollution complexes are estimated by peat stratigraphic study in the Appalachians by Schell et al. (1986). In Pennsylvania, enrichment factors greater than 100 are reported for Cl, N and S, and 10 to 40 for Pb, Br, Ca and Sb.

Increases of certain trace metals including Pb and Zn start in lake sediment dating to the mid- to late-1800's in northern New England and the Adirondacks (Norton, 1986). In the upper part of sediment profiles in acidic (pH $\leqslant$ 5.5) lakes, Zn accumulation rates decrease as a result of increased leaching due to acidification and/or sediment diagenesis. Decreases in sedimentary accumulations of Ca and Mn relative to Ti probably result from increased leaching of Ca and Mn by acidified waters. Accumulation rates of V start increasing in sediment dating 1920-1940, reflecting the upswing in fuel oil consumption.

5. RECONSTRUCTION OF LAKE pH BY ANALYSIS OF SEDIMENTARY REMAINS OF DIATOMS

Battarbee and Charles (1986) describe pH reconstructions based on diatoms from Scotland, Scandinavia, continental Europe, Canada and U.S.A., and demonstrate that acidification, probably due to acidified precipitation, has occurred in certain lakes in all these regions. Geographic distributions of the lakes shown to have been acidified and the chronology of acidification in these lakes are consistent with geographic patterns of precipitation chemistry and with what is known of the history of acidic emissions. The authors point out that the diatom technique is still the only reliable one for accomplishing detailed reconstruction of lake pH. Charles et al. (1986) imply that sedimentary remains of silica-scaled chrysophytes may soon be used for this purpose, and Norton (1986) indicates that sediment chemistry can be used for inferring the crossing of certain pH thresholds.

Taylor and Duthie (1986) indicate a relationship between (1) abundance of sedimentary remains of the diatoms *Cyclotella stelligera* and *C. kutzingiana* and (2) depth of shield lakes in Ontario, but no relationship with pH. In other geographic regions, investigators have found relationships between the distributions of these species and pH and have used the species for paleolimnologic reconstruction of pH. Taylor and Duthie's (1986) results demonstrate that the extrapolation of diatom pH calibrations from one region to another for use in reconstruction of lake pH is a risky procedure.

6. PRECIPITATION CHEMISTRY

Altwicker and Johannes (1985) characterized the differences in precipitation chemistry between the "North East Region" (including

Adirondacks and northern new England areas) and the "North Central Region" (including the northern Great Lakes region) in terms of the ratio of equivalents of (1) "Sum(+)" i.e. $Ca^{++} + Mg^{++} + NH_4^+ + K^+ + Na^+$ to (2) "Sum(-)", i.e. $SO_4^= + NO_3^- + Cl^-$. The authors pointed out a clear difference between the "non-acidic (pH > 4.5)" "North Central Region" with a ratio of ca. 1:1 and the "acidic (pH < 4.5)" "North East Region" with 1:>2. A comparison was made of ratios from the 1950's (Junge sites) with ratios from the late 1970's and early 1980's for these two regions and also for the "Midwest" and "East Central" regions. Decreased pH was inferred from increases of "Sum(-)" in all but the "North Central Region." This is consistent with results of the PIRLA Project (Charles et al., 1986) and of fishery/water chemistry studies (Haines and Baker, 1986; Stewart et al., 1986). The methodological approach of Altwicker and Johannes (1985) is useful for discerning spatial and temporal trends of acidity of precipitation when reliable measurements of pH are not available, but because of possible problems with the quality of older data on cations and anions, the approach still needs to be used with caution.

