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Paleolimnological evidence for recent acidification of Big Moose Lake, Adirondack Mountains, N.Y. (USA)

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Abstract. Big Moose L. has become significantly more acidic since the 1950s, based on paleolimnological analyses of sediment cores. Reconstruction of past lakewater pH using diatom assemblage data indicates that from prior to 1800 to ca. 1950, lakewater pH was about 5.8. After the mid-1950s, the inferred pH decreased steadily and relatively quickly to about 4.6. Alkalinity reconstructions indicate a decrease of about 30 μeq · l^{-1} during the same period. There was a major shift in diatom assemblage composition, including a nearly total loss of euplanktonic taxa. Chrysophyte scale assemblages and chironomid (midge larvae) remains also changed in a pattern indicating decreasing lakewater pH starting in the 1950s. Accumulation rates of total Ca, exchangeable and oxide Al, and other metals suggest recent lake-watershed acidification. Cores were dated using ^{210}Pb, pollen, and charcoal. Indicators of watershed change (deposition rates of Ti, Si, Al) do not suggest any major erosional events resulting from fires or logging. Accumulation rates of materials associated with combustion of fossil fuels (polycyclic aromatic hydrocarbons, coal and oil soot particles, some trace metals, and sulfur) are low until the late 1800s-early 1900s and increase relatively rapidly until the 1920s-1930s. Peak rates occurred between the late 1940s and about 1970, when rates declined.

The recent decrease in pH of Big Moose L. cannot be accounted for by natural acidification or processes associated with watershed disturbance. The magnitude, rate and timing of the recent pH and alkalinity decreases, and their relationship to indicators of coal and oil combustion, indicate that the most reasonable explanation for the recent acidification is increased atmospheric deposition of strong acids derived from combustion of fossil fuels.

Introduction

Acid deposition and its ecological effects are a major environmental concern, and the Adirondack region is one of the areas where possible effects have received much attention (Altshuller and Linthurst, 1984; National Research Council, 1986). This is especially true for the acidification of aquatic systems in the Adirondacks. However, assessing trends of lake and stream acidification has been difficult because there is little good

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historical data on precipitation or surface water chemistry to compare with current conditions (National Research Council, 1986). In the absence of a historical data base, paleoecological analysis of lake sediments is one of the most effective approaches for assessing trends in atmospheric deposition and acidification (e.g. Battarbee, 1984; Charles and Norton, 1986; Smol *et al.*, 1986).

The purpose of this paper is to provide a reconstruction of the acidification history of an Adirondack lake for which there are both previous paleoecological data (Charles, 1984) and independent water chemistry and fisheries evidence (Schofield and Driscoll, 1987; NYSDEC) suggesting recent acidification, and to assess the potential causes of the acidification. Our approach involves reconstruction and correlation of 1) trends in lakewater pH, alkalinity, and Al; 2) watershed disturbance history; and 3) trends in deposition of materials derived from the combustion of fossil fuels and from industrial activities. These reconstructions are used to evaluate three alternative hypotheses for the inferred recent acidification of Big Moose Lake: 1) long-term natural acidification; 2) acidification due to watershed disturbance; and 3) increased deposition of strong acids.

Information on lake acidification is provided by remains of diatoms, chrysophytes and chironomids, and by metals. Data on deposition of by-products of fossil fuel combustion are determined by analysis of soot and fly-ash particles, polycyclic aromatic hydrocarbons (PAH), sulfur, and certain trace metals in the sediments. Watershed disturbances are ascertained by a review of historical records and from knowledge of local residents. Changes in sediment characteristics such as pollen, charcoal, and metals can be correlated with the disturbance history.

Several paleolimnological studies of Adirondack lakes have provided information on trends in lake acidification and combustion of fossil fuels (Charles, 1984; Del Prete and Galloway, 1983; Del Prete and Schofield, 1981; Holdren, *et al.*, 1984; Smol *et al.*, 1984b; Galloway and Likens, 1979; Heit *et al.*, 1981; Mitchell *et al.*, 1984; Norton, 1986). Several of these studies indicate that lakes with a current pH less than about 5.0 have acidified recently and that net accumulation rates of PAH and trace metals (Pb, Zn, Cu, V) have increased substantially since about the turn of the century.

Analyses were performed by the authors as follows: Charles (diatoms, watershed history), Engstrom, (humics), Fry (S isotopes), Hites (PAH), Norton (^{210}Pb dating, total metals), Owen (S,C,N,H), Roll (PAH), Schindler (S,C,N,H), Smol (chrysophytes), Uutala (chironomids), White (sequential extraction of metals, MINEQL simulation), Whitehead (pollen) and Wise (charcoal, soot).

Big Moose Lake and watershed Big Moose L. (43°49′02″N; 74°51′23″W) is located in the Moose River drainage basin in the southwestern Adirondacks (Fig. 1). It has a surface area of 515 ha, watershed area of 8760 ha, maximum depth of 22 m and is at an elevation of 556 m.

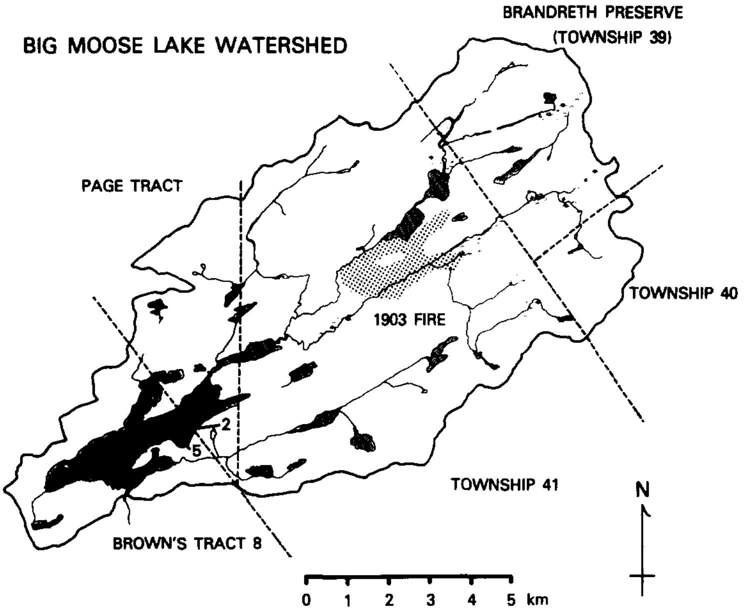


Figure 1. Watershed map of Big Moose L. showing township boundaries and location of 1903 fire (shaded area). Dots indicate locations where cores 2 and 5 were taken. A bathymetric map is in Odell (1932).

Monthly surface water pH measurements ranged from 4.60 to 4.96 during August 1977 to July 1978. For this same period, alkalinity ranged from -19.5 to $1.1\,\mu\mathrm{eq.l^{-1}}$, and total Al ranged from 320 to $595\,\mu\mathrm{g.l^{-1}}$. Average concentration of Ca was $99\,\mu\mathrm{eq.l^{-1}}$, of Mg was $34\,\mu\mathrm{eq.l^{-1}}$ and of SO_4 was $150\,\mu\mathrm{eq.l^{-1}}$ (Driscoll, 1980). Current (1983–1984) annual average lakewater pH is 5.1; alkalinity is $1\,\mu\mathrm{eq.l^{-1}}$ (Driscoll *et al.*, 1987).

Information on watershed characteristics is published elsewhere: geology (Newton *et al.*, 1987) and vegetation (Cronan *et al.*, 1987).

The disturbance history of the watershed (Fig. 1) is important because land use changes can affect several sediment core characteristics. The following account is based on publications by the Association for the Protection of the Adirondacks (1913); New York State Department of Conservation (1916); Donaldson (1921); Whited (1928); and personal communication with William Marleau, retired Forest Ranger and lifelong resident. The watershed in Townships 40 and 41 and the Page Tract (Fig. 1) is state owned and nearly all is in the Pigeon Lake Wilderness area. Most of the remainder is privately owned. The first camp on Big Moose L. was constructed in 1876. Several more camps and a few resort hotels were built by 1890. There are now about 150 residences, mostly seasonal, around the lake, an average of about six per km of shoreline. Big Moose

Road, which runs along the south side of the lake, was put in during 1895–1896. Around 1924, Martins Road was built along the northwest shore of the lake. The first logging operation was in Brown's Tract 8 and occurred between 1895 and 1904. Legal restrictions specified that softwood removed had to be at least ten inches in diameter at a distance two feet above the ground and hardwoods to be at least 12 inches in diameter. New York State purchased this land, and no logging has occurred since 1904. The Page Tract was logged from 1903 to 1906, primarily for red spruce, under the same restrictions as above. Logs were collected in North Bay, floated across Big Moose L., and then driven down the Moose River to a lumber mill. The Page Tract was logged a second time for hardwoods and softwoods during the period 1913–1914. From 1912–1915 Brandreth Preserve was logged, primarily for softwoods.

