Journal of Paleolimnology **5**: 267–284, 1991.

Variability in diatom and chrysophyte assemblages and inferred pH: paleolimnological studies of Big Moose Lake, New York, USA

Donald F. Charles[1], Sushil S. Dixit[2], Brian F. Cumming[2] & John P. Smol[2]
[1]*Indiana University, c/o U.S. EPA Environmental Research Laboratory, 200 SW 35th Street, Corvallis, OR 97333, USA*; [2]*Department of Biology, Queen's University, Kingston, Ontario K7L 3N6, Canada*

Received 2 August 1989; in revised form 19 July 1990; accepted 8 November 1990

Key words: variability, diatoms, chrysophytes, acidification, paleolimnology, Adirondacks

Abstract

We measured variability in the composition of diatom and chrysophyte assemblages, and the pH inferred from these assemblages, in sediment samples from Big Moose Lake, in the Adirondack Mountains of New York. Replicate samples were analyzed from (1) a single sediment core interval, (2) 12 different intervals from each of 3 separate cores, and (3) 10 widely spaced surface sediment samples (0–1 cm). The variability associated with sample preparation (subsampling, processing, and counting) was relatively small compared to between-core and within-lake variability. The relative abundances of the dominant diatom taxa varied to a greater extent than those of the chrysophyte scale assemblages. Standard deviations of pH inferences for multiple counts from the same sediment interval from diatom, chrysophyte, and diatom plus chrysophyte inference equations were 0.04 (n = 8), 0.06 (n = 32), and 0.06 (n = 8) of a pH unit, respectively. Stratigraphic analysis of diatoms and chrysophytes from three widely spaced pelagic sediment cores provided a similar record of lake acidification trends, although with slight differences in temporal rates of change. Average standard deviations of pH inferences from diatom, chrysophyte and diatom plus chrysophyte inference equations for eight sediment intervals representing similar time periods but in different cores were 0.10, 0.20, and 0.09 pH unit, respectively. Our data support the assumption that a single sediment core can provide an accurate representation of historical change in a lake. The major sources of diatom variability in the surface sediments (i.e., top 1.0 cm) were (1) differences in diatom assemblage contributions from benthic and littoral sources, and (2) the rapid change in assemblage composition with sediment depth, which is characteristic of recently acidified lakes. Because scaled chrysophytes are exclusively planktonic, their spatial distribution in lake sediments is less variable than the diatom assemblages. Standard deviations of pH inferences for 10 widely spaced surface sediment samples from diatom, chrysophyte and diatom plus chrysophyte inference equations were 0.21, 0.09, and 0.16 of a pH unit, respectively.

Introduction

The number of new paleolimnological studies has increased exponentially during the past decade. Many of these studies have focused on assessing the influence of cultural disturbances (e.g., eutrophication, acid precipitation) on lakes. Considerable progress has been made in several analytical and interpretive procedures, and new techniques are continually being developed (Smol, in press). However, relatively little progress has been made in the measurement, assessment, and reporting of error and variability associated with paleoecological studies. Methods exist (Birks, 1985; Esterby & El-Shaarawi, 1981a, b; Kreis, 1986, 1989; Kreis *et al.*, 1989; Birks *et al.*, 1990), but are rarely used.

Several questions are frequently asked. What error is associated with the subsampling, processing, and analysis of sediment? How well does a single sediment core represent an entire lake? How accurate are inferences of limnological characteristics inferred from calibration data sets based on surface sediment samples? More generally, what are the sources of variability in paleolimnological studies, and how important are they?

Many factors potentially contribute to variability in sediment core analyses. Although variability may be introduced during the sediment coring, subsampling, and analysis procedures, horizontal and vertical variability in lake sediments is thought to be of prime importance. This spatial variability may be influenced by sediment focusing, differential transport of diatom and chrysophyte remains, influence of tributaries, spatial variability in lakewater chemistry, biological and physical mixing of sediment, and diagenesis (e.g., chemical diffusion, dissolution of siliceous remains) (Davis & Ford, 1982; Sweets, 1983; Anderson, 1989).

This paper is part of the variability study component (Kreis, 1986, 1989) of the Paleoecological Investigation of Recent Lake Acidification I (PIRLA I) Project (Charles & Whitehead, 1986). This study was designed to assess the variability in diatom and chrysophyte assemblages within a lake, and the variability associated with enumerating and inferring pH from these assemblages. The results presented in this paper serve as a partial basis for assessing the uncertainty associated with the diatom and chrysophyte analyses of all PIRLA I study lakes. The analyses were performed using the best techniques available in the period 1986 to 1988. Since that time, more sophisticated, accurate, and precise techniques have been developed (e.g. weighted averaging; Birks *et al.*, 1990). Many results presented here may not be applicable to pH inferences based on these more recently developed techniques.

Our study had three major components: (1) counting replicate samples taken from a single sediment interval in order to quantify the variability associated with subsampling, processing, and counting; (2) analyzing three widely spaced cores to assess within-lake variability; and (3) analyzing surface sediment samples taken from 10 widely spaced sites to characterize within-site and among-site (lakewide) spatial variability.

A major conclusion of this study is that a single sediment core can adequately represent the overall trends that have occurred in a lake.

Study site

Big Moose Lake is a relatively large (515 ha), deep (24 m), acidic (pH about 5.0) lake in the southwest Adirondacks, the quadrant with the highest percentage of acidic lakes (Brakke *et al.*, 1988). Big Moose Lake is considered the largest acidic lake in the Adirondacks. It has been studied extensively, primarily with respect to the effects of acidic deposition (Driscoll, 1980; Charles, 1984; Charles *et al.*, 1987; Driscoll & Newton, 1985; Smol, 1986; Rudd, 1987). There is considerable evidence, including paleolimnological (Charles *et al.*, 1987) and historical fish data (Schofield & Driscoll, 1986), that the lake has acidified recently.

Methods

All sediment samples (1 cm^3) for diatom and chrysophyte analysis were subsampled in the

laboratory using calibrated glass syringes with the ends removed. Sediment was digested with nitric acid and potassium dichromate. Slides were counted using research quality microscopes with oil-immersion objectives at 1000 or 1250×. Unless specifically mentioned elsewhere, a minimum of 500 valves and 500 chrysophyte scales were counted for each analysis. Methods are described in more detail elsewhere (Charles, 1985; Smol, 1986; Charles & Whitehead, 1986).

To quantify the variability associated with subsampling, processing, and counting, we used the sample scheme developed for the PIRLA project by Kreis (1986; Fig. 1). We used the 5.0 cm to 7.0 cm interval of Big Moose Lake core 3 as our study sample. Donald Charles counted diatoms on the top half and bottom half of coverslips from slides 1, 5, 9, and 13. Brain Cumming made eight chrysophyte counts from different areas of coverslips from slides 2, 6, 10, and 14 (a total of 32 counts). Counts were made on different areas of the slides to assess the overall variability in the distribution of remains on the cover slips.

To assess between-core variability, we analyzed cores from three sites located approximately 0.5 to 1.0 km from each other. Cores were taken with a 10 cm diameter piston corer with a clear Lucite tube, modified from the design of Cushing & Wright (1965). Cores 2s, 6s, and 8s (Fig. 2) were taken from depths of 13, 18, and 24 m, respectively. Core 2s was taken on 4 August 1982, 6s on 17 July 1985, and 8s on 19 July 1985. The cores were extruded in 1 cm intervals (to 30 cm) in the field. All diatom analyses for these cores were performed by D. Charles, while chrysophyte scale analyses were performed by John Smol. Only 400 diatom valves per interval were counted for core 2s. Analyses of ^{210}Pb activity for cores 2s, 6s, and 8s were performed in Stephen A. Norton's laboratory (University of Maine, Orono; Blake & Norton, 1986). Michael Binford (Harvard University) calculated the ^{210}Pb dates using the constant rate of supply (CRS) model. He also calculated corresponding standard deviations (Binford, 1990). We were most interested in determining how closely the three cores agreed in temporal pattern, in particular how well assemblage composition and inferred pH agreed at corresponding points in time. To accomplish this comparison, we analyzed eight intervals selected from each core in such a way that sets of intervals from the cores had similar dates. The interval selection was done by R.G. Kreis, Jr., using the following mathematical procedure (Kreis, 1986). First, ^{210}Pb dates were determined for the midpoint of

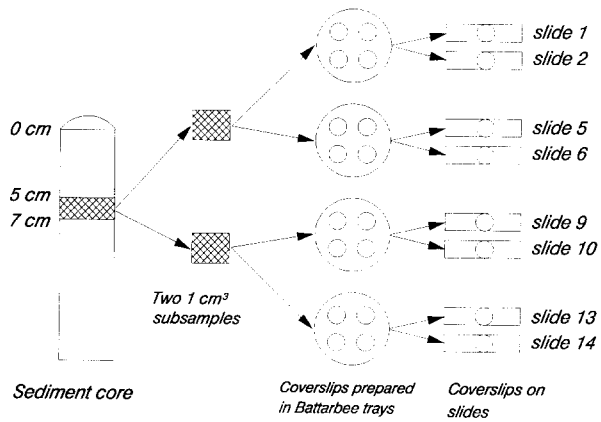


Fig. 1. Design of within-interval intra-laboratory variability study. The 5.0 cm to 7.0 cm interval of Big Moose Lake core 3 was used for this study. Four slides were made from coverslips prepared in each Battarbee tray. Only two of the four cover slips from each tray were used in this study. Diatoms were counted on top and bottom halves of slides 1, 5, 9, and 13. Eight chrysophyte counts were performed on different locations of slides 2, 6, 10, and 14. Results of these analyses appear in Figures 3, 4, and 5 (and Appendices A and B).

