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Effects of acidic deposition on North American lakes: palaeolimnological evidence from diatoms and chrysophytes

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Analysis of sediment diatom and chrysophyte assemblages is the best technique currently available for inferring past lake water pH trends. Use of this approach for assessing the ecological effects of acidic deposition is increasing rapidly. As of August 1989, sediment core inferred pH data existed for at least 150 lakes in North America and cores from about 100 more lakes are being analysed. Equations for inferring past pH are based on at least 15–20 calibration data-sets involving about 700 lakes.

Palaeolimnological studies indicate that recent acidification has been caused by acidic deposition in the Adirondack Mountains (New York), northern New England, Ontario, Quebec and the Canadian Atlantic provinces. Inferred pH decreases are commonly as much as 0.5–1.0 pH units. With the exception of one lake, no acidification trends were observed in regions currently receiving low deposition of strong acids (e.g. Rocky Mountains and Sierra Nevada in the western United States). Slight or no trends towards decreasing pH were observed in study lakes receiving moderately acidic deposition (upper Mid-west and northern Florida). The amount of inferred acidification (increase in H^+ concentration) correlates with the amount of S and N loading and the ability of watersheds and lakes to neutralize acid inputs, and is generally consistent with current lake-acidification theory.

In most cases, the primary cause of recent acidification (post-1850) is acidic deposition, as opposed to land-use changes or natural processes, though these may be contributing factors. Acid loading has decreased in some regions since 1970 (e.g., northeastern United States). Some lakes have become less acidic in response, but others continue to lose acid neutralizing capacity. Many currently acidic lakes were naturally acidic ($pH < 5.5$) before the onset of anthropogenic acidification. These lakes are typically small (less than 10 ha‡) are located at moderately high elevations, have thin or peaty soils, or are located in outwash deposits. Many of these have acidified further recently.

Introduction

Acidification of lakes by atmospheric deposition of strong acids is a major environmental issue in North America and causes and effects have been studied intensively. Several research projects have been implemented to determine the acidity status of lakes before the onset of acidic deposition, and to estimate their response to strong acid inputs. Information from these studies is necessary to fully assess the effects of acidic deposition on aquatic resources and to accurately predict the nature and extent of response to future changes in deposition. Historical changes have been assessed by (i) comparison of recent and historical water chemistry, fish and diatom data, (ii) use of empirical and dynamic models and (iii) analysis of palaeoecological data (National Research Council 1986). Other than the sparse historical chemistry and fisheries

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‡ 1 ha = 10^4 m^2.

information, which is usually difficult to interpret, palaeoecological studies have provided the most direct indication of trends in past lake pH and acid neutralizing capacity (ANC), the rate and magnitude of the change and possible causes of the change (Battarbee 1984; Charles & Norton 1986; Smol *et al.* 1986; Battarbee & Charles 1986, 1987; Davis 1987; Charles *et al.* 1989; Battarbee, this symposium).

The purpose of this paper is to summarize what we have learned in North America from palaeolimnological studies about the nature and extent of recent acidification in different regions, and the role of acidic deposition and other factors as causes of observed changes.

METHODS FOR INFERRING PAST pH AND ASSESSING ACIDIFICATION CAUSES

Before 1989, most pH reconstructions used Index α (Nygaard 1956; Meriläinen 1967), index B (Renberg & Hellberg 1982) and multiple regression approaches (see, for example, Charles (1985)). The standard error for the pH inference equations based on these indices ranges between 0.25 and 0.4 pH units (Battarbee 1984; Charles & Norton, 1986; Smol *et al.*, 1986; Charles *et al.* 1989). A multiple regression technique, similar to that for pH, has been developed to infer alkalinity (Charles *et al.* 1990). New techniques have been developed to infer pH by using both diatoms and scaled chrysophytes (Charles & Smol 1988). These are particularly useful in acidic lakes ($pH < 5.0$), because chrysophytes appear more sensitive to pH changes in these ranges than do diatoms (Smol 1986, 1987). Also, methods based on canonical correspondence analysis (ter Braak 1986; ter Braak & Van Dam 1988) and weighted averaging (Birks *et al.* and Kingston & Birks, this symposium) are now being used to reconstruct pH, ANC, DOC, and Al for lakes in the Adirondacks (Charles & Smol 1990) and New England (Davis *et al.*, this symposium).