The only significant forest fire occurred in 1903 (Fig. 1). The fire was severe; the area remained open for many years after the burn. Township 41, representing about 40 percent of the watershed, has never been logged.

On November 25, 1950, hurricane force winds blew down extensive areas of Adirondack forests. Some of Township 41 was affected, but precise locations have not been mapped. A large percentage of the trees along the steep northwest shore were leveled. This was private property and many owners removed the downed trees.

From 1950 to about 1960, DDT was used extensively in the watershed to control black flies. Plaster blocks impregnated with DDT were placed in streams.

Methods

Sediment cores were taken with a 10 cm diameter piston corer with clear Lucite tube, modified from the design of Cushing and Wright (1965). The cores were extruded vertically in the field. They were sectioned at 0.5 cm intervals from the top to 30 cm, and at 1.0 cm intervals below. Sediment was placed in plastic Whirl-pak bags and stored at 4°C.

Measurements of ^{210}Pb were made on approximately 0.1 g of air-dried (90°C, 48 hr) sediment which was processed according to the methods of Eakins and Morrison (1978). Activity of ^{210}Pb was measured on a Tracor Northern (TN-1710) alpha spectrometer using counting times of 20,000 to 100,000 seconds. Chronology of ^{210}Pb was calculated from the ^{210}Pb activity profile, using the constant rate of supply (CRS) model of Appleby and Oldfield (1978). Below about 1850 ± 25 yr the CRS model typically fails mathematically. Chronology below 1872 (set off by a dashed line in the figures) was estimated using a constant initial concentration (CIC) model (Krishnaswami *et al.*, 1971), based on the part of the activity-depth profile where the cumulative mass-ln ^{210}Pb activity relationship is linear. The CIC ages are only approximate.

Activity of ^{137}Cs was determined by packing a known mass of dry sediment into small Petri dishes with standard geometry. Sediment was held in place with a small plastic piston, taped to the Petri dish. This assembly was then counted on a GeLi detector for, in most cases, 20,000 seconds.

Methods for diatom analysis are in Charles (1984, 1985); chrysophyte analysis techniques are in Smol (1986).

Chironomid head capsule remains were sorted from 3-ml subsamples of wet sediment from the available intervals of core 5 using the methods of Warwick (1980). The collected remains were slide-mounted in euparal for identification.

Slides for pollen and charcoal counts were prepared using modifications of techniques outlined by Faegri and Iverson (1975) (Whitehead *et al.*, 1986). The pollen sum was at least 150 grains, usually >250.

Techniques for charcoal counting and identification were modified from Swain (1973; pers. comm.). Criteria for identification of charcoal and soot were based on analyses of charcoal made in the laboratory, soot collected from a coal fired power plant, McCrone (1973), and discussions with K. Tolonen, I. Renberg, and A. Swain. Charcoal fragments were tallied according to size classes using a graticule. The total areas of charcoal and soot particles were measured and presented as a ratio to total pollen (μm^2/pollen grain). This ratio is assumed to be proportional to accumulation rate of charcoal because pollen accumulation rate is assumed to be relatively constant.

Sediment samples for analysis of total S, C, H, and N were dried at 90 °C for 48 hours prior to analysis. Total S was determined by oxidation with NaOBr followed by HI-reduction using a modified Johnson-Nishita apparatus (Landers *et al.*, 1983). C, H, and N were determined on a Perkin-Elmer Model 240C elemental analyzer (Culmo, 1969). The technique for measurement of $\delta^{34}S$ is described by Fry (in press). Isotopic values are reported relative to Canyon Diablo Troilite with a precision of $\pm 0.2‰$.

Water content of sediment was determined by heating a known mass of wet sediment to constant weight (90 °C, ca. 48 hours). Loss on ignition was determined by heating sediment at 550 °C for three hours.

Samples for total metal analysis were prepared by putting 0.1000 g of ashed sediment in solution using the method of Buckley and Cranston (1971). Standards were made up in the same Buckley and Cranston matrix to simulate a typical sediment. Vanadium and Pb were analyzed by flameless atomic absorption spectrophotometry (AAS) (Perkin-Elmer 703 and HGA-2200 graphite furnace). All other elements were analyzed using flame AAS. Silica (SiO_2) was determined by difference.

Sequential chemical leaching to extract Al, Fe, and trace metals associated with a series of sediment phases was performed using the techniques of Tessier *et al.* (1979). Extracts of 5-ml sediment samples were analyzed for metal concentrations using atomic absorption spectrophotometry (Instrumentation Laboratory, Video 12), calibrated with matrix-matched standard solutions and deuterium background correction.

Sedimentary humic materials were analyzed by a spectrophotometric method for dissolved tannin and lignin as modified for lake sediments (Engstrom and Hansen, 1985). Humic components were extracted from dried sediment samples in 0.1 N KOH, treated with a mixture of tungsto- and molybdo-phosphoric acids, and measured for absorbance at 700 nm.

PAH analyses were performed using a Hewlett-Packard 5985B GC/MS. Procedural blanks and analyses of a reference sample (NBS Urban Air Particulate SRM # 1649) were analyzed.

More detailed descriptions of the above methods are in Charles and Whitehead (1986).

Results and discussion

Sediment core description and analysis

Core descriptions Sediment core numbers 2 and 5 were taken from the main basin of Big Moose L. (Fig. 1). Core 2 (54 cm long) was taken 4 August 1982 in 13.7 m of water; Core 5 (27 cm long) was taken 3 August 1983 at 18 m water depth. The surface layer (less than 1 cm) of each core

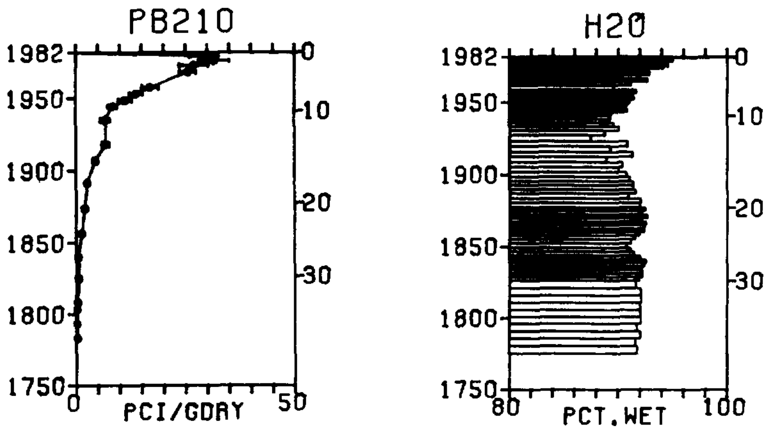
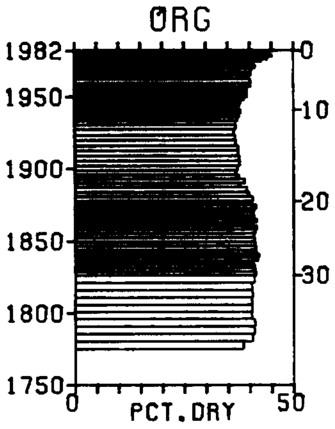