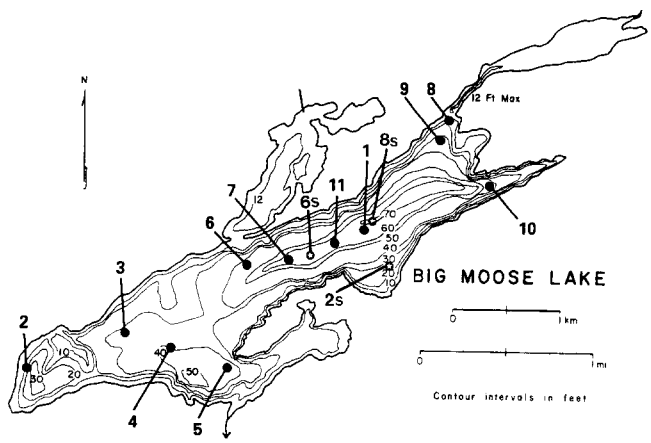


Fig. 2. Location of sediment core sites in Big Moose Lake, N.Y. Solid dots represent surface sediment samples (0.0 cm to 1.0 cm). Circles with stars represent cores that were analyzed stratigraphically (cores 2s, 6s, and 8s).

each core interval. Second, the program SLOTSEQ (Gordon, 1973) was used to choose the set of eight intervals from the three cores for which the dates matched most closely. Third, the selections made in step two were modified slightly to insure that the period 1865–1985 was adequately represented in all cores. Sediments from the final selection of intervals were used for diatom and chrysophyte analysis.

To characterize within-site and lakewide spatial variability, we used surface sediment samples (0.0 cm to 1.0 cm) collected at 10 sites (Fig. 2) with a sediment corer based on the design of Hongve (1972). The most distant sites (2 and 10) are more than 3 km apart. All samples were taken in water deeper than 10 m, since cores for paleolimnological studies would usually not be taken at a shallower depth in a lake as deep as Big Moose Lake. Sites were chosen to maximize expected variability in assemblage composition. For example, sites 3, 6, 9, and 10 are located opposite the entry of major tributaries. At sites 1, 6, and 11, three samples were taken from different sides of an anchored boat to provide an indication of within-site variability. The top 1.0 cm interval of each core was used for analysis. D. Charles enumerated the diatom valves and S. Dixit counted the chrysophyte scales.

All three chrysophyte counters (B. Cumming, S. Dixit & J. Smol) worked in the same laboratory. They cross-checked their taxonomy and verified consistency in enumeration by examining each other's specimens frequently and by periodically analyzing the same slides and comparing counts and identifications. All data were entered and maintained in the PIRLA Data Base Management System (DBMS) (Charles *et al.*, 1989). Diatom (DI pH), chrysophyte (CI pH), and diatom plus chrysophyte inferred pH (D + CI pH) were calculated using equations described by Charles & Smol (1988). Species diversity (H′) was calculated using Shannon & Weaver's (1949) diversity index (Pielou, 1966). Species diversity was calculated only to help characterize the structure of assemblages and as a measure of the ecological information content of individual assemblages.

Results and discussion

The major diatom taxa encountered in the Big Moose Lake sediments were *Achnanthes marginulata* Grun.; *Anomoeoneis serians* v. *brachysira* (Bréb. *ex* Kütz) Hust.; *Asterionella ralfsii* v. *americana* Körn; *Cyclotella stelligera* Cl. *et* Grun.; *Fragilaria acidobiontica* Charles (Charles, 1986); *Fragilaria virescens* v. *exigua* Grun.; *Frustulia magaliesmontana* Cholnoky; *Frustulia rhomboides* v. *saxonica* (Rabh.) De T.; *Melosira nygaardii* Camburn; *Navicula tenuicephala* Hustedt; *Tabellaria flocculosa* v. *flocculosa* strains III, III p, and IV *sensu* Koppen; and *Tabellaria quadriseptata* Knuds. All diatom count data are presented in Charles (1987a, b). The common chrysophyte taxa found were *Mallomonas crassisquama* (Asmund) Fott; *Mallomonas hamata* Asmund; *Mallomonas hindonii* Nicholls; *Mallomonas acaroides* v. *muskokana* Nicholls; *Synura echinulata* Korsh.; and *Synura sphagnicola* Korsh. Smol (1986) has detailed the recent chrysophyte history of Big Moose Lake.

Variability in subsampling, sample preparation, and counting

Subsampling, sample preparation, and counting are potentially important sources of variability in sediment analysis. The replicate count study was undertaken to quantify the combined error attributable to these three factors. Diatom taxa showed larger amounts of variability in the relative abundances of dominant taxa in replicate counts (Fig. 3) than the chrysophyte scales (Fig. 4), although the variability in both algal groups was small. Percentage estimates of nearly all diatom and chrysophyte taxa have standard errors less than 2% (Appendix A, B). Although estimates of chrysophyte taxa relative abundances were less variable than estimates for diatom taxa relative abundances, the variability in the percentage of diatom valves in pH categories (e.g., acidobiontic, acidophilic) was similar to the variability in the percentages of chrysophyte scales in pH categories (e.g., Group 1, Group 2)

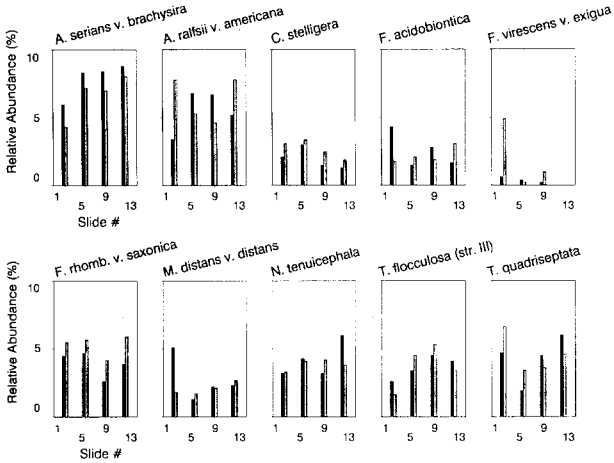


Fig. 3. Percentages of the 10 most common diatom taxa found on slides 1, 5, 9, and 13 from the 5 cm to 7 cm interval, core 3, Big Moose Lake. Dark bars represent counts from the top of each slide, light bars from the bottom portion of each slide. For more details, see Appendix A, Fig. 1.

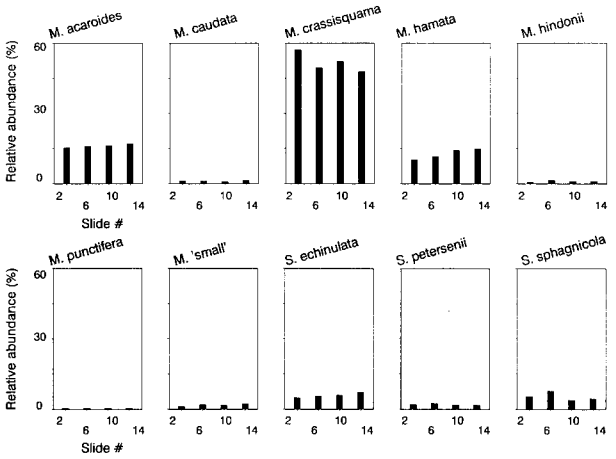


Fig. 4. Percentages of the 10 most common chrysophyte taxa identified on slides 2, 6, 10, and 14 from the 5.0 cm to 7.0 cm interval, core 3, Big Moose Lake. Each bar represents an average of eight replicate counts performed on different portions of the slides. For more details, see Appendix B, Fig. 1.