7. INTEGRATIVE PALEOECOLOGICAL APPROACHES, AND MODELLING

Charles et al. (1986) describe the PIRLA Project and give some of the early results of the project. They demonstrate the effectiveness of multiparameter and multidisciplinary approaches in paleoecological studies. The sedimentary contents may be used in two ways: first, as a record of changes outside the lake, both in the atmosphere and in the terrestrial watershed, and second, as a record of responses of the lake to atmospheric and terrestrial changes. Charles et al. (1986) show that the evaluation of both aspects of the sedimentary record is complementary for the understanding of the history and effects of acidic precipitation. The PIRLA Project covers four acid sensitive regions of North America where lake sediment cores have been analyzed for biological indicators (including diatom and chrysophyte remains) of past water chemistry. Inferred chemical trends are interpreted by comparison with accumulations in the same cores of airborne contaminants associated with acid deposition such as polycyclic aromatic hydrocarbons, soot particles, and trace metals. An important goal of the project is the estimation of errors associated with the paleoecological reconstructions. This is being accomplished by replicate determinations for several of the parameters at each major step in the procedure, including analyses of multiple cores from at least one lake in each region. The PIRLA investigators have demonstrated that certain lakes now with pH 4.4 to 5.0 in the Adirondack Mts., N.Y., and in northern New England have been acidified (by acidic precipitation) by $\leq$ 1 pH unit starting in the 1920's to 1950's depending on the particular lake. These lakes were all naturally less than pH 6 prior to the recent acidification. By historical study of changes in the watersheds (e.g., logging, forest fire, forest succession) it has been possible for several lakes to exclude watershed changes as causes of the acidification. Study lakes now with pH greater than 6.0 in these areas show no evidence of recent acidification. Lakes studied in the northern Great Lakes region (one of which is pH 4.4) show no evidence of recent acidification. This probably results from the different precipitation chemistry in this region compared with the Adirondacks and New England.

Wright et al. (1986) reconstruct water pH back to pre-pollution times in four lakes using a model (MAGIC) that accepts inputs for historical trends in acidic air pollutants as well as data on the capacity of watershed soil to buffer and otherwise alter such pollutants. These authors demonstrate that terrestrial processes "damp, delay, and moderate" the responses of lakes to acid deposition. Major responses of lakes have occured over only 1 to 3 decades compared to the longer term, slower increase of acid deposition that started earlier. The time-series lake pH responses generated by the model are in reasonable agreement with reconstructions of pH based on sedimentary diatom remains.

8. CONCLUDING COMMENTS

Any retrospective study is likely to give an incomplete and only roughly quantitative picture of chemical and biological changes relating to acidification. Nevertheless, we believe that historical and paleoecological studies such as those presented at Muskoka and highlighted here can contribute, if used with appropriate care, to our information base on trends of acidification. Ingenuity and persistence in uncovering old records, and the development of increasingly sophisticated techniques for determining trends from these records and from lake sediment and peat stratigraphies are contributing to our understanding of acidic precipitation and its effects. Particularly encouraging is the agreement now emerging among the results of widely different approaches such as the modelling of trends in acidification, study of spatial and temporal patterns of precipitation chemistry, comparison of new and old biological and chemical data for terrestrial and aquatic systems, analyses of sediment/stratigraphic "records" of airborne contaminants, and environmental inference based on sedimentary diatom remains and other sedimentary indicators of past conditions. For example, the contrasting acidification history of the heavily impacted Adirondacks and the lightly impacted northern Great Lakes region (except for point source areas like Sudbury) has been demonstrated by historic studies of precipitation chemistry and fisheries as well as sediment studies. Because of the heavy impacts in the Adirondacks, and therefore the relative ease in demonstrating these impacts, the area is the best historically documented one in North America for demonstrating the effects of regional acid deposition including lake acidification and fishery losses. For other regions, less comprehensive but similar historic data demonstrate lake acidification, loss of fisheries and other effects of acidic deposition.

As a final comment, we point to what we perceive as a major difficulty in interpreting historical and paleoecological data. This difficulty derives from the co-occurrence of natural and anthropogenic processes and the diverse ways that airborne contaminants may affect terrestrial and aquatic systems. The difficulty may be partly overcome by increasing our understanding in general of ecosystem function and watershed biogeochemistry. Notably in short supply is good comparative information on the variation in response of ecological systems to natural perturbations. Such information can be obtained from long-term ecological study and monitoring in relatively unpolluted areas, and by sophisticated paleoecological study. Support for such fundamental and long-term studies is at least as important as for studies of pollution effects themselves, because without knowledge of non-anthropogenic variation it is impossible to place anthropogenic variation in a meaningful context.

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