Diatom and chrysophyte data are being used not only to infer the past pH trend of a lake but also, in many cases, to suggest the causes of the changes. There are three major possible causes of regional acidification of low-alkalinity lakes in North America: (i) long-term natural acidification, (ii) catchment disturbances, such as fires, blowdown, logging, and ensuing responses of vegetation and soils and (iii) atmospheric deposition of strong acids. These possible causes, and the use of palaeolimnological techniques to determine their importance, are discussed in detail in Charles *et al.* (1989) and Battarbee (this symposium).

RECENT LAKE ACIDIFICATION TRENDS IN REGIONS OF NORTH AMERICA

Diatom data-sets from several regions (figure 1; table 1) have been assembled and reviewed for the purpose of evaluating recent acidification trends in North America (see Charles & Norton (1986) and Charles *et al.* (1989) for locations of lakes and for tables of diatom inferred (DI) pH data and lake characteristics; results from some completed studies are as yet unpublished and are not included in table 1). Data were selected for lakes having: (i) current alkalinity less than 200 $\mu eq\ l^{-1}$; (ii) minimal or, if not minimal, well-known watershed disturbance of influence from local emission sources and (iii) adequate quality and quantity of diatom or chrysophyte data. Inferred pH values were based on calibration sets developed for regions in which the study lakes are located.

In general, the study lakes represent the most acidic lakes in each region. Most of the lakes in the Adirondacks (12), upper Mid-west (9), and northern Florida (6), and some in New

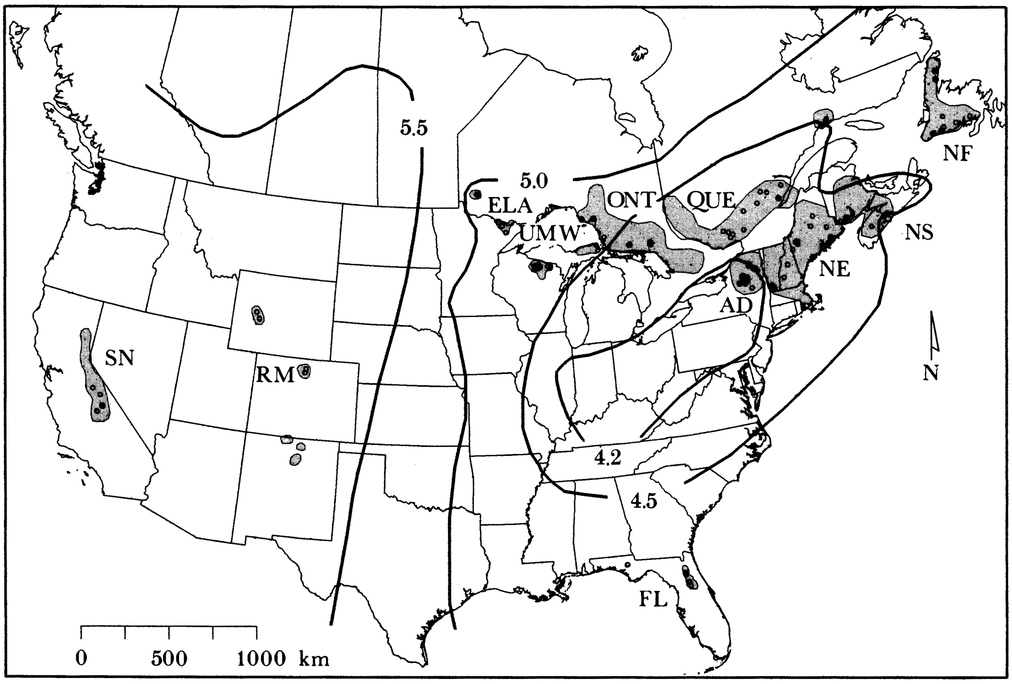

Figure 1. Locations in North America of palaeolimnological studies using diatom and chrysophyte assemblages to infer recent trends in lake acidity status. Shaded regions indicate areas covered by calibration data sets. Solid symbols represent sites where recent acidification is indicated. Open symbols represent sites where no change or an increase in pH has been inferred. See text for further explanation. See Charles *et al.* (1989) for tables of measured and inferred pH for the study lakes. Isopleths of precipitation pH are from Barrie (1984). Lakes in New Mexico are not included in Charles *et al.* (1989). Data available (Lynch *et al.* 1988) do not indicate any significant recent acidification. (AD, Adirondack Park, New York; ELA, Experimental Lakes Area, Ontario, Canada; FL, northern Florida; NE, New England; NF, Newfoundland, Canada; NS, Nova Scotia and New Brunswick, Canada; ONT, Ontario, Canada; QUE, Quebec, Canada; RM, Rocky Mountains; SN, Sierra Nevada.)