(Fig. 5). Standard deviations of DI, CI, and D + CI pH inferences for multiple counts from the same sediment interval were 0.04 (n = 8), 0.06 (n = 32), and 0.06 (n = 8) of a pH unit, respectively. The chrysophyte counts used to calculate the D + CI pH values were designated by randomly selecting two of the eight chrysophyte

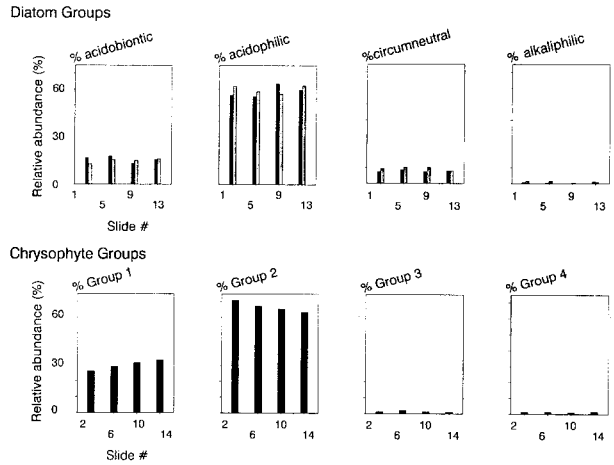


Fig. 5. Bar graphs showing relative abundance of diatoms and chrysophytes in their respective pH categories as described by Charles & Smol (1988). The dark and light bars for the diatom replicate counts represent single counts from the top and bottom portions of the slides, respectively. The dark bars for the chrysophytes each represent the average of eight replicate counts. For more details, see Appendices A and B.

counts performed on each of the slides and matching them with the two diatom counts made on the top and bottom half of each slide. The D + CI pH inference had a standard deviation between the pH values inferred for diatoms alone and for chrysophytes alone. Overall, the variability associated with subsampling, sample preparation, and counting is negligible.

Within-lake variability (inter-core variability)

A major assumption made in most paleolimnological studies is that the record provided by a single sediment core adequately represents temporal trends in a lake's history. We tested this assumption for Big Moose Lake by analyzing three widely spaced cores (2s, 6s, and 8s; Fig. 2).

We found no indication of significant bioturbation or other mixing in the recent sediments of the cores, based on (1) examination of profiles of unsupported ^{210}Pb activity, (2) the relationship between dates and cumulative dry mass (Fig. 6), (3) and direct observation of the sediment core.

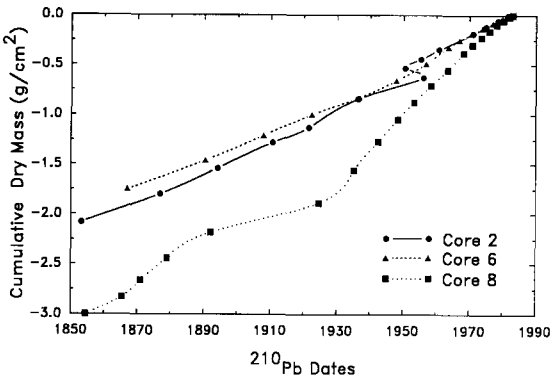


Fig. 6. Cumulative dry mass versus ^{210}Pb date for cores 2s, 6s, and 8s from Big Moose Lake.

At sites 2s and 6s the sediment accumulation rate has remained fairly constant for the past 130 years (about 15 $\mu g\ cm^{-2}$ since 1930); at site 8s, it is more variable (Fig. 6). The sedimentation rate was faster at site 8s than at sites 2s and 6s, probably because site 8s is in the deepest part of the lake and receives sedimentary materials from a larger region.

Profiles of dominant diatom (Fig. 7) and chrysophyte taxa (Fig. 8) are similar in the three cores, but the relative percentages and rates of change differ. Assemblage composition appears to be affected by factors such as depth, distance from shore, and sediment accumulation rate. Despite some floristic differences, DI pH trends are similar for the three cores (Fig. 9). The main difference observed among DI pH profiles (Fig. 9) is that the fastest changes occur earlier in the shallowest core (2s, 1953 to 1973) than in the deeper water cores (6s, 1962 to 1978; 8s, 1953 to 1978). The estimated time at which inferred pH decreased below 5.5 varies from 1955 (2s) to 1967 (6s) to 1970 (8s).

Factors that might be responsible for the differences among cores are: (1) variability in ^{210}Pb dates, (2) variability in sediment accumulation rates, and (3) differential deposition of planktonic versus littoral taxa. The first of these, uncertainty in dating, can account for some of the differences. Standard deviations of the ^{210}Pb dates are about 4, 2, and 1.5 years for cores 2s, 6s, and 8s, respectively. The faster sedimentation rate at site 8s (nearly twice that at site 2s) and the smaller dating standard error of core 8s means that this core should provide finer temporal resolution of limnological change and therefore a slightly different pattern of change. The second potential source of among-core variability is the relative influence of sediment mixing at sites with differing accumulation rates. During a several-year period of lake change, mixing can cause some of the newly deposited sediment particles to be transferred farther down in the sediment, where they can potentially indicate that changes occurred earlier than they did, or at least earlier than would be indicated by a core with a faster sedimentation rate. Another consequence of the mixing is that rates of change would appear to have occurred more slowly. Thus, differences in accumulation rate may explain why the pH appears to have decreased later and faster at site 8s than at sites 6s and 2s. The third possible cause of difference in timing among the cores is the variation in rates of loss of all euplanktonic diatom taxa, primarily circumneutral, and the rates of increase in benthic diatom taxa, primarily acidobiontic and acidophilic. The decline in DI pH occurs in two main phases for all three cores. First, there is a gradual pH decline driven by a steady loss of circumneutral euplanktonic taxa (primarily *Cyclotella stelligera*). This is followed by a more rapid pH decline driven by an increase in acidobiontic benthic taxa. The difference in timing of the post-1950 pH decrease could thus be due partially to variation in lag-time in the transport and deposition of benthic acidobiontic diatoms. As distance from core site to the littoral zone increases, the time required for transport of littoral forms increases. required for transport of littoral forms increases. Thus, the post-1950 pH decrease could have been later in core 8 because this site is farther from shore, and the transport of benthic diatoms to that point took longer.

This latter hypothesis can be tested by examining changes in chrysophyte stratigraphy, taking advantage of the fact that all our chrysophyte taxa are planktonic. Because chrysophytes accumulate directly from overlying water, there should be no difference in rate of transport of scales to core

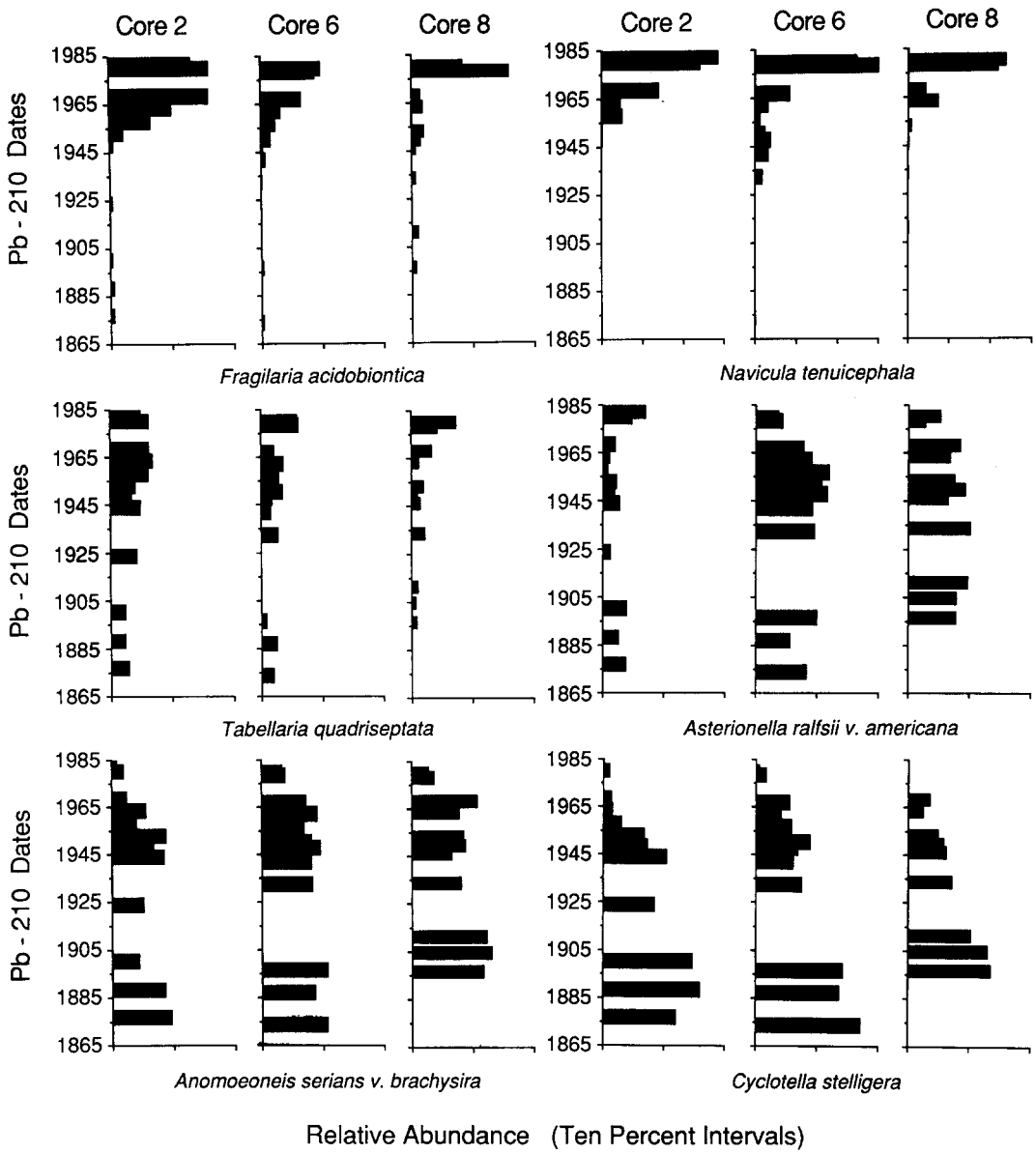


Fig. 7. Profiles of common diatom taxa in Big Moose Lake cores 2s, 6s, and 8s. The horizontal axis is divided into 10% intervals.