Figure 2. Geochemical characteristics of Big Moose L. core 2. Profiles of ^{210}Pb and ^{137}Cs activity (pCi.g^{-1}), percent water, percent organic matter, and concentrations of Fe, Si, and Ca expressed in the oxide form as weight percent of ignited sediment. Vertical axes are ^{210}Pb dates and core depth. Lead-210 dates extend only to about 1850; dates prior to that time are extrapolations of CIC model dates. On the date-depth graph, the line extending below 35 cm depth represents CIC model dates, the other line represents CRS model dates.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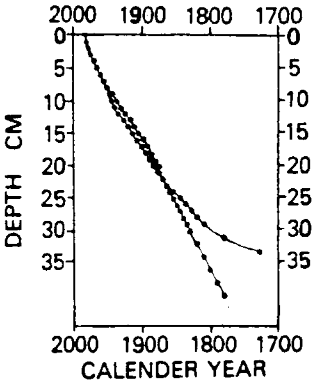
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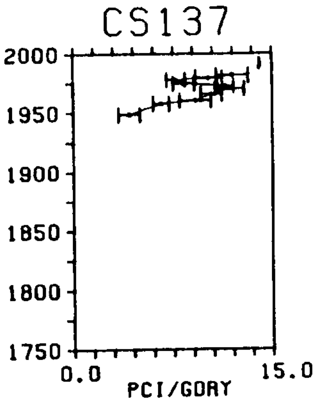
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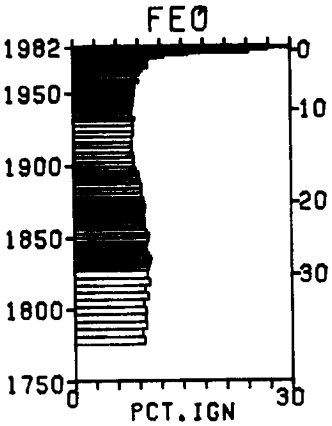
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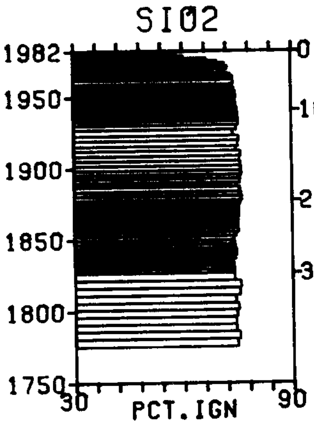
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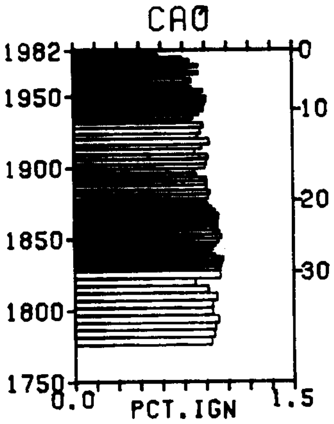
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was reddish brown. From 1 to 5 cm, sediment was brown with some green and reddish brown mottling. Sediment below about 5 cm was firm, dark brown gyttja. No invertebrates were observed during subsampling, nor was there any obvious evidence of sediment mixing.

^{210}Pb chronology The ^{210}Pb chronology for core 2 (Fig. 2, Table 1) is based on an 18 point curve (Fig. 2); values for unmeasured intervals were based on linear interpolation. This yields a very slight overestimation of these values and also a very slight overestimation of integrated unsupported ^{210}Pb.

Additionally, we assumed a surface interval activity for ^{210}Pb of 33 pCi.g^{-1} dry wt, only slightly higher than the value of the 2.5 cm interval of sediment just beneath it. We interpret this zone (0 to 3.0 cm) to be mixed, or alternatively as a period of increasing sedimentation rate. We believe that the latter explanation is more probable because many chemical parameters vary appreciably through these intervals. However, some mixing must have occurred, or else the sediment would be laminated. The precise value of surface activity does affect the chronology, but only by a few years (Table 1) distributed over a 100 year time span, for sediment intervals with assumed activity values ranging from 28 to 40 pCi.g^{-1} dry wt.

Unfortunately, the core was not sufficiently long to determine background supported ^{210}Pb with certainty. We chose a background of 0.3 pCi.g^{-1} dry wt at a depth of 33 cm. Choosing 0.1 pCi.g^{-1} dry wt at 40 cm as background has little effect on the chronology. The CRS chronology extends to a depth of 21 cm (ca. 1872). Below that depth, ages have

Table 1. Analysis of sensitivity of CRS model dates to choice of ^{210}Pb surface and background levels, Big Moose L. core 2. Activities and background depth used to calculate dates in Figure 2 are shown in the top row. The profile of ^{210}Pb data that were used for selection of activities and depths presented in this table are shown in Figure 2.

Surface	Background		CRS model dates for core intervals (cm)				
^{210}Pb Activity (pCi·g^{-1})	Core Depth (cm)	^{210}Pb Activity (pCi·g^{-1})	5 cm	10 cm	15 cm	20 cm	25 cm
33	33	0.3	1964.6	1941.0	1908.6	1877.3	1837.3
35	33	0.3	1964.6	1941.0	1908.6	1877.3	1837.3
40	33	0.3	1964.5	1940.9	1908.5	1877.2	1837.3
30	33	0.3	1964.6	1941.1	1908.7	1877.4	1837.4
25	33	0.3	1964.7	1941.1	1908.7	1877.4	1837.5
33	39	0.2	1964.9	1941.9	1911.1	1882.7	1850.0
33	26	0.6	1963.8	1938.6	1902.0	1862.2	1783.2
30	39	0.3	1964.6	1941.1	1908.7	1877.5	1837.8
30	36	0.3	1964.6	1941.1	1908.7	1877.5	1837.8

been estimated crudely by extrapolating the age-depth relationship (slope) for the CIC model below 21 cm. This procedure is based on the assumption that no significant changes in sedimentation rate have occurred over the period of extrapolation.

The core 5 ^{210}Pb profile is very similar to that of core 2. The only apparent difference is in sedimentation rate, 0.25 cm.yr^{-1} for core 5 and 0.20 for core 2, averaged for the period 1900–1982. The concentration of ^{210}Pb is constant in mid-profile of both cores (10–14 cm in core 2, Fig. 2) because of either a period of mixing or a period of very high sedimentation rate. If the former, dates below this zone will be in error. Several other parameters show sharp change over this sediment interval indicating that mixing is probably not important.

^{137}Cs stratigraphy The ^{137}Cs stratigraphy (Fig. 2) has been determined for part of the core, although Davis *et al.*, (1984) and Heit and Miller (1987) have demonstrated that ^{137}Cs dating is generally unreliable in slowly sedimenting, acidic lakes. There is no similarity between these data and the well established pattern for ^{137}Cs atmospheric deposition over the last 40 + years. Consequently, the identification of the 1961–3 peak in deposition is not possible from concentration data alone. However, if it is assumed that the ^{210}Pb chronology is accurate, the ^{137}Cs can be age-corrected for decay. This yields a broad peak of activity, 15.6–15.8 pCi.g^{-1} dry wt with poor

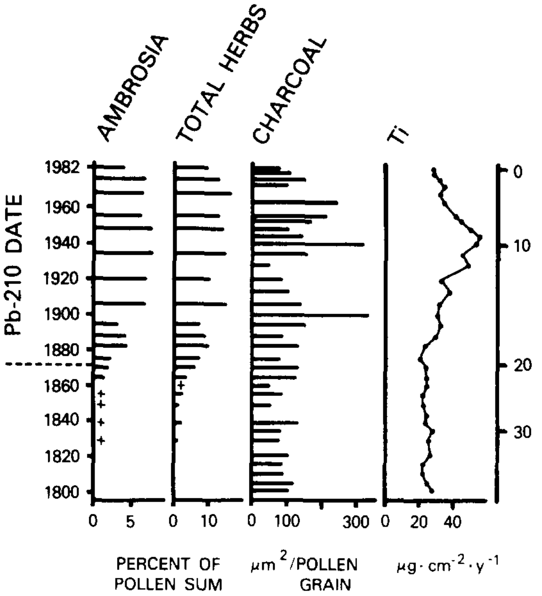

Figure 3. Sediment indicators of watershed and regional disturbance history, Big Moose L., core 2.

resolution from about 1960 to 1970. Furthermore, if the true peak activity is ca. 15 pCi.g^{-1}, the surface activity is at least an order of magnitude too high. A variety of explanations for this type of pattern have been advanced, but with our data, a full explanation is not possible (see Davis *et al.*, 1984; Heit and Miller, 1987).

Pollen Pollen stratigraphy (Fig. 3) is important primarily as a means of identifying the sediment intervals that correlate with European settlement and land clearance that began in the Adirondacks ca. 1860–1870. A sharp increase in *Ambrosia* (ragweed) pollen, increases in other weedy taxa, and a general increase in pollen of herbs indicate this settlement horizon. The increase in these pollen categories in Big Moose L. occurs between 22.5 and 23.5 cm (Fig. 3), 1860–1865 according to ^{210}Pb-dating, and corresponds closely with known regional land clearance dates. Other weedy taxa (e.g., *Plantago* and *Rumex*) and cultivars such as *Zea* (maize) occur above this level, but not below it. There are no significant trends evident in the curves for dominant tree types.

Charcoal Charcoal data (Fig. 3) enable us to identify years during which there were major forest fires. Extensive fires occurred in the Adirondacks in 1903 (Suter, 1904) including some of the Big Moose L. watershed. The charcoal peak recorded at 16 cm (^{210}Pb date 1902) probably represents the 1903 fire. Several fires also occurred in the Adirondacks in the late 1800s and also in 1905 and 1908, which may explain the "tails" on either side of 16 cm. We have no immediate explanations for the peak at 10 cm (ca. 1938) or the broad maximum at about 4 cm (ca. 1960).