Table 1. Acidification trends for North American lakes based on difference in di pH between surface (modern) and pre-1850 sediment core assemblages. Lakes were determined to have become more acidic if di pH decreased by 0.2 pH units or more. Regions are listed in decreasing order of current acid deposition loading. Acidification categories are divided according to pre-1850 di pH (above or below pH 5.5)

(See text for explanation. Data on which this table is based are presented in Charles *et al.* (1989).)

		no acidification		acidification	
region	pre-1850 pH:	< 5.5	⩾ 5.5	< 5.5	⩾ 5.5
Adirondacks		1	6	6	6
Northern New England		7	1	5	1
Ontario		0	1	1	5
Quebec		1	11	0	1
New Brunswick/Nova Scotia		0	5	2	7
Newfoundland		0	2	0	1
Upper Midwest		3	6	1	4
Northern Florida		3	1	1	1
Rockies		0	7	0	0
Sierra Nevada		0	4	0	1
total		15	44	16	26

England, (3), were studied as part of the Paleoecological Investigation of Recent Lake Acidification (PIRLA) project funded by the Electric Power Research Institute (Charles & Whitehead 1986). Chrysophyte data are available for most lake studies in the Adirondacks, New England, Ontario and Quebec, but not for the other regions. Major changes in diatom stratigraphy are usually accompanied by changes in chrysophyte stratigraphy and they indicate the same pH trend.

(a) *United States of America*

Diatom and chrysophyte assemblages in Adirondack lakes indicate significant recent acidification (figure 1, table 1). All 11 clearwater lakes with current pH less than 5.5 have acidified recently. The acidification histories of most are substantiated by several lines of evidence, including stratigraphies of diatom, chrysophyte, chironomid, and cladoceran remains; Ca:Ti and Mn:Ti ratios; sequentially extracted forms of Al; and historical fish data (Charles *et al.* 1987, 1989, 1990). The pH of Big Moose Lake, Queer Lake, and Honnedaga Lake declined about 1 unit from before 1800 to the present. Diatoms and chrysophytes in Deep Lake, Barnes Lake, Lake Arnold, Merriam Lake, Upper Wallface Pond and Woods Lake indicate a recent drop in pH from about 5.0–5.5 to around 4.7–4.9. These lakes are likely to have been naturally acidic and to have acidified further recently. Shifts in assemblage composition (Charles *et al.* 1990; Smol & Dixit 1990) suggest that increased concentrations of Al or other metals, and decreased organic matter (Davis *et al.* 1985; Davis 1987) may have accompanied the pH decline. Acidification trends appear to be continuing in some lakes, despite recent reductions in atmospheric sulphur loading.

All clearwater lakes with current pH greater than 6.0 have acidified only slightly or not at all, reflecting the ability of the lake–catchment systems to neutralize acid inputs. Diatoms and chrysophytes in high DOC lakes and bogs suggest a relatively small pH change, as would be expected in highly coloured acidic waters buffered by organic acids.

The primary cause of recent acidification is clearly the increased atmospheric deposition of strong acids derived from combustion of fossil fuels, though other factors may play a role. Natural processes and catchment disturbances cannot account for the rapid changes in water chemistry that have occurred (see, for example, Whitehead *et al.* (1986)). For many of the lakes, sediment core profiles of Pb, Ca, V, Zn, S, polycyclic aromatic hydrocarbons (PAH) and carbonaceous particles provide a record of deposition of materials associated with fossil fuel combustion beginning in the late 1800s and early 1900s. The onset of acidification began after that time (Charles *et al.* 1990).

As part of the recently initiated PIRLA II project (Charles & Smol 1990), funded by the U.S. Environmental Protection Agency (EPA), recent (0–1 cm) and pre-1850 (> 30 cm) sediment core intervals of 37 lakes statistically selected as part of EPA's Eastern Lake Survey (Landers *et al.* 1988) were analysed to determine historical pH and ANC trends. All of the 17 lakes with current pH less than 5.8 declined in pH and ANC (J. P. Smol, personal communication). This further corroborates findings based on palaeolimnological and other studies indicating that acidic deposition has caused widespread acidification of Adirondack lakes.