sites 2, 6, and 8. Therefore, if the above hypothesis was true, there should be a discrepancy between the onset of chrysophyte changes and the onset of benthic diatom changes, and that discrepancy should increase with increasing distance from the shore. However, as shown in Fig. 8, the chrysophyte changes are in agreement with changes in the diatom taxa, and suggest a more recent post-1950 acidification in the core most distant from shore (8s) compared with the cores closer to shore (6s and 2s). Thus the planktonic : littoral diatom ratio hypothesis cannot by itself explain the temporal differences in diatom stratigraphy and inferred chemistry among the cores. The most logical explanation for the difference in timing of recent changes is the differences in sediment accumulation rates, as discussed above, although variability in dating and pH inference

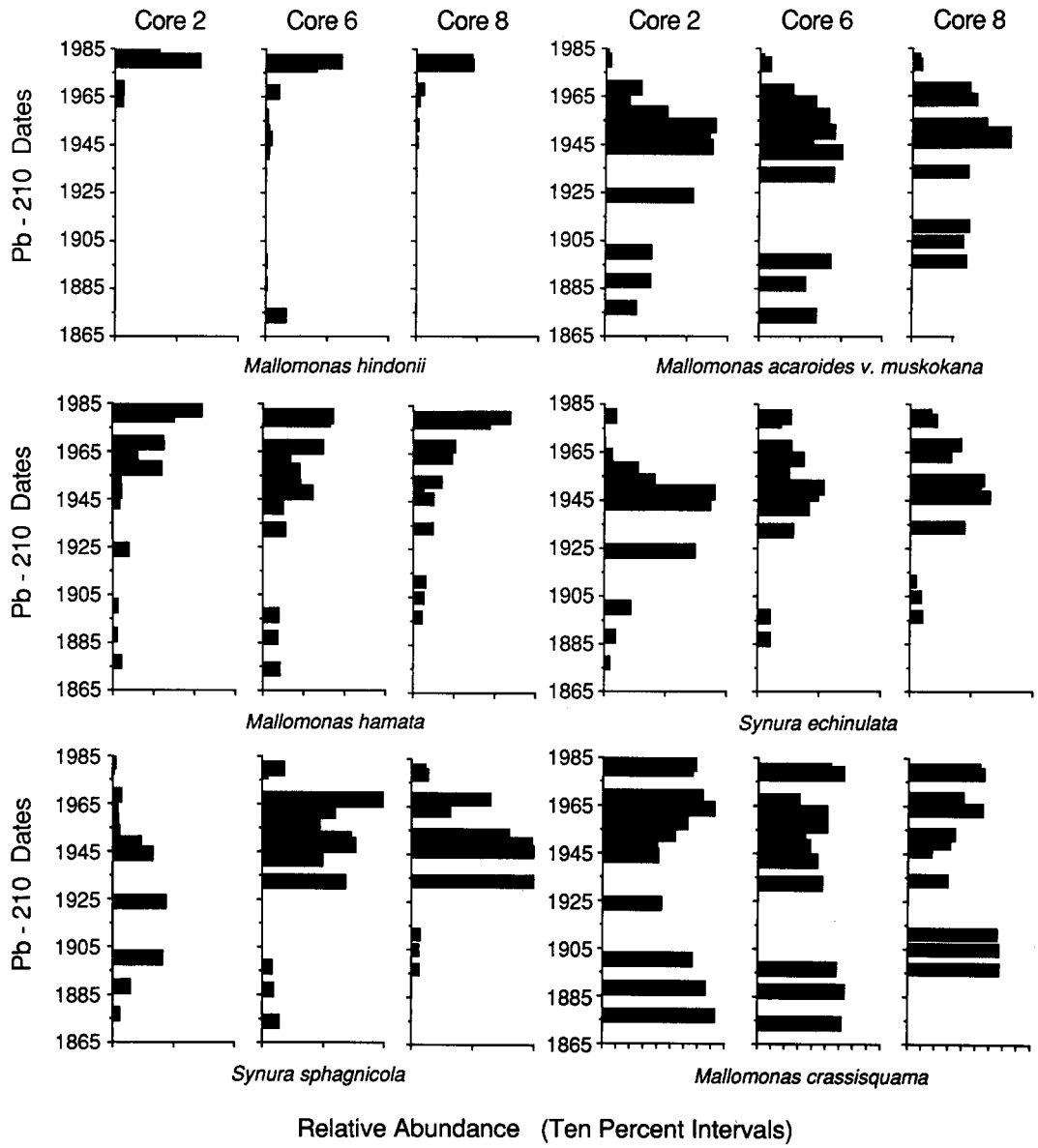


Fig. 8. Profiles of common chrysophyte taxa in Big Moose Lake cores 2s, 6s, and 8s. The horizontal axis is divided into 10% intervals.

calculations may also contribute. It is also important to note that there are relatively few data points covering the period of rapid change, and analyses of more intervals might show that the differences in timing are not as large as our current data indicate.

Variability among inferred pH profiles was examined by comparing DI, CI, and D + CI pH values for closely matched levels of cores 2s, 6s, and 8s (Fig. 10). The DI and D + CI pH profiles have similar trends, but CI pH values were as much as 0.7 pH unit lower. The gradual departure of CI pH from close agreement at the top of the core to ≈ 1900 appears to be related to the high percent abundance of *M. crassisquama* in the lower portion of the cores (60–80%). This taxon occurs in lakes having a wide range of pH and thus may not be a good pH indicator. Charles &