Diatoms Analysis of sediment diatom assemblages is currently the most effective procedure for reconstructing the pH history of acidic, oligotrophic lakes like Big Moose. Diatom valves are siliceous, preserve well and are abundant in sediments (Battarbee, 1984). Most importantly, distributions of individual taxa correlate closely with lake water pH and related factors (Battarbee, 1984; Charles, 1985; Charles and Norton, 1986; Davis *et al.*, 1985).

Big Moose L. diatom stratigraphy has been reported previously (Charles, 1984); results are summarized here. More than 200 taxa were identified from the core. Assemblages were diverse. For most of the core, counts of 400 to 450 valves included about 80–100 taxa. The number decreased above ca. 5.0 cm, reaching a low of 49 taxa at the surface. No taxon ever comprised more than 20 percent of an assemblage.

The stratigraphy of dominant diatoms within the core (Fig. 4) indicates an acidification trend beginning in the 1950s. The acidobiontic taxa *Navicula tenuicephala* Hustedt and *Fragilaria acidobiontica* Charles (Charles, 1986) increased significantly toward the top of the core while the euplanktonic form *Cyclotella stelligera* Cl. et Grun. decreased. In a study of sediment diatom assemblage-water chemistry relationships among 38 Adirondack lakes (Charles, 1985), the two acidobiontic taxa were not encountered in sediment assemblages of lakes that had a pH greater than 5.7; the indifferent, *C. stelligera* was nearly always found at pH's above 6.0. The percentages of valves assigned to Hustedt (1939) pH categories (Fig. 4) suggests an acidification trend, as does the decline in percentage of euplanktonic taxa. Among surface sediment assemblages of 38 Adirondack lakes, euplanktonic taxa were absent or very rare in the 15 lakes with a pH less than 5.8–6.0. The decline in accumulation rate of valves parallels, and is probably caused by, the decrease in euplanktonic taxa.

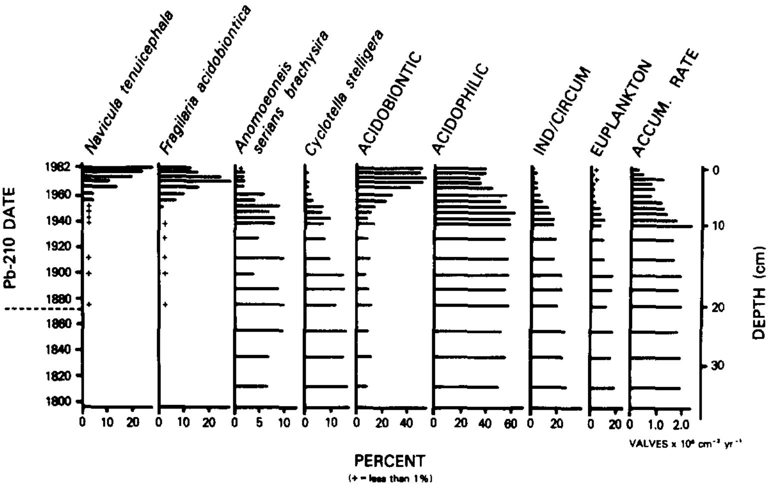

Figure 4. Dominant diatom taxa, percentages of diatoms in pH categories, percent of euplanktonic diatoms, and diatom valve accumulation rates in Big Moose L. core 2. Hustedt (1939) pH categories: ACIDOBIONTIC, best development at pH < 5.5; ACIDOPHILIC, generally occur at pH < 7; CIRCUMNEUTRAL, INDIFFERENT, occur at pH around 7. In previous papers (Charles 1984, 1985), *N. tenuicephala* was called *Stauroneis gracillima* Hust. and *F. acidobiontica* was called *F. virescens* var. 1. The euplanktonic diatoms identified were *Cyclotella stelligera, C. comta,* and *Melosira ambigua* (Grun.) Müller. Data are discussed in more detail in Charles (1984).

Mallomonadacean chrysophytes Scales of 20 mallomonadacean species were found in the top 40 cm of sediment core 2, but only eight taxa ever represented more than 2% of the total scale sum (Fig. 5). Throughout the lower portion of the core (i.e., pre-1890), the assemblage is overwhelmingly dominated by the generalist *Mallomonas crassisquama* (Asmund) Fott, with lesser amounts of *M. acaroides* Perty *em* Iwanoff, *M. punctifera*

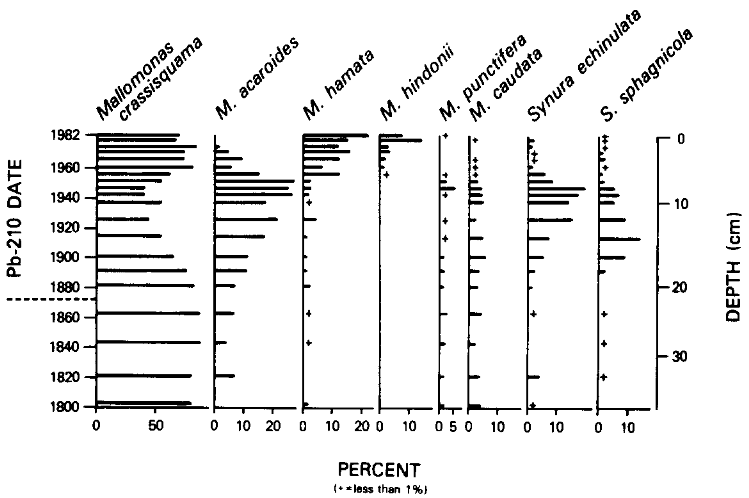

Figure 5. Dominant mallomonadacean chrysophyte taxa in Big Moose L. core 2. Relative abundance is expressed as percent of total scales counted. Data are discussed in more detail in Smol (1986).

Korsh., and *M. caudata* Iwanoff *em.* Krieger. Near the 16-cm level, (about 1902) *M. acaroides, Synura echinulata* Korsh, and *S. sphagnicola* Korsh. increase in relative frequency and continue to maintain moderate populations until 7 cm (about 1955). Based on a study of the relationship of mallomonadacean taxa with limnological characteristics in 38 Adirondack lakes (Smol *et al.*, 1984a; Smol, 1986), these latter three taxa appear to be acidophilic, and it may be argued that the lake began to acidify slightly near the turn of the century.

A second species shift starts near the 7-cm level (about 1950s) when acidobiontic taxa such as *Mallomonas hindonii* Nicholls and *M. hamata* Asmund increase in relative frequency, while more alkaliphilous taxa, such as *M. caudata*, become rare. The changes in Mallomonadaceae in Big Moose Lake (Smol, 1986) coincide with shifts of acidobiontic diatoms (Fig. 4). Also, they are similar to those recorded in the recent sediments of Deep Lake (Smol *et al.*, 1984b), and Upper Wallface Pond (Christie and Smol, 1986).

The accumulation rates of scales (Smol, 1986) indicates that Mallomonadaceae were usually more abundant in Big Moose L. after 1950. This is in marked contrast to the decrease in planktonic diatoms, which occurred during the same period. Possible explanations include reduced competition (e.g., for silica) with diatoms and increased water transparency, which may accompany lake acidification. The latter could lead to increased populations of many deep water chrysophyte species.

Chironomid remains Chironomid larvae usually dominate the macrobenthos in lake sediments, and their headcapsule remains have been used for reconstructing historical lake conditions (e.g., Warwick, 1980). Alterations in chironomid assemblages have been inferred to respond to increased acidity from both anthropogenic (Henrikson *et al.*, 1982) and natural causes (Walker *et al.*, 1985).

The numbers of chironomid head capsules in Big Moose L. core 5 were relatively low, and showed much variation, ranging from 6 to 55.5 per 3-ml sample, with a mean of 19.4. Head capsule accumulation rates and taxonomic richness showed no pattern with sediment depth. The recent increase in *Zalutschia* nr. *briani*, and the decreases in Tanytarsini taxa, *Micropsectra* and *Zavrelia* gp. around 1950 (Fig. 6) were statistically significant. *Z.* nr. *briani* is currently most common in the more acidic Adirondack lakes. Reductions in the Tanytarsini have been observed in Scandinavian acidified lakes (Wiederholm and Eriksson, 1977; Raddum and Saether, 1981; Henrikson *et al.*, 1982). Moreover, similar increases in the abundance of *Z.* nr. *briani* and decreases in the abundance of *Micropsectra* have been observed in stratigraphies from other acidic Adirondack lakes (Uutala, unpubl. information). Thus, the observed variations in these taxa are indicative of increased acidity in Big Moose L. after 1950.