In New England, changes in sediment diatom assemblage composition indicate recent acidification of some lakes. However, most of the pH trend data indicate no change or only a slight decrease in pH from pre-1800 to be present (Norton *et al.* 1985; Charles *et al.* 1989; Davis *et al.* 1990; Ford 1986, 1990). Fluctuations in some of the profiles appear to be related to watershed events (Davis *et al.* 1983). Sediment chemistry data for Mud Pond, Haystack Pond, and Little Long Pond indicate post-1900 increases in materials associated with the combustion of fossil fuels (e.g. total Pb and V) (Davis *et al.* 1990). The DI pH of Duck Pond, a kettle pond on Cape Cod, Massachusetts, suggests a slight recent acidification trend (pH 5.2–5.0), though this pond has been naturally acidic for thousands of years, with a mean DI pH for its entire history (about 12000 years) of 5.2 ± 0.3 pH units (Winkler 1988).

Lakes in the Upper Mid-west differ as a group from those in the northeast in that most are seepage lakes and are very dilute (conductivities as low as 9 μS cm^{-1}). There is no indication of acidification in Minnesota lakes (three lakes studied); and there is evidence of post-1900 pH declines in four of nine Wisconsin lakes; one of two lakes studied in Michigan has become slightly more acidic (Charles *et al.* 1989; Kingston *et al.*, this symposium). These results are generally consistent with the strong gradient of decreasing precipitation pH from west to east (see, for example, figure 1). McNearney Lake in Michigan is a naturally acidic lake (pre-1800 DI pH = 4.9); its pH has not declined, but current Al concentrations are high. Concentrations of S, Pb, Cu, V and polycyclic aromatic hydrocarbons increase towards the surface of the cores, but they are not as great as concentrations in the northeastern United States (Kingston *et al.* 1990).

Northern Florida has the largest percentage of lakes with pH less than 5.0 (12%) of all regions in the United States (Landers *et al.* 1988). Analysis of pre-1850 sediment core diatom assemblages indicates that four of six PIRLA lakes had low pH values due to natural causes (Sweets *et al.* 1990). Low base cation concentrations are probably attributable to the low cation exchange capacity and low base saturation of the deep coarse sands in which the lakes are situated, and to isolation from the local groundwater table (Floridan aquifer) by the clay-rich Hawthorne formation. The high SO_4^{2-} concentrations, which contribute most to the acidity, apparently result from high evapoconcentration rates (Pollman & Canfield 1990). Lake Barco and Lake Suggs have become more acidic recently, with DI pH decreases of about 0.5 pH units. There are two possible causes: acidic deposition and a decrease in the regional groundwater table (Sweets *et al.* 1990; Pollman & Canfield 1990).

The Rocky Mountain and Sierra Nevada lakes may be considered control or reference lakes. They all have low alkalinity (most with alkalinity < 60 μeq l^{-1}) and are therefore sensitive to increased input of strong acids, but do not currently receive precipitation with an annual average pH lower than about 5.0 (see, for example, Barrie (1984)). Current SO_4^{2-} concentrations are typically less than 20 μeq l^{-1}. Changes in the diatom stratigraphy of most Rocky Mountain lakes are relatively minor, occur gradually and do not indicate recent acidification (Baron *et al.* 1986). The same is true for Sierra Nevada lakes (see, for example, Holmes *et al.* (1989), but there is evidence of trends of both increasing and decreasing pH, particularly based on analysis of floristic changes (M. Whiting, personal communication). Some of the trends began well before 1900. Causes are not clear, but may include effects of volcanic eruptions during the past few thousand years, land-use changes in nearby valleys that have caused changes in dry deposition of particulates containing base cations, and increased episodic acidification events following summer rainstorms (M. Whiting & D. Whitehead, personal communication).

(*b*) *Eastern Canada*

In contrast to studies in the United States, in which the goal has been to assess the effects of acidic substances transported long distances, a large percentage of the Canadian studies have focused on lakes that are near large point sources of sulphurous oxide (SO_x) and metal emissions (e.g. Sudbury, Wawa), near mining effluents, or on lakes that have been manipulated (e.g. limed or acidified). Several studies deal with lakes that are strongly influenced by organically rich soils and bogs. Nevertheless, in all lake regions studied thus far where acidic precipitation occurs, diatoms and chrysophytes have indicated a recent pH decrease in at least some lakes. The floristic changes are similar to those recorded in the northern United States and some areas of Europe.