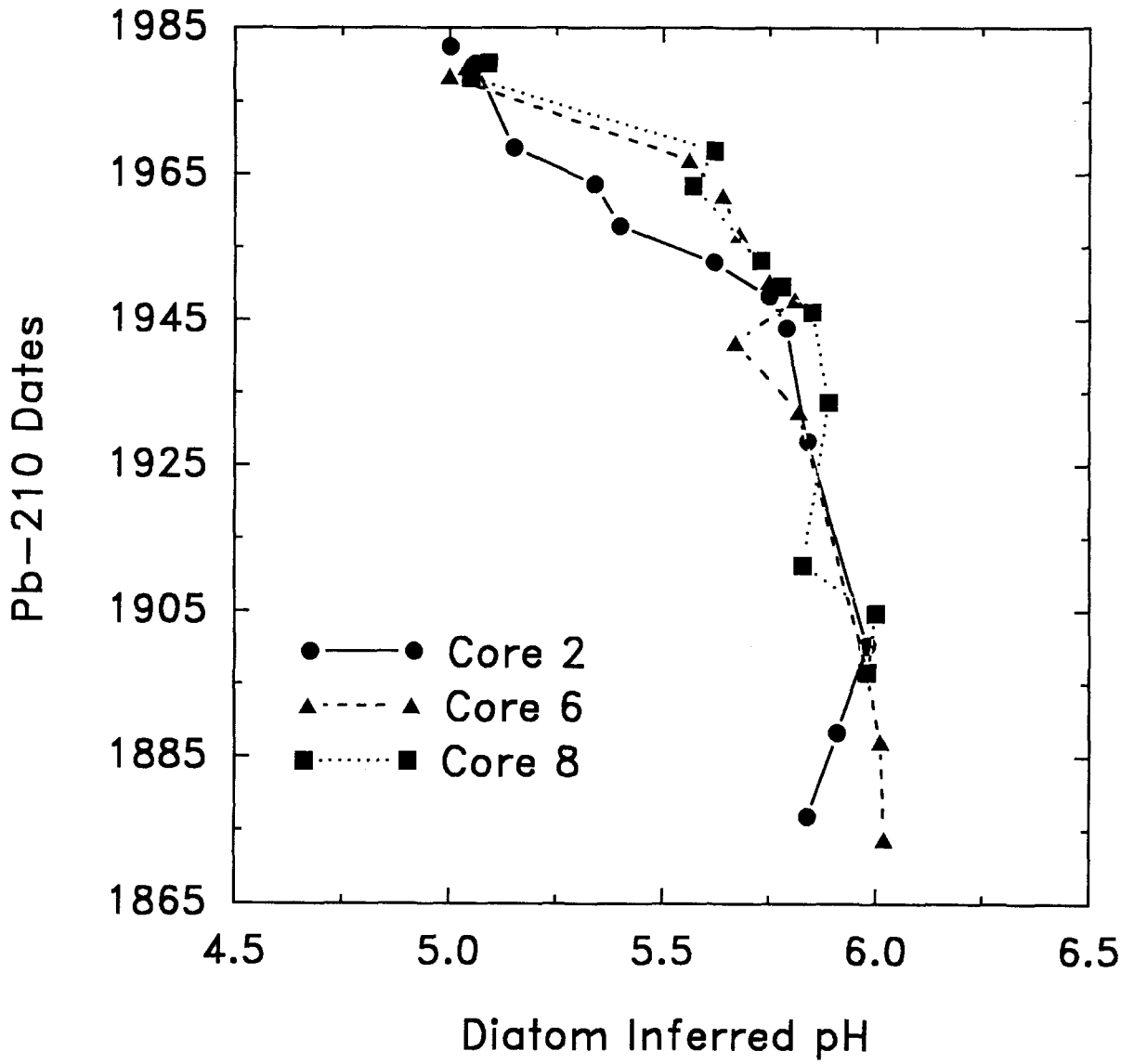


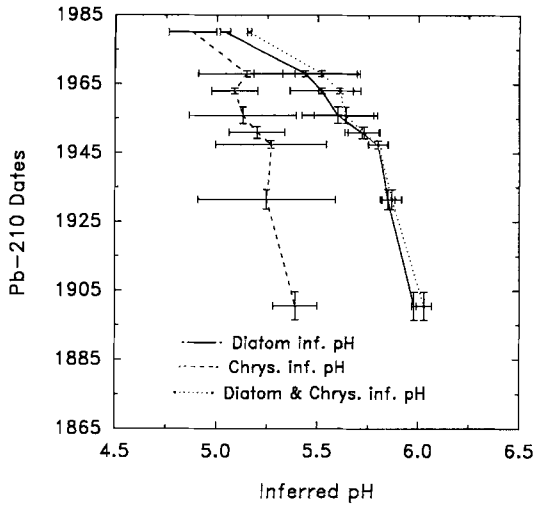
Fig. 9. DI pH profiles for cores 2s, 6s, and 8s, Big Moose Lake calculated by means of inference equations from Charles & Smol (1988).

Smol (1988) have shown that the chrysophyte inference techniques based on pH categories are not sensitive enough to provide accurate pH inferrences for cores in which abundance of *M. crassisquama* changes dramatically. However, this deficiency can be overcome in future studies by taking advantage of the recent advances made in CI pH models (Dixit *et al.*, 1989, 1990; Cumming *et al.*, in press), which incorporate calibration coefficients for individual taxa.

Surface sediment variability

We examined surface sediment assemblages for two reasons; first, to learn more about the variability of diatom and chrysophyte assemblages throughout the lake, and second, to quantify the extent to which this variability translates into variability of inferred pH values.

Both diatom and chrysophyte assemblages showed greater variability in assemblage com-



position among the 10 sites examined than within each site (i.e., the 3 replicate samples taken at each of sites 1, 6, and 11) (Figs. 11 and 12). Eight common diatom taxa comprised between 40% and 70% of the total diatom sum, whereas six common chrysophytes constituted at least 90% of the total counts. Most of the common taxa were present in all sites, but in varying percen-

Fig. 10. DI, CI, and DI + CI pH for eight matched samples for cores 2s, 6s, and 8s from Big Moose Lake. Each point shown is the average of the three values with corresponding dates. Horizontal bars represent the average standard deviations calculated from sets of three points for each profile.

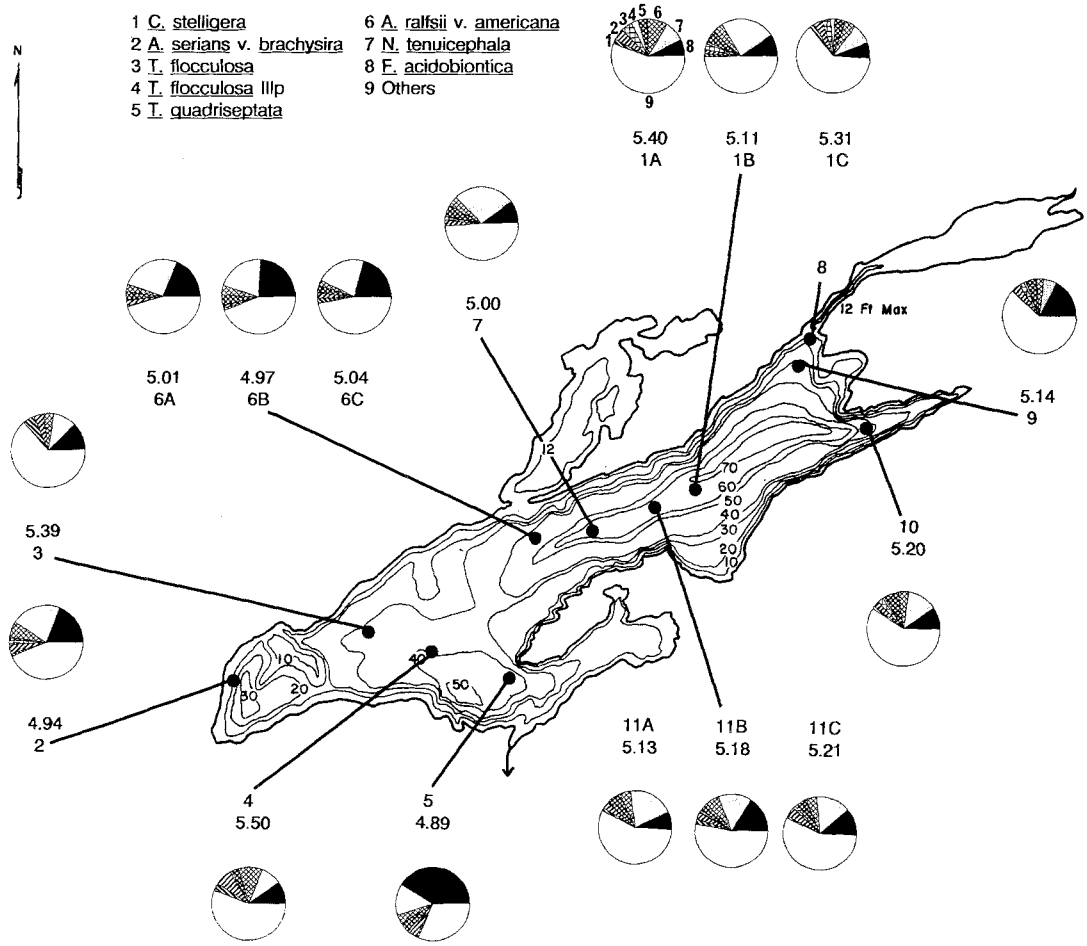


Fig. 11. Percentages of common diatom taxa in 0.0 cm to 1.0 cm surface sediment samples of Big Moose Lake and associated DI pH values. Sample eight was not analyzed because it was taken from shallow water depth.

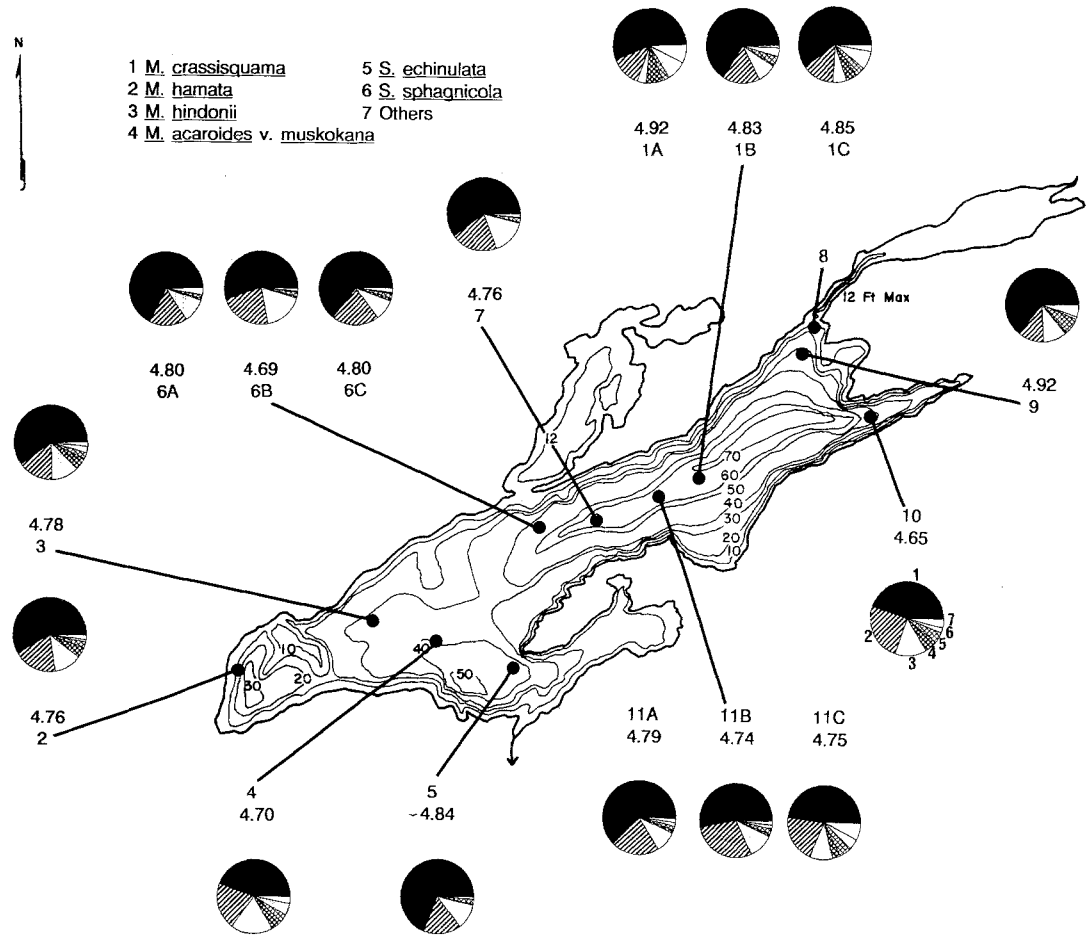


Fig. 12. Percentages of common chrysophyte taxa in 0.0 cm to 1.0 cm surface sediment samples of Big Moose Lake and associated CI pH values. Sample eight was not analyzed because it was taken from shallow water depth.

tages. For example, the most common diatom taxon, *F. acidobiontica*, and the most common chrysophyte, *M. crassisquama*, ranged from 7% to 41% and from 44% to 69%, respectively. The variation in chrysophyte assemblage composition is less than that for diatoms, probably because the chrysophytes are all euplanktonic, and are not affected by the spatial variation in the ratio of inputs of littoral to inputs of euplanktonic forms as are the diatom assemblages.