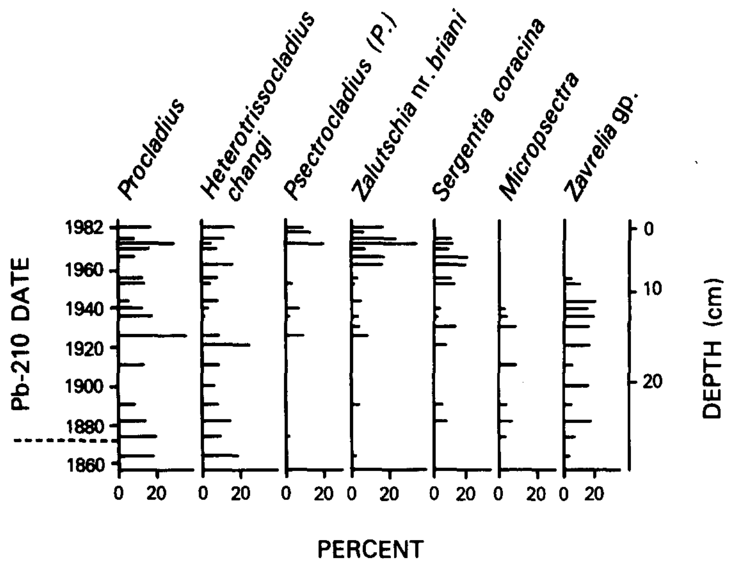

Figure 6. Important chironomid taxa in Big Moose L. core 5. Relative abundance is expressed as percent of total head capsule count. Only *Zalutschia* nr. *briani*, *Micropsectra* and *Zavrelia* gp. showed significant variation ($P < 0.05$) based on the Kolmogorov-Smirnov test for goodness of fit of discrete data (Zar, 1984).

Increases in the relative abundance of *Psectrocladius (P.)* and *Sergentia coracina* have been observed in clear water acid lakes in Scandinavia (Raddum and Saether, 1981; Henrikson *et al.*, 1982). Though similar trends were indicated in Big Moose L., neither was significant. The sample sizes for *Psectrocladius (P.)* were too small to be conclusive. *S. coracina* is often the dominant profundal chironomid in Adirondack lakes, regardless of pH, and may not be positively affected by acidification (Uutala, unpubl. information).

Diatom inferred pH, H^+, and alkalinity Diatom inferred (DI) pH was calculated using index alpha (Nygaard, 1956), index B (Renberg and Hellberg, 1982) and multiple regression (MR) equations based on the percentage of diatoms in pH categories (Charles, 1984, 1985). Coefficients for the equations were calculated using surface sediment diatom assemblage and water chemistry data for 37 Adirondack lakes (Charles, 1985). A weighted average DI pH (Index WA) was then calculated from these three sets of pH values (Fig. 7)

$$\text{Index WA} = \frac{\text{pH}_a + \text{pH}_B + (1.18 \times \text{pH}_{MR})}{3.18}$$

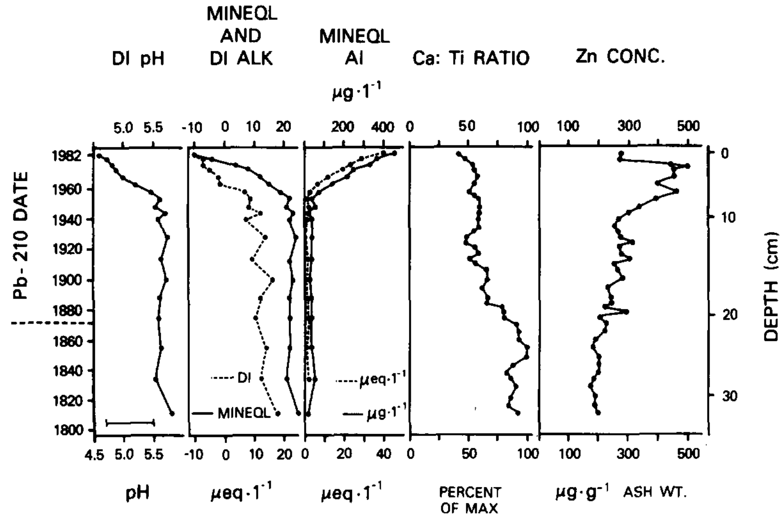

Figure 7. Sediment characteristics (core 2) and computer simulation results indicating recent acidification of Big Moose L. The diatom inferred (DI) pH (Index WA) is a weighted average of slightly modified index alpha, index B and MR equation pH values presented in Charles (1984). Bar represents 95% CI of DI pH for an individual point, based on the predictive relationship determined from the calibration data set. See text for discussion of MINEQL calculations.

where the coefficients are the standard errors of the respective inference equations (Charles, 1985). The standard error for this equation based on 37 Adirondack lakes is ± 0.28 pH units; $r^2 = 0.94$. The averaging procedure smooths the pH profile, and makes it easier to distinguish fluctuations detected by all three indices from those expressed by individual indices. The latter may result from particular sensitivity of an index to changes in a single diatom pH category.

Alkalinity was calculated using a multiple regression equation derived like the pH MR equation, by doing a regression of pH categories with alkalinity instead of pH (Charles, unpublished data). The relationship between DI and measured alkalinity was nearly as good as for pH ($r^2 = 0.91$; SE $= \pm 16\,\mu eq.l^{-1}$ alkalinity). It is important to note that the inferred pH and alkalinity are not independent in that they are both derived from the same diatom data. Advantages of reconstructing alkalinity in addition to pH are that alkalinity is measured on a linear scale, and that it serves as a direct measure of lakewater acidification.

Diatom inferred pH and alkalinity are relatively constant from 1800 (and back to at least 1700, but data not shown) to the 1950s. Values of DI pH and alkalinity then decline to 1982. The rates of changes are rapid, and magnitudes of the changes are relatively great. The DI pH decreased by about 1 pH unit (5.8 to 4.6) in about 30 years (1950–1980). This corresponds to an increase in H^+ of about $25\,\mu mol.l^{-1}$. DI alkalinity decreased by about $30\,\mu mol.l^{-1}$ over the same time period.

To determine if variability of surface sediment diatom assemblages within Big Moose L. might be great enough to suggest that a single core would not be representative of changes within the entire lake, diatoms in 0–1 cm surface sediment samples from 10 locations throughout the lake were analyzed (Charles, unpublished data). There were four dominant taxa in the assemblages, all classified as acidobiontic. Their relative abundance varied widely (e.g., < 10 to 40 percent). However, DI pH values from all locations ranged only from 4.5 to 5.1, suggesting strongly that had cores from other locations been analyzed, similar results would have been obtained.

Computer simulations (MINEQL) We used a computer program that calculates chemical equilibrium of aqueous systems (MINEQL, Westall *et al.*, 1976), and 1977–1978 water chemistry data (Driscoll, 1980) to provide a generalized reconstruction of alkalinity and Al concentrations in Big Moose L. surface water (Charles, 1984) based on the DI pH profile (Fig. 7). The simulated alkalinity values decreased by about $30\,\mu eq.l^{-1}$, declining fastest during the 1950s. The average total dissolved Al increased by over $300\,\mu g.l^{-1}$ during the same time span.

Both DI alkalinity and MINEQL-simulated alkalinity indicate decreases of about $30\,\mu eq.l^{-1}$ in Big Moose L. since the 1950s. This is considerably less than the ca. 100 μeq.l^{-1} decline predicted for Adirondack lakes using some early acidification models (e.g., Hendrey *et al.*, 1980).

Wright's (1983) acidification model is more realistic than earlier models because it assumes that base cation concentrations will increase by some factor (F) because greater SO_4 and NO_3 loading will cause increased cation leaching from the watershed. Agreement between Wright's acidification model and changes in DI alkalinity can be evaluated in part by determining an F-factor based on the diatom data and comparing it with the range suggested by Wright. Assuming a pre-1800 SO_4 concentration of 31 μeq.l^{-1} (Wright, 1983), and current concentrations of ions as measured by Driscoll (1980) (average sum of base cations about 160 μeq.l^{-1}, SO_4 about 150 μeq.l^{-1}), the pre-1800 base cation concentration would have been about 70 μeq.l^{-1} for the pH to have been 5.8. This also assumes no change in Cl (10 μeq.l^{-1}) and NO_3 and NH_4 concentration (undetectable). Changes in HCO_3^-, $RCOO^-$ and Al species concentrations were determined from output of the MINEQL program. The calculated F-factor is more than 0.5, on the high side of Wright's suggested range for an F-factor, but because the calculations are rough, it is not unreasonable. It is similar to some values calculated for other Adirondack lakes (Wright, 1983). The important conclusion is that the rate of watershed cation output has probably increased significantly in the past 30–50 years. This is also supported by preliminary results of application of the ILWAS model to acidification trends in Big Moose L. (G.F. Davis., unpubl. data).