In Ontario, Dickman *et al.* (1984) and Dixit & Dickman (1986) studied acidification of lakes in the Wawa area, northeast of Lake Superior and downwind of a major smelting operation. They inferred that the pH in Lake CS and Lake B had markedly declined. During the past 200 years, other lakes had been rather acidic, one lake had relatively stable pH, and one had fluctuating pH (Fortescue 1984). The acidification of Lake CS and Lake B in the past 30–50 years is apparently attributable to emission of S from Wawa, Ontario, in the 1940's and 1950's (Dickman *et al.* 1984). Forest fires and logging may also have affected diatom stratigraphy and lakewater pH.

Dixit *et al.* (1987, 1988) used diatoms and chrysophytes to infer the pH history of two lakes (Hannah and Clearwater) near Sudbury, an area of major smelting operations. In Hannah Lake, acidification started soon after the roasting of ore began at Copper Cliff in the 1880s. Between about 1800 and 1975, the DI pH declined from about 6.0 to 4.6. After liming in 1975, the DI pH increased. In Clearwater Lake, the diatom assemblages indicated that acidification occurred after the installation of tall stacks at Copper Cliff in the 1920s. The pH declined from about 6.0 in *ca.* 1930 to about 4.2 by *ca.* 1970. Acidification appears to have stopped after that time.

Chrysophyte scales from a variety of Ontario lakes are being used to infer pH change (K. Nicholls (Ontario Ministry of the Environment) and J. P. Smol, unpublished data). Chrysophytes indicate a decrease in lakewater pH in Algonquin Park, in the Parry Sound region, and in Pukaskwa National Park. Davidson (1984) and Dickman *et al.* (1988) studied the artificially acidified Lake 223 in the Experimental Lakes Area by using a variety of techniques and found that the diatom flora in a core from the lake showed good agreement with the known plankton history.

Cores from Key Lake and Lake C-22 in the Matamek Watershed in northeastern Quebec were studied by Hudon *et al.* (1986). In the recent sediments of Key Lake, there was a decrease in the number of circumneutral diatom taxa and an increase in acidobiontic forms; however, no statistical increase in acidity could be inferred. Similarly, in Lake C-22 there has been a slight tendency toward greater acidification in the past 20 years, but the trend was less distinct than that shown in Key Lake.

In a study of several lakes in Quebec located in a strip 150 km wide north of the St Lawrence River, Dixit and others found either a small change or no change in inferred pH (Dixit 1988; Charles *et al.* 1989). Analysis of four of the lakes suggested a recent minor pH reduction. Chrysophytes changed much more strikingly than diatoms in recent sediments of several lakes, but again suggesting only minor acidification.

Delorme *et al.* (1983) inferred pH trends for Kejimkujik Lake (central Nova Scotia), a presently acidic ($pH = 4.8$) site in a drainage basin of organic rich soils and bogs. Since those results were published, the core has been reanalysed by using more recent taxonomic information. Instead of a significant increase in DI pH, only a slight increase is now inferred

(H. Duthie, personal communication). The present low pH of the lake cannot be attributed entirely to atmospheric loading; acid conditions have persisted for at least the last 1000 years, probably because of organic acids.

A study of three Nova Scotia lakes and four New Brunswick lakes showed that DI pH declines in the unbuffered lakes (e.g. a decline from 6.1 to 5.3 for Big Indian Lake), but not in the higher alkalinity lakes (Elner & Ray 1987). The changes occurred over about the past 70 years, coincident with assumed increases in acidic precipitation.

Diatom inferred pH profiles for seven lakes in Newfoundland indicate declines of about 0.2–0.3 pH unit in three of the lakes (Scruton *et al.* 1987*a*, *b*). The pH changes were probably caused by atmospheric sources, as well as by possible watershed disturbances (e.g. forest fire) and natural processes. These small changes in inferred pH are consistent with the relatively low level of acidic deposition in Newfoundland.

Assessment of trend data and possible acidification causes

Considerable high-quality data now exist with which to make assessments of acidification trends in North America. As of August 1989, sediment core DI pH data existed for about 150 lakes. Reports on studies of about another 100 lakes will probably appear within the next two years. The pH inference equations on which the DI pH data were calculated are based on 15–20 calibration data sets for North America involving a total of about 700 lakes (Charles *et al.* 1989). The predictive equations based on these data sets have a good ability to infer pH. With few exceptions, the surface sediment DI pH values agree with current measured pH within about 0.1–0.4 units (Charles *et al.* 1989).