The variation in the percentages of diatom and chrysophyte taxa in pH categories (e.g., 29% to 61% for acidophilic diatoms), and the pH calculated using these percentages is much less than the variation in percentages of individual taxa. Inferred pH ranged from 4.89 to 5.50 for diatoms alone, 4.65 to 4.92 for chrysophytes alone, and 5.04 to 5.47 for diatoms plus chrysophytes (Table 1; Figs. 11 and 12). Standard deviations of DI, CI, and D + CI pH inferences for the 10 widely spaced surface sediment samples were 0.21, 0.09, and 0.16 of a pH unit, respectively. The range of inferred values is less than 2 standard deviations (0.25 pH units) of the predictive equations.

One-way analysis of variance was used to determine if significant differences occurred among the three sites (1, 6, and 11; Table 2) where the replicate samples were collected. Group means for DI pH were significantly different at the $P < 0.05$ level, but not at the $P < 0.01$ level. The same result was obtained for percentages of

Table 1. Site, diatom and chrysophyte assemblage data, and inferred pH for Big Moose L. surface sediment samples[a].

Site	Depth (m)	Diatom diversity	F. acb. + N.ten.	DI[b] pH	Chrysophyte diversity	CI[b] pH	DI ± CI[b] pH
5	12	2.63	55	4.89	1.56	4.84	5.07
6B	13	2.99	45	4.97	1.16	4.69	5.04
2	10	3.13	41	4.94	1.34	4.76	5.05
6A	13	3.15	45	5.01	1.27	4.80	5.17
6C	13	3.17	43	5.04	1.25	4.80	5.17
7	23	3.29	37	5.00	1.57	4.76	5.10
1B	24	3.42	34	5.11	0.96	4.83	5.25
11A	18	3.53	28	5.13	0.98	4.79	5.23
4	15	3.56	19	5.50	1.16	4.70	5.45
10	18	3.62	23	5.20	1.08	4.65	5.19
11B	18	3.55	31	5.18	1.12	4.74	5.22
11C	18	3.58	27	5.21	1.17	4.75	5.25
3	10	3.72	22	5.39	1.52	4.78	5.44
9	10	3.77	23	5.14	1.11	4.92	5.30
1A	24	3.80	16	5.40	1.34	4.92	5.47
1C	24	3.96	16	5.31	1.57	4.85	5.40
x	16	3.43	32	5.15	1.26	4.79	5.24
SD	5	0.35	12	0.18	0.21	0.08	0.14

[a] Sites are listed in order of increasing diversity of diatom assemblages. Number of taxa identified per site ranged from 61 to 100.

[b] DI = diatom inferred, CI = chrysophyte inferred, SD = standard deviation.

The pH of Big Moose Lake surface water was about 5.0 at the time the sediment cores were taken.

dominant diatom and chrysophyte taxa. This indicates that among-site variability is greater than within-site (sampling) variability.

Relationships among DI pH, assemblage diversity, and the sum of the percentages of the acidobiontic taxa, *Fragilaria acidobiontica* plus *Navicula tenuicephala* are very strong (Table 1). Clearly, a high abundance of these acidobiontic taxa causes low diversity and low DI pH. These relationships are similar to those for diatom assemblages in cores 2s, 6s and 8s.

Although the variability in DI pH among sites was not overwhelming, we wanted to learn more about the causative factors. Likely candidates were: (1) spatial variation in water chemistry, (2) differences in contribution of source area (e.g., littoral vs. pelagic zone), and (3) differences in the time intervals represented by each 0.0–1.0 cm sample.

Spatial differences in water chemistry may have had some influence on assemblage composition, but probably not much. Available water chemistry data (Charles, 1984; Driscoll, 1980; Driscoll & Newton, 1985) suggest there is relatively little spatial variability. Laboratory measurements of surface sample pH in the fall of 1974 for five sites throughout the lake ranged from 4.9 to 5.0 (Charles, unpublished data). Monthly surface samples taken between July 1978 and August 1987 ranged from 4.60 to 4.96; the lowest values occurred from January to April (Driscoll, 1980).

We can discern no clear relationships between depth of site, distance from shore, or geographic location and inferred pH, planktonic : littoral ratio, or percentage of common taxa. In earlier surface sediment variability studies, where samples were taken from pelagic as well as littoral zones, strong habitat dependent distributions were identified for diatoms (Meriläinen, 1971; Renberg, 1978; DeNicola, 1986; Dixit & Evans, 1986; Jones & Flower, 1986; Earle *et al.*, 1988). Perhaps differential contributions from source

areas did not have as much influence on the composition of the samples we analyzed because all our samples were taken from > 10 m of water depth, and valves and scales were dispersed more widely than they would have been if samples had been taken closer to shore in shallower water, as was done in the other studies. Another possibility is that spatial and source habitat influences are real and important, but are not clearly discernible because temporal factors also have a strong influence on assemblage composition, as discussed below.

The third potential source of variability is the difference in time period represented by each sample. This difference is potentially important in a lake with changing algal populations, but difficult to assess. It is clear from examination of rapid changes in diatom and chrysophyte composition and in inferred pH near the surface of cores 2s, 6s, and 8s (Figs. 7, 8, and 9) that variability among surface samples could be significant if the samples represent different time periods. There are at least three possible sources of temporally related variability. One is sedimentation rate. A 1.0 cm sample at a site with a fast sedimentation rate represents less time than a similar depth interval sample from a site with a slower sedimentation rate. Another source is sediment mixing. The amount of time represented by a surface sample can increase as a function of increased mixing depth. A third source of temporal variability is that surface sediment samples taken with a Hongve corer are not always precisely 1.0 cm in thickness. A sample slightly less than 1.0 cm may represent less time than a sample slightly greater than 1.0 cm. Because sedimentation and mixing rates are not known for the sample sites, it is impossible to directly assess the importance of the first two factors. However, variability due to imprecision in collection of 1.0-cm samples can be evaluated by comparing results among the triplicate surface cores taken at sites 1, 6, and 11. The three samples taken at each site should have similar sediment accumulation and mixing rates and most within-site differences should be due to coring variability. Standard deviations for triplicate values of DI pH at these three sites were 0.15, 0.04, and 0.04 of a pH unit. These values are relatively small compared with the standard deviation of 0.21 for all surface sample sites. We can therefore say that sampling variability probably accounts for only a small part of the overall variability among surface samples.

We are then left with the conclusion that variability is related primarily to differences in contributions from source areas or differences in the time periods represented, the latter being a function of variability in sedimentation and mixing rates throughout the lake. For example, an assemblage with low DI pH and low diversity due to a high proportion of acidobiontic taxa could occur at near-shore sites close to major sources of benthic acidobiontic diatoms, or could be located in deep water sites with high sedimentation rates where surface samples represent a short period of time and contain only diatoms representing the most recent acidic conditions. We cannot quantify the importance of the two for the lake overall, or for specific sites.

We have identified and quantified several sources of variability in analysis of diatom and chrysophyte assemblages (Table 2). In general, variability among samples was not extensive, and is less than the standard error of the predictive techniques. Variability in analytical procedures (subsampling, processing, and counting) was relatively small compared to within-lake variability. No distinct spatial or temporal patterns can be identified in the distribution of littoral versus planktonic diatom assemblages.

Our study provides information that can be used in designing future sampling programs. Data for calibration sets might more accurately represent current limnological conditions if multiple samples were taken and pooled, either before or after analysis. Before taking cores, surface sediment samples from different water depths could be examined briefly to determine the optimal site for coring based on (1) relative proportions of littoral and planktonic diatoms, (2) the combination of diatom and chrysophyte assemblages, and (3) sedimentation rate and corresponding temporal resolution.

Table 2. Sources and estimates of variability associated with analysis of diatom and chrysophyte assemblages in cores and surface sediments[a].