Percent water and loss on ignition There is a strong correlation between water content and organic content (loss on ignition) in Big Moose L. core 2 (Fig. 2), and core 5, which is typical for oligotrophic lakes. In core 2, there is a long-term decline from ca. 1875 to a minimum in the 12.5–13.0 cm interval (1926), followed by an increase toward the sediment surface. The simplest explanation for this trend is that disturbance within the watershed has resulted in the increasing sedimentation of progressively more organic-poor material.

Total metals The shape of the concentration profiles of Mg, Ti, Na, K, and to a lesser extent Al (Charles and Norton, 1986), are similar and have a reciprocal relationship with organic content (Fig. 2). Accumulation rates (μg.cm^{-2}.yr^{-1}), calculated as proportion of total ash weight × concentration of ash (μg.cm^{-3}) × sedimentation rate (cm.yr^{-1}), of these elements increase significantly in the 1920s to a peak in the late 1940s and then decline toward recent times to values nearly equivalent to background values. The accumulation rate of Ti (Fig. 3), a good indicator of watershed erosion, starts increasing in the late 1800s, when watershed disturbance began occurring. There is no clear explanation for the 1940–1950s peak. The concentration of SiO_2 varies only a few percent in the lower part of the core, but decreases by about 20 percent near the surface. Nearly all of the decrease is accounted for by the proportional increase in Fe (Fig. 2). However, the accumulation rate of Si decreases toward the core surface to less than background rates, and may reflect input of biogenic Si in the form of diatom frustules (Fig. 4).

The concentrations of Fe and Mn behave independently from the major elements, and are enriched in surface sediments. This enrichment is diagenetic and ephemeral, migrating upward as the sediment accumulates. The surface enrichment of Fe (nearly all in the oxide form) causes a reciprocal decline in all other elements, effectively diluting them, including ^{210}Pb.

Both the Ca concentration and Ca:Ti ratio profiles (Fig. 7) show gradual decreases since 1850 or so, the greatest changes being near the surface of the core. The Ca:Ti ratio is indicative of the trend in Ca accumulation rate independent of the input of inorganic particulates due to changing watershed erosion patterns. The simplest interpretation is that the slight decline in organic content (and organics are typically 20 to 30% CaO) and/or acidification of the lake water with associated leaching of Ca from the detritus compensates for the general increase in alkalis and alkaline earths. The importance of acidification is supported by the decrease in near surface Ca concentration, Ca accumulation rate, and Ca:Ti ratio values. They are only 60 percent of background values, whereas organic content is equal to background.

Deposition rates of total Pb (Fig. 8) increase from background values starting about the 1860s, and increase by a factor of 25 by ca. 1970. About 95 percent of the increase is from atmospheric inputs, the rest is due to an increase in gross sedimentation of watershed materials. Copper accumulation rate (Fig. 8) increases less distinctly; surface values are 3 times

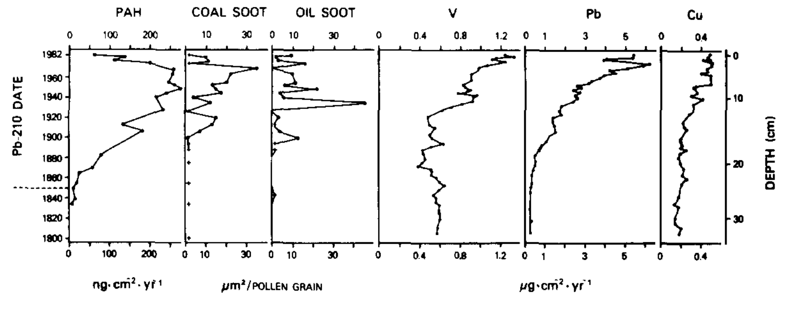

Figure 8. Sediment indicators of fossil-fuel combustion and industrial activity. Profiles of V, Pb, and Cu are based on measurements made on every 0.5 cm interval of core 2. Polycyclic aromatic hydrocarbon (PAH) data is for core 5. A 6–9 percent error is associated with the total PAH concentration determination, based on extraction and analysis of replicate sediment samples.

background values. Zinc concentration (Fig. 7) and accumulation rate increase irregularly starting about 1880 and parallel that of Pb. The peak occurs at 4 cm. Concentration of Zn declines sharply near the sediment surface to values only slightly above background. The decline is consistent with lake water acidification (Kahl and Norton, 1983) and/or diagenesis related to elevated lake water SO_4 and Zn concentration (Carignan and Tessier, 1985). Vanadium, derived largely from oil burning, increases above background after 1935, consistent with increasing oil consumption in the U.S.

Sequential extraction of metals Acid deposition may mobilize metals from the terrestrial ecosystem to lakes where they may be retained in lake sediments. Factors affecting the chemical form and accumulation of these metals in sediments include lakewater pH, concentrations of the metal, other substances which may react with it, and time (Driscoll, 1980; White and Driscoll, 1985). Selective sequential extractions can help to determine the forms in which metals may be bound within sediments, thereby yielding information on changes in these factors that cannot be determined from analysis of total metals alone.

Aluminum is one of the most important metals in the Big Moose system (Driscoll *et al.*, 1987). Schafran and Driscoll's (1987) research implies that significant quantities of Al are retained in Dart's L. (an acidic lake downstream from Big Moose) during low flow periods, and deposited in the sediment. The Al is retained in an acid-labile matrix, which also appears to enhance retention of Pb (White and Driscoll, 1985). In Big Moose L. sediments, the concentration of acid-labile Al forms (exchangeable and oxide fractions, Fig. 9) increases towards the surface. Major increases occur during the 1950s and 1960s. These changes indicate decreasing lakewater pH and increasing Al concentration in the water. The oxide forms of Pb also increase during this period, probably due to increased complexation with oxide forms of Al (White and Driscoll, 1985). The decline in exchangeable Al above 6 cm (1964) may be a result of increasing lakewater H^+ concentration. The H^+ ions would compete for exchange sites on adsorbing surfaces (either in the water column or at the sediment-water interface).

Polycyclic aromatic hydrocarbons Most PAHs enter the environment through the combustion of fossil fuels. They are preferentially adsorbed onto combustion particulates such as soot or fly ash, transported through the atmosphere, and eventually, deposited in aquatic systems. They become incorporated into the sediment, where they remain as a stable component of the stratigraphic record.

The overall PAH profile for Big Moose L. (Fig. 8) is similar to those obtained in previous studies (Gschwend and Hites, 1981). A low, constant

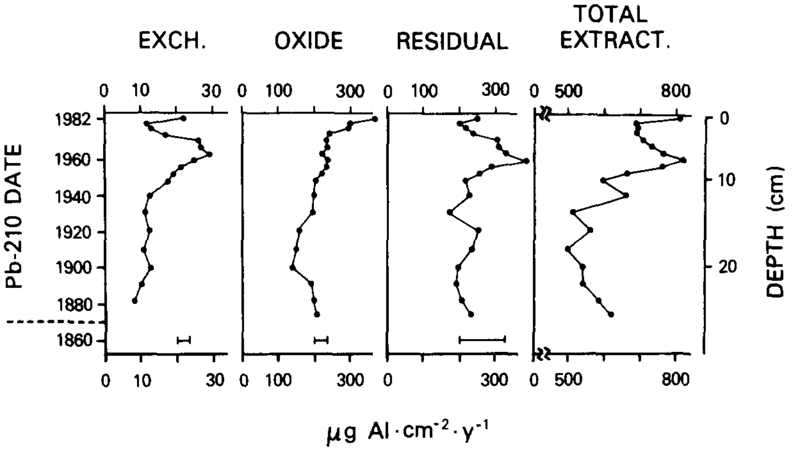

Figure 9. Accumulation rates of sequentially extracted forms of Al in Big Moose L. core 5 (exchangeable, oxide, residual, total extracted). Bars represent the standard deviation of all points in each profile.

level is observed prior to about 1880. This is followed by a sharp increase that corresponds to the large increases in combustion that occurred at the turn of the century. Based on the results obtained here, we conclude that Big Moose L. has experienced a large influx of PAH which implies a large influx of combustion particulates. The decline in PAH accumulation rate starting in the 1970s reflects the recent decrease in combustion of coal and oil in the Northeast (Husar, 1986).