Palaeoecological data now available are sufficient to conclude that lake acidification has occurred in the Adirondack Mountains (New York), New England, Ontario, Quebec, the Atlantic provinces, the Upper Mid-west, and Florida (figure 1, table 1; Charles *et al.* 1989).

Based on palaeolimnological and other data, the primary cause of recent lake acidification in most of the above regions is acidic deposition derived from combustion of fossil fuels, although catchment changes and natural long-term processes may play a minor role. Data for the Upper Mid-west and Florida strongly suggest that acid deposition may be the cause for acidification of some lakes, but the evidence is not sufficiently strong to suggest that acidic deposition has caused significant acidification of many lakes within those regions. The relative importance of these possible causes was evaluated by using the hypothesis testing criteria described by Charles *et al.* (1989). It is clear that pH declines in most areas cannot be accounted for by natural long-term processes (the rates of change are too fast) or by catchment changes, although these probably contributed to the process in some areas. In the majority of cases, DI pH declines occurred after the onset of acidic deposition (post-1850–1960), as palaeoecological evidence (e.g. Pb, V, PAH, carbonaceous particles) demonstrates. All regions where pH declines have been inferred receive relatively high levels of acidic deposition.

Taken together, the DI pH profiles exhibit a continuum of acidification trends that have been classified arbitrarily into four basic patterns (Charles & Norton 1986; Charles *et al.* 1989; table 1). Two represent trends and two represent no trend. The patterns are: (i) background pH greater than about 6.0 and no overall change in pH; (ii) relatively rapid decline in pH from the range of 5.7–6.0 to less than 5.0 (some pH declines start in pH ranges above 6.0); (iii) pH about 4.8–5.2 throughout the entire profile, and no overall trend and (iv) decline from the range of pH 4.8–5.3 to as low as about 4.3.

The most rapid changes in DI pH and sediment core diatom composition occur when DI pH decreases from a value above approximately 5.7–6.0 to below 5.0 (pattern 2). A smaller pH drop is observed for lakes with pre-1850 DI pH values of less than 5.5 (pattern 4). These patterns are consistent with the logarithmic nature of the pH scale and the response of sample lake-water pH to titration with strong acid in the laboratory. The pre-1850 water chemistry of lakes with patterns 1 and 2 and patterns 3 and 4 represent the dominant pre-1850 buffering systems in the studied regions: bicarbonate in the higher pH lakes, organic acids and Al species in the lower-pH lakes. Declines in pH in the latter group (pattern 4) should be interpreted carefully. Though pH may have decreased only slightly, increases in Al may have been substantial, because the change in Al per pH unit is greater in the pH range 4.5–5.0 than in the range 5.5–6.0 (Driscoll *et al.* 1984; Sullivan *et al.* 1989).

Lakes with pre-1850 DI pH less than 5.5 deserve special attention. First, they represent what have been considered 'naturally' acidic lakes, and second, it is difficult to explain their past chemistry and how it may have changed during the process of acidification (Charles *et al.* 1989). Many lakes of this type have been studied. In the Adirondacks, northern New England, and northern Florida (table 1), at least 40% of the lakes have pre-1850 DI pH less than 5.5. There are two probable reasons for this high percentage. First, a region may have a high proportion of naturally acidic lakes due to its geologic setting (e.g. Florida), or second, because of conscious site-selection criteria, only the more acidic lakes in a region may have been chosen for study, many of which were found to be naturally acidic (e.g. New England). It seems probable that organic acids were an important cause of acidic conditions in many lakes in acid sensitive areas before 1850 (Patrick *et al.* 1981; Davis *et al.* 1985). Also, if the pH was about 5.0, Al concentrations may have been moderate at that time, although much of the Al would have been complexed with organic compounds (Driscoll *et al.* 1984).

As low pH (5.0–5.5) lakes have become more acidic, changes in Al and organic-acid concentrations have probably been important factors affecting pH and alkalinity (see, for example, Sullivan *et al.* (1989)). The output of dissolved Al from the watersheds of these lakes should have increased with increased inputs of strong acids (Driscoll *et al.* 1984), except perhaps for seepage lakes in outwash deposits. This is consistent with the fact that most of the lakes examined that have current pH less than 5.5 have concentrations of total Al greater than 100–200 $\mu g\ l^{-1}$; the concentration in some lakes is as high as 600–700 $\mu g\ l^{-1}$ (see, for example, National Research Council (1986), appendix table E.3).

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