	Variability due to sample preparation and analysis		Variability among surface sediment samples		Variability among triplicate cores	
	Mean Inf. pH	SD	Mean Inf. pH	SD	Ave.	Range (min → max)
DI pH	5.54	0.04 (n = 8)	5.16	0.21 (n = 16)	0.10	0.02 → 0.15
CI pH	4.92	0.06 (n = 32)	4.79	0.09 (n = 10)	0.20	0.11 → 0.34
DI + CI pH	5.56	0.06	5.25	0.16	0.09	0.01 → 0.19

[a] Data for counting, processing, and subsampling variability were obtained from the replicate counts, data for inter-core variability from the triplicate core study, and data for surface sediment variability from that study. Variability is expressed as standard deviations (pH units).

Conclusions

1. The variability associated with subsampling, processing, and counting is relatively small compared to within-core and among-core variability.
2. Analysis of a single pelagic core accurately represents the overall acidification trend in Big Moose Lake, although some differences in timing occur and appear to be due to differences in sediment accumulation rates and transport processes.
3. Variability in diatom and chrysophyte assemblages among surface samples is caused primarily by: (a) relative input of littoral versus planktonic forms, as determined by such factors as geographic location within the lake, water depth, and distance from shore, and (b) the time period represented by each sample, which is a function of depth of the surface core (0 to 1.0 cm) actually taken, the sedimentation rate, and sediment mixing.
4. Variation in composition of surface sediment assemblages, due to the factors described above, may be an important source of error in diatom and chrysophyte assemblages used in calibration data sets for acidifying low pH lakes, especially those with slow sedimentation rates.
5. Values of pH inferred from surface sediment assemblages are less variable than the percentages of individual taxa comprising those assemblages.
6. The variation among surface sediment CI pH values was less than the variation among DI pH and D + CI pH values. However, as discussed in Charles & Smol (1988), inferences based solely on chrysophytes are not as accurate and precise as those for diatoms, and must therefore be interpreted with caution.
7. Standard deviations of DI, D + CI, and CI pH calculated for multiple samples from: (a) the same sediment core interval, (b) intervals with corresponding ^{210}Pb dates from three separate cores, and (c) surface sediment samples (0 to 1.0 cm) from 10 widely spaced sites are all less than the standard error of the correlation between inferred and measured pH for the calibration data sets used to derive the equations. Hence, the error associated with the predictive equations is greater than any of the within-lake variability or processing and analytical errors measured in this study.

These conclusions support the assumption that inferences from a single sediment core from the deeper part of a lake can provide an accurate representation of historical water chemistry changes.

Acknowledgements

This paper is contribution number 31 of the Paleoecological Investigation of Recent Lake Acidification (PIRLA) Project, funded by the Electric Power Research Institute (RP-2174-10). Support was also provided by a grant from the National Science Foundation (BSR-861722), and by the U.S. Environmental Protection Agency (Cooperative Agreement No. CR813933 with Indiana University). The paper has been subjected to the EPA's peer and administrative review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

We thank the several people who contributed to this effort. Deborah Sorucco prepared all microscope slides for counting of diatoms and chrysophytes. Harith Ahmad, P. Roger Sweets, and Allen Uutala were responsible for retrievals from the PIRLA data base. Eric Rusack entered much of the count data into computer files. Susan Christie provided many helpful editorial suggestions. We also thank Françoise Gasse for serving as guest editor.

References

Anderson, N. J., 1989. A whole-basin diatom accumulation rate for a small eutrophic lake in Northern Ireland and paleoecological implications. J. Ecol. 77: 926–946.

Binford, M., 1990. Calculation and uncertainty analysis of ^{210}Pb dates for PIRLA project lake sediment cores. J. Paleolim. 3: 253–267.

Birks, H. J. B., 1985. Recent and future mathematical developments in quantitative palaeoecology. Palaeogeogr., Palaeoclimatol., Palaeocol. 50: 107–147.

Birks, H. J. B., J. M. Linee, S. Juggins, A. C. Stevenson & C. J. F. ter Braak, 1990. Diatoms and pH reconstruction. Phil. Trans. r. Soc., Lond. B 327: 263–278.

Blake, G. & S. A. Norton, 1986. Lead-210 dating. In D. F. Charles and D. R. Whitehead (eds). Paleoecological Investigation of Recent Lake Acidification (PIRLA): Methods and project description. EPRI EA-4906. Electric Power Research Institute, Palo Alto, CA: 9–1 to 9–4.

Brakke, D. F., D. H. Landers & J. M. Eilers, 1988. Chemical and physical characteristics of lakes in the Northeastern United States. Envir. Sci. Technol. 22: 155–163.

Charles, D. F., 1984. Recent pH history of Big Moose Lake (Adirondack Mountains, New York, U.S.A.) inferred from sediment diatom assemblages. Verh. int. Ver. Limnol. 22: 559–566.

Charles, D. F., 1985. Relationships between surface sediment diatom assemblages and lakewater characteristics in Adirondack lakes. Ecology 66: 994–1011.

Charles, D. F. & J. P. Smol, 1988. New methods for using diatoms and chrysophytes to infer past pH of low-alkalinity lakes. Limnol. Oceanogr. 33: 1451–1462.

Charles, D. F., 1986. A new diatom species, *Fragilaria acidobiontica*, from acidic lakes in northeastern North America. In J. P. Smol, R. W. Battarbee, R. B. Davis & J. Meriläinen (eds). Diatoms and lake acidity. Dr W. Junk, Dordrecht, The Netherlands: 35–44.

Charles, D. F., 1987a. Diatom counts of Adirondack lake surface sediment samples. PIRLA Unpublished Report Series, Report Number 11, Indiana University, Bloomington, IN.

Charles, D. F., 1987b. Diatom counts of Adirondack lake surface sediment samples. PIRLA Unpublished Report Series, Report number 12, Department of Biology, Indiana University, Bloomington, IN. 393 pp.

Charles, D. F. & J. P. Smol, 1988. New methods for using diatoms and chrysophytes to infer past pH of low-alkalinity lakes. Limnol. Oceanogr. 33: 1451–1462.

Charles, D. F. & D. R. Whitehead, (eds) 1986. Paleoecological Investigation of Recent Lake Acidification (PIRLA): Methods and Project Description. EPRI EA-4906 Electric Power Research Institute, Palo Alto, CA. 228 pp.

Charles, D. F., J. P. Smol, A. J. Uutala, P. R. Sweets & D. R. Whitehead, 1989. The PIRLA DataBase Management System. INQUA – Commission for the Study of the Holocene. Newsletter of the Working Group on Data Handling Methods. 2: 3–6.

Charles, D. F., D. R. Whitehead, D. R. Engstrom, B. D. Fry, R. A. Hites, S. A. Norton, J. S. Owen, L. A. Roll, S. C. Schindler, J. P. Smol, A. J. Uutala, J. R. White & R. J. Wise, 1987. Paleolimnological evidence for recent acidification of Big Moose Lake, Adirondack Mountains, N.Y. (USA). Biogeochemistry 3: 267–296.

Cumming, B. F., J. P. Smol & H. J. B. Birks, 1991. The relationship between sedimentary chrysophyte scales (Chrysophyceae and Synurophyceae) and limnological characteristics in 25 Norwegian lakes. Nord. J. Bot. (in press).

Cushing, E. J. & H. E. Wright, Jr., 1965. Hand operated piston corers for lake sediments. Ecology 46: 380–384.

Davis, M. B. & M. S. Ford, 1982. Sediment focusing in Mirror Lake, New Hampshire. Limnol. Oceanogr. 27: 137–150.

DeNicola, D. M., 1986. The representation of living diatom communities in deep-water sedimentary diatom assemblages in two Maine (USA) lakes. In J. P. Smol, R. W. Battarbee, R. B. Davis & J. Meriläinen (eds). Diatoms and Lake Acidity. Dr W. Junk Publishers, Dordrecht, The Netherlands: 73–85.

Dixit, S. S. & Evans, 1986. Spatial variability in sedimentary algal microfossils and its bearing on diatom-inferred pH reconstructions. Can. J. Fish. aquat. Sci. 43: 1836–1845.

Dixit, S. S., A. S. Dixit & J. P. Smol, 1989. Relationship between chrysophyte assemblages and environmental variables in seventy-two Sudbury lakes as examined by canonical correspondence analysis (CCA). Can. J. Fish. aquat. Sci. 46: 1667–1676.

Dixit, S. S., J. P. Smol, D. S. Anderson & R. B. Davis, 1990. Utility of scaled chrysophytes for inferring lakewater pH in northern New England. J. Paleolim. 3: 269–286.

Driscoll, C. T., 1980. Chemical characterization of some dilute acidified lakes and streams in the Adirondack region of New York State. Ph.D. dissertation, Cornell University, Ithaca.

Driscoll, C. T. & R. M. Newton, 1985. Chemical characteristics of Adirondack lakes. Envir. Sci. Technol. 19: 1018–1024.

Earle, J. C., H. C. Duthie, W. A. Glooschenko & P. B. Hamiliton, 1988. Factors affecting the spatial distribution of diatoms on the surface sediments of three Precambrian shield lakes. Can. J. Fish. aquat. Sci. 45: 469–478.