Previous sediment studies (Gschwend and Hites, 1981) indicated low PAH fluxes to remote aquatic systems, whereas sediments from more urbanized systems exhibited much greater fluxes, reflecting the greater input of combustion particulates from nearby point sources. Interestingly, Big Moose L. PAH accumulation rates are similar to those for the urban aquatic systems. Accumulation rates were 1–2 orders of magnitude greater than those to remote New England lakes for corresponding time periods. Data obtained here do correlate, however, with other Adirondack lake studies (Heit *et al.*, 1981). These very high fluxes may be due, in part, to the location of the Adirondack region with respect to emission sources. Atmospheric loadings of other combustion related materials such as sulfur are greater in the Adirondacks than other remote regions (Altshuller and Linthurst, 1984).

Soot particles Soot from coal and oil provides a record of combustion of these fossil fuels that may also correlate with atmospheric deposition of S (e.g., Webber *et al.*, 1985). Coal soot increases in the late 1800s and peaks between 1950–1970 (Fig. 8). Oil soot begins increasing in the early 1900s, reflecting the lag of oil use behind coal use.

Total S and S isotopes Sulfur compounds can be used as paleolimnological indicators of S input to lakes (Holdren *et al.*, 1984; Mitchell *et al.*, 1984, 1985a; Nriagu, 1984; Fry, in press). Studies on lakes from Ontario (Nriagu and Coker, 1983), the Adirondacks (Mitchell *et al.*, 1984) and New England (Mitchell *et al.*, 1985b) all indicate historical increases in S concentration beginning in the mid-to late-1800s, which correspond to the hypothesized period of increased SO_4 emission to the atmosphere (Husar, 1986). However, interpretation of sediment profiles is difficult because S enters lakes in different forms from different sources, and because sediment processes can alter forms and concentrations. Despite these complexities, the sulfur profile can be used to infer an approximate S deposition history. This is because the combination of all important processes incorporating S in sediments will lead to higher total S accumulation rate if S deposition and lakewater concentration increase.

Total S concentrations in Big Moose L. cores 2 (analyzed by Owen and Schindler) and 5 (analyzed by Fry) (Fig. 10) were similar, both indicating an historical increase of S loading to the lake.

The initial S increase in the sediment profiles may result from a combination of two processes: 1) an increase in S input to the sediment

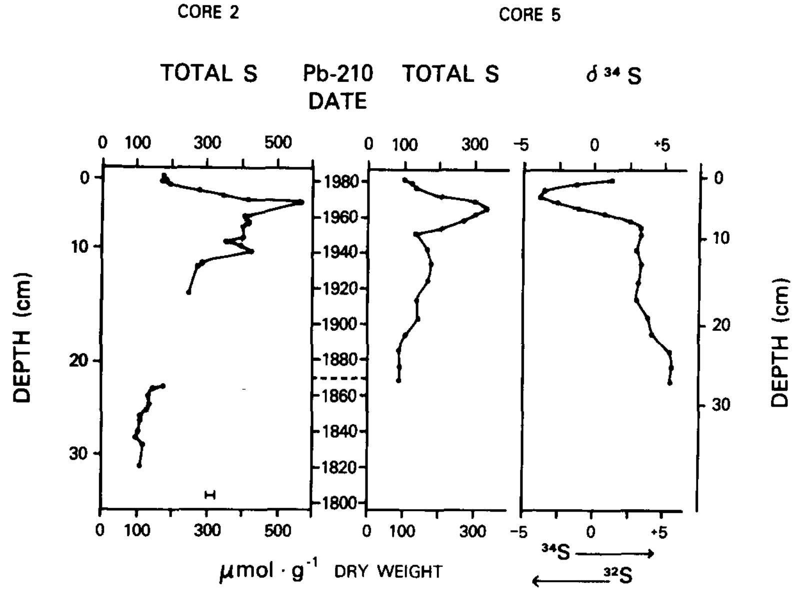

Figure 10. Total S concentration (cores 2 and 5) and S isotope ratio profile in core 5. There is a gap in the total S profile for core 2 because no sediment was available for analysis. Bar for core 2 represents average of all standard errors determined for each point in the profile. Standard errors for each point were based on four analyses.

resulting from an increase in sulfur loading to the lake and watershed (David and Mitchell, 1985) and 2) S diffusing downward from overlying sediment (e.g., Holdren *et al.*, 1984). The decline in S toward the surface (post-1970) may be due both to ongoing sediment processes, and the recent reduction in atmospheric S loading (Husar, 1986). Because of these uncertainties the only conclusion adequately supported by the data is that S loading increased to the lake sometime after the mid to late 1800s.

Bacterial reduction of S is an important mechanism incorporating S into the sediments of Big Moose L. (Rudd *et al.*, 1986a; Nriagu and Soon, 1985), and can contribute alkalinity to lakewater (Cook and Schindler, 1983). Analysis of S isotopes provides information on changes in rates of this process (Fry, in press). Bacterial S reduction is S-limited in many freshwater lakes such as Big Moose, where water column SO_4 concentrations are low, $< 200\,\mu eq.l^{-1}$ (Ingvorsen *et al.*, 1981). Increasing lakewater SO_4 concentration increases the rate of bacterial S reduction (Cook and Schindler, 1983). Bacteria preferentially use the lighter ^{32}S isotope, which leads to enrichment of ^{32}S (lower $\delta^{34}S$ value) as inorganic sulfides produced during sulfate reduction are stored in sediments (Fry, in press). The $\delta^{34}S$ profile for Big Moose L. (Fig. 10) suggests increasing sulfur concentration starting in the late 1800s, and possibly a further significant increase in the 1950s. The sharp increase in the $\delta^{34}S$ values at the top of the core may result from a decline in SO_4 loading to the lake, and probably more importantly, from surface oxidation and loss of ^{32}S enriched sulfides and sulfide-containing materials.

Total C, N, and H Concentrations of C, N, and H in sediments are potentially useful indicators of changes in organic matter decomposition, productivity, or allochthonous inputs that may be related to acidification (e.g., Rao *et al.*, 1984a, 1984b). For example, if the rate of decomposition decreases, the C:N ratio can be expected to increase. The profiles of C, N, and H (mean values of about 15, 1, and $22\,mmol.g^{-1}$ dry wt respectively, for core 2) parallel the percent organic profiles (Fig. 2) and exhibit no major fluctuations. The C:N and other ratios are nearly constant throughout the core. This suggests that no significant changes in processes affecting production or decomposition of organic matter have occurred.

Humic materials Organic compounds including humic acids are important water chemistry components, and can contribute significantly to color and lake acidity (e.g., Cronan and Aiken, 1985). Decreasing lakewater pH and increasing Al concentration can lead to increased loss of these compounds to the sediments. Because Big Moose L. is currently a sink for dissolved organic carbon and alumino-organic solutes (Driscoll *et al.*, 1987) we decided to analyze sedimentary humic materials to assess potential historical changes in water color and DOC resulting from changes in sedimentation of dissolved humic acids (e.g., Engstrom and Hansen, 1985; Davis *et al.*, 1985). Concentration of sedimentary humics varied little from mean values of 36.3 $mg.g^{-1}$ dry wt and 88.5 $mg.g^{-1}$ organic matter, respectively. Humic content per gram dry matter paralleled the percent organic profile (Fig. 2). This trend is eliminated by normalization to organic matter which removes the influence of organic clastics. Although the core analyzed for humic materials was not dated, a similar decline in organic content, evident in the dated cores (2 and 5), suggests the humic content profile would be similar in these cores. Because humic content was measured only in relative units (mg tannic $acid.g^{-1}$) the actual proportion of organic matter extracted as humic material cannot be calculated.

Analysis of Acidification Trends and Potential Causes

Lake and watershed acidification

Big Moose L. DI pH decreased relatively rapidly from about 5.8 to 4.6, and DI alkalinity by about 30 $\mu eq.l^{-1}$, starting in the 1950s (Fig. 7). The recent acidification trend is also strongly indicated by changes in diatom and chrysophyte flora (Figs. 4, and 5), and deposition rates of Ca (Fig. 7), and Al fractions (Fig. 9). Changes in chironomid stratigraphy (Fig. 6), and Zn concentration (Fig. 7) also suggest recent declining pH. The earliest measurements were colorimetric; in 1948, measured pH was 6.0 (NYSDEC), in 1960 and 1965 it was 5.2 (NYSDEC), and in 1977 it was 5.5 (NYSDEC). Later measurements made with pH meters gave pH readings of 4.9 in 1974 (D. Charles, unpublished data), 4.6–5.0 during 1977–1978 (Driscoll, 1980), and an average of 5.1 for the period 1983–1985 (Driscoll *et al.*, 1987). These data are generally consistent with DI pH trends, but are not strong evidence on their own, because the earlier colorimetric data cannot be considered as precise or accurate as the later data, and colorimetric data for low alkalinity water are often biased toward higher values. Sufficient descriptions of procedures were not recorded at the time measurements were made, so it is impossible to attempt a correction of the values (e.g., Kramer and Tessier, 1982). Historical data for Dart's L., which receives most of its water from Big Moose L., are also pertinent. Colorimetric pH was 6.7 in August 1931 (NYSDEC); current annual average pH is 5.1 (Driscoll *et al.*, 1987). The timing and pattern of fish population declines and extinctions in Big Moose L. also suggest recent acidification, major changes being widely observed in the late 1940s (Schofield and Driscoll, 1987).

The current combination of Al concentration and pH are toxic to many fish species which have disappeared or been reduced in numbers in Big Moose L. (Johnson *et al.*, 1987; Schofield and Driscoll, 1987). The reconstruction of lakewater Al concentrations (Fig. 7) using the MINEQL program and the trend of increasing deposition of exchangeable and oxide

Al fractions in the sediment (Fig. 9) both suggest that the concentration of Al in Big Moose L. has increased. The increase of *Fragilaria acidobiontica* (Fig. 4) may also be indicative of higher Al concentration (Charles, 1986). The period of most rapid increase appears to have started after about 1960, after DI pH dropped below about 5.2.

Dissolved organic carbon (DOC) and water color may have decreased in Big Moose L. as a result of decreasing pH and increased Al concentration. Support for this idea includes the ongoing loss of DOC in Big Moose L., Dart's Lake (Driscoll *et al.*, 1987; Effler *et al.*, 1985), Woods L. (Cronan and Aiken, 1985), theoretical considerations and laboratory studies (Almer *et al.*, 1978), limited historical data, and diatom and chrysophyte stratigraphy. Water color of Dart's L. (immediately downstream from Big Moose L.) was described as "brown" in August 1931 (NYSDEC), but currently has no noticeable brown color (C. Schofield, pers. comm.). Abundance of diatom taxa (e.g., *Anomoeoneis serians* var. *brachysira* and *Frustulia rhomboides* var. *saxonica*) that have been shown to be proportional to water color in Norwegian lakes (Davis *et al.*, 1985), decreased in the 1950s (Charles, 1984; Fig. 3). Recent changes in chrysophyte flora and accumulation rates suggest increases in water clarity (Smol, 1986). However, concentration of extracted sediment humic materials and total C, N, and H are relatively constant throughout the Big Moose L. core, suggesting no major change in organic matter (OM) accumulation rate. This latter data cannot be interpreted as strongly indicating no change in water color or increased deposition of OM because watershed outputs of humics may have declined, offsetting an increased proportion of dissolved organic material reaching the sediment. A decrease in watershed outputs might occur because solubility of soil humic materials is apparently reduced at lower pH (Ghosh and Schnitzer 1980; Ritchie and Posner, 1982).

Alternative hypotheses for recent acidification

There are three logical alternative hypotheses to consider as possible explanations of recent acidification of lakes like Big Moose (Charles, 1984; Charles and Norton, 1986). They are: (I) long-term natural acidification caused by factors such as depletion of leachable cations from the watershed, soil development, and increased spread of peatland-type vegetation (e.g., *Sphagnum*) in the watershed causing increased uptake of cations and increased output of hydrogen ions and organic acids (e.g., Rosenquist, 1978); (II) disturbance in watershed vegetation (e.g., fires, logging) followed by regrowth of vegetation and increased uptake of cations from the soil and ground water, which in turn would lead to reduced cation supply to the lake; and (III) increased atmospheric deposition of strong acids. Each of these hypotheses can be evaluated using sediment data to determine if any can be falsified.

(I) Long-term natural acidification Rates of natural acidification, as revealed by paleolimnological analyses of complete lake histories (Battarbee, 1984; Charles and Norton, 1986), are too slow to account for the relatively rapid pH changes after 1950 inferred for Big Moose L. Declines in pH of one unit (pH range 5–6) due to natural processes associated with ecosystem development take hundreds to thousands of years (e.g., three Adirondack High Peaks lakes, Whitehead *et al.*, 1986). There is no evidence of recent increased development of peatland vegetation in the watershed. The gradual decline in DI pH and Ca concentration occurring from the 1800s and 1900s may be related to natural processes.

(II) Watershed disturbance Watershed disturbance and vegetation regrowth cannot explain the recent pH decline in Big Moose L. because: 1) it is unlikely that vegetation regrowth of a low-productivity Adirondack forest could sufficiently reduce watershed output of cations (Nilsson *et al.*, 1982; Martin *et al.*, 1984); 2) there is no logical temporal relationship between vegetation changes and stratigraphic indicators of acidification; and 3) the intensity and magnitude of watershed disturbance events were not major relative to the size of the watershed. At least 30 to 40 percent of the watershed has not been burned or logged. Most of the watershed disturbances which did occur happened between 1870 and 1915. None involved more than 25 percent of the watershed. If disturbance could cause significant acidification, the acid neutralizing capacity of the lake is low enough that at least some evidence of acidification during or immediately following this period should exist, even if only slight. None does.

Because accumulation rates of erosion indicators (Ti, Si, Na) peak around the onset of recent acidification (Fig. 2, 3), it is important to consider potential relationships. Explanations for the increases include a major watershed disturbance and the possibility that the 1950 hurricane force winds resuspended some surface sediment in shallower areas, resulting in its redeposition in deeper areas. There is no record of major disturbance in the 1940s–1950s except the 1950 windstorm, and the amount of vegetation blown down during that event (not more than 20 percent of the watershed) is not great enough to account for the increased acidity by itself. It was probably not greater than the amount of disturbance that occurred in the late 1800s to early 1900s, which resulted in no detectable acidification. Watershed disturbance may have contributed to recent acidification, but it cannot be considered the primary cause.

(III) Increased atmospheric deposition of strong acids The sediment record, in conjunction with other data, supports the hypothesis that the recent acidification of Big Moose L. was caused primarily by increased acid deposition associated with the combustion of fossil fuels.

Acidic deposition is currently being deposited in the Big Moose region, and the SO_4 from that deposition is primarily responsible for the low pH in Big Moose L. (Driscoll and Newton, 1985). There is very strong evidence that the atmospheric S and N being deposited are derived mostly from the combustion of fossil fuels and that there is a roughly linear relationship between emissions of S and atmospheric deposition of S in the eastern U.S. (National Research Council, 1983). Emissions of S are known to have increased significantly from the early 1900s to near the present (Husar, 1986), and therefore sulfate deposition has presumably increased by a factor of about five; (National Research Council, 1986; Wright, 1983). Therefore earlier Big Moose L. SO_4 and Al concentration should have been lower, and pH would have been higher. Thus independent historical data, and current understanding of lake acidification mechanisms indicate that increased acid deposition could have resulted in a decline of lakewater pH and increase in Al concentration at least as great as that inferred from the sediment record.

The timing, magnitude, and rate of DI pH and alkalinity decrease in Big Moose L. (Fig. 7) are consistent with the hypothesis that the changes were caused by acid deposition. The rapid.decrease began in the 1950s following a period of increased deposition of SO_4 and NO_3 starting in the 1900s and peaking in the period 1940 to 1970. Increased SO_4 and NO_3 loadings are the only mechanism which can reasonably account for a pH and alkalinity decrease as great and as rapid as that inferred to have occured. Watershed and within-lake processes have probably modified the influence of increased acid deposition, most likely through changes in cation output from the watershed (G.F. Davis unpubl. data) and SO_4 reduction in the sediments (e.g., Rudd *et al.*, 1986b). This has resulted in DI pH changes (Fig. 7) having occured later and faster than would be expected on the basis of the inferred patterns of fossil fuel combustion (Fig. 8).

Soot particles, PAH, and vanadium (Fig. 8) all reflect increasing atmospheric deposition of materials associated with combustion of fossil fuel. Coal soot and PAH, the best indicators of coal combustion, increase in the early 1900s, and have peak accumulation rates between about 1945 and 1970. The best oil combustion indicators, oil soot and vanadium, also increase in the early 1900s, but show a sharper increase starting in the 1940s. Total S and S isotope data (Fig. 10) indicate increased SO_4 loading from at least early in the century, and possibly before. These data thus suggest a strong correlation between increases in combustion of fossil fuels and SO_4 loading, especially during the 1940s, and increased acidification beginning in the 1950s.

Evaluation of the three alternative hypotheses and their logical consequences indicates that I and II are not supported by the sediment record, but that III is. Therefore, the most reasonable explanation for the recent acidification of Big Moose L. is increased atmospheric deposition of strong acids, though natural acidification and processes associated with watershed disturbance may have played minor contributing roles.

Acknowledgments

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