Esterby, S. R. & A. H. El-Shaarawi, 1981a. Likelihood inference about the point of change in a regression regime. J. Hydrobiol. 53: 17–30.

Esterby, S. R. & A. H. El-Shaarawi, 1981b. Inference about the point of change in a regression model. J. App. Stat. 30: 277–285.

Gordon, A. D., 1973. A sequence comparison statistic and algorithm. Biometrika 60: 197–200.

Hongve, D., 1972. En bunnhenter som er lett a lage. Fauna 25: 281–283.

Jones, V. J. & R. J. Flower, 1986. Spatial and temporal variability in periphytic diatom communities: paleoecological significance in an acidified lake. In J. P. Smol, R. W. Battarbee, R. B. Davis & J. Meriläinen (eds). Diatoms and Lake Acidity. Dr W. Junk Publishers, Dordrecht, The Netherlands: 87–94.

Kreis, R. G., Jr., 1986. Variability study. In D. F. Charles & D. R. Whitehead (eds). Paleoecological Investigation of Recent Lake Acidification (PIRLA): Methods and Project Description. EPRI EA-4906. Electric Power Research Institute, Palo Alto, CA, USA: 17–1 to 17–19.

Kreis, R. G., Jr., 1989. Variability study – interim results. In D. F. Charles & D. R. Whitehead (eds). Paleoecological Investigation of Recent Lake Acidification (PIRLA): 1983–1985. EPRI EN-6526. Electric Power Research Institute, Palo Alto, CA, USA: 4–1 to 4–48.

Kreis, R. G., Jr., J. C. Kingston, K. E. Camburn & R. B. Cook, 1989. Diatom-pH relationships in the northern Great Lakes region for predicting past lake acidity. In D. F. Charles & D. R. Whitehead (eds). Paleoecological Investigation of Recent Lake Acidification (PIRLA): 1983–1985. EPRI EN-6526. Electric Power Research Institute, Palo Alto, CA, USA: 10–1 to 10–35.

Meriläinen, J., 1971. The recent sedimentation of diatom frustules in four meromictic lakes. Ann. bot. fenn. 8: 160–176.

Pielou, E. C., 1966. Shannon's formula as a measure of specific diversity: its use and misuse. Am. Nat. 100: 463–465.

Renberg, I., 1978. Paleolimnology and varve counts of the annually laminated sediment of Lake Rudetjärn, Northern Sweden. Early Norrland 11: 63–92. Stockholm.

Rudd, J. W. M. (ed.), 1987. Acidification of the Moose River System in the Adirondack Mountains of New York State. Biogeochemistry 3: 1–296.

Schofield, C. L. & C. T. Driscoll, 1986. Fish species distribution in relation to water quality gradients in the North Branch of the Moose River Basin. Biogeochemistry 3: 63–85.

Shannon, J. C. & W. Weaver, 1949. The mathematical theory of communication. Univ. Illinois Press, Urbana, IL.

Smol, J. P., 1986. Chrysophycean microfossils as indicators of lakewater pH. In J. P. Smol, R. B. Battarbee, R. B. Davis & J. Meriläinen (eds). Diatoms and Lake Acidity. Dr W. Junk, Dordrecht, The Netherlands: 275–287.

Smol, J. P. Paleolimnology – recent advances and future challenges. In R. DeBernardi, G. Giussani & L. Barbanti (eds). Scientific Perspectives in Theoretical and Applied Limnology. Mem. Ist. Ital. Idrobiol. 47: (in press).

Sweets, P. R., 1983. Differential deposition of diatom frustules in Jellison Hill Pond, Maine. Masters thesis. University of Maine, Orono, ME.

Appendix A. Diatom replicate count data for Big Moose Lake, core 3, 5.0 cm to 7.0 cm interval.[a]

Slide/ cover slip half	Anom. brach.	Aster. ralfsii amer.	Cycl. stell.	Frag. acb.[b]	Frag. vir. exig.	Frust. rhomb. sax.	Melos. distans	Nav. tenuic.	Tabell. flocc. str. III	Tabell. quad.	Num. of taxa	Diversity H′	DI[b] pH	Pct. acb.[b] diat.	Pct. acf.[b] diat.	Pct. cir.[b] diat.	Pct. alk.[b] diat.
1T	6.0	3.4	2.1	4.3	0.6	4.5	5.1	3.2	2.6	4.7	117	4.20	5.49	16.9	56.4	7.5	0.9
1B	4.3	7.8	3.1	1.8	4.9	5.5	1.8	3.3	1.6	6.6	108	4.10	5.56	13.0	61.9	9.5	1.6
5T	8.3	6.8	3.0	1.5	0.4	4.7	1.3	4.3	3.4	1.9	117	4.11	5.50	17.9	55.6	8.7	0.4
5B	7.2	5.3	3.4	2.1	0.2	5.7	1.7	4.1	4.5	3.4	119	4.18	5.61	15.8	58.6	10.4	1.7
9T	8.4	6.7	1.5	2.8	0.2	2.6	2.2	3.2	4.5	4.5	122	4.13	5.52	13.3	63.6	7.5	0.2
9B	7.0	4.2	2.5	1.9	1.0	4.2	2.1	4.2	5.3	3.6	133	4.29	5.56	15.3	57.1	10.2	0.6
13T	8.8	5.2	1.3	1.7	0.0	3.9	2.3	6.0	4.1	6.0	123	4.11	5.53	15.9	59.6	8.2	1.1
13B	8.0	7.8	1.9	3.1	0.0	5.9	2.7	3.8	3.4	4.6	114	4.06	5.51	16.3	62.3	8.0	1.0
x	7.3	5.9	2.4	2.4	0.9	4.6	2.4	4.0	3.7	4.4	119	4.15	5.54	15.5	59.4	8.8	0.9
SD[b]	1.5	1.6	0.8	0.9	1.6	1.1	1.2	0.9	1.2	1.5	7	0.07	0.04	1.7	3.0	0.5	0.5

[a] Percentages of the 10 most common taxa, inferred pH, and other data. See Fig. 1 for diagram of replicate count design. See text for full taxonomic names.
[b] acb = acidobiontic; acf = acidophilic; cir = circumneutral; alk = alkaliphilic; DI = diatom inferred; SD = standard deviation.

Appendix B. Chrysophyte replicate count data for Big Moose Lake, core 3, 5.0 cm to 7.0 cm interval.[a]

Slide Cover-slip	M. acar.	M. caud.	M. cras.	M. hama.	M. hind.	M. punc.	M. 'small'	S. ech.	S. pete.	S. spha.	Num. of taxa	Diversity H'	CI[b] pH	DI + CI[b] pH	Pct. Group 1	Pct. Group 2	Pct. Group 3	Pct. Group 4
Slide 2	(n = 8)																	
x	15.26	1.18	57.20	10.20	0.63	0.37	1.25	4.94	2.08	5.42	12.50	1.45	4.96	5.58	26.39	70.88	1.47	1.25
SD	2.45	0.39	2.15	1.04	0.28	0.17	0.39	1.08	0.59	1.46	1.12	0.06	0.05	0.03	2.08	1.65	0.54	0.46
Slide 6	(n = 8)																	
x	15.94	1.09	49.59	11.50	1.46	0.40	1.92	5.60	2.44	7.80	12.88	1.65	4.94	5.59	29.38	67.34	1.95	1.34
SD	1.37	0.35	4.20	1.61	0.51	0.20	0.62	1.10	0.91	1.81	1.27	0.14	0.04	0.06	2.06	2.67	0.73	0.63
Slide 10	(n = 8)																	
x	16.19	0.97	52.25	14.21	1.06	0.51	1.63	5.99	1.85	3.97	12.75	1.53	4.88	5.56	31.90	65.69	1.23	1.18
SD	3.12	0.24	5.28	1.84	0.41	0.40	0.76	1.14	0.76	1.07	1.92	0.14	0.05	0.04	3.96	4.35	0.76	0.39
Slide 14	(n = 8)																	
x	17.02	1.53	47.87	14.83	1.10	0.48	2.33	7.28	1.64	4.54	13.50	1.60	4.90	5.53	33.46	63.65	1.23	1.64
SD	2.46	0.51	6.12	2.26	0.44	0.21	0.79	1.20	0.48	1.08	0.87	0.12	0.06	0.03	4.78	5.00	0.28	0.42
Overall	(N = 32)																	
x	16.10	1.19	51.72	12.68	1.06	0.44	1.78	5.95	2.00	5.43	12.91	1.56	4.92	5.57	30.28	66.89	1.47	1.35
SD	2.51	0.44	5.86	2.58	0.51	0.28	0.77	1.42	0.76	2.02	1.40	0.14	0.06	0.05	4.35	4.53	0.67	0.52

[a] Percentages of the 10 most common taxa, inferred pH, and percentage of taxa in pH groups. Values are the average of 8 counts/slide. The DI + CI pH was estimated by randomly selecting a chrysophyte count from each slide to match each diatom count.

[b] CI = chrysophyte inferred; DI = diatom inferred; SD = standard deviation.