Limnol. Oceanogr., 44(3, part 2), 1999, 757–773
© 1999, by the American Society of Limnology and Oceanography, Inc.

Algal responses to dissolved organic carbon loss and pH decline during whole-lake acidification: Evidence from paleolimnology

P. R. Leavitt
Limnology Laboratory, Department of Biology, University of Regina, Regina, Saskatchewan S4S 0A2

D. L. Findlay
Department of Fisheries and Oceans, Central and Arctic Region, Freshwater Institute, 501 University Crescent, Winnipeg, Manitoba R3T 2N6

R. I. Hall[1]
Limnology Laboratory, Department of Biology, University of Regina

J. P. Smol
Paleoecological Environmental Assessment and Research Lab (PEARL), Department of Biology, Queen's University, Kingston, Ontario K7L 3N6

Abstract

Fossil pigment analyses and 19 year-long historical records were used to quantify whole-lake algal response to changes in optical and chemical properties following experimental acidification of Lake 302 with H_2SO_4 (south basin, 302S; 1981–1989) or HNO_3 (north basin, 302N; 1982–1986) and HCl (1987–1989). Undisturbed sediments were collected by freeze-coring, sectioned in approximately annual intervals, and analyzed for fossil carotenoids, chlorophylls, and derivatives by high performance liquid chromatography. Concentrations of fucoxanthin (diatoms, chrysophytes, some dinoflagellates) were correlated with algal standing crop ($r^2 = 0.67$, $P < 0.05$; 1978–1989) and increased 6-fold following acidification of Lake 302S with H_2SO_4 from pH 6.6 to 5.0, consistent with observed reductions in dissolved organic carbon (DOC) from 7 to 4.5 mg liter^{-1}, improved water clarity, and increased biomass of deep-water chrysophytes. However, fucoxanthin concentrations declined to baseline values in sediments from 1988 to 1990, concomitant with severe acidification to pH 4.5, continued DOC loss (<1.5 mg liter^{-1}) and an estimated 8-fold increase in the penetration of UVb radiation (UVR-b). Increased penetration of ultraviolet radiation (UVR) was recorded also by increased relative abundance of pigments characteristic of UVR-transparent environments. In contrast, pigments from green algae (Chl *b*, pheophytin *b*, lutein-zeaxanthin) doubled during acidification with H_2SO_4, while those from cryptophytes (alloxanthin) were unaffected and diatoxanthin from diatoms declined. Patterns of ubiquitous β-carotene, Chl *a*, and pheophytin *a* suggested that total algal biomass increased ~200–400% by the mid-1980s, but declined to near-baseline under severe acidification. Variance partitioning using redundancy analysis captured 80–83% of variation in fossil chlorophylls and carotenoids and suggested that the direct effects of pH were greater (~50% of total variance) than those of irradiance (~12%), but that ~20% of variance was attributable to factor interactions. Fossil concentrations of pigments from green algae and diatoms increased ~100% following acidification of Lake 302N to pH 6.1, but there were few signals of deep-water blooms, possibly because DOC remained 3.5–5.0 mg liter^{-1}. Such complex interactions between pH, DOC, and light may help explain the high variability of algal biomass response to lake acidification.

Lake acidification can impact algal communities through both biotic and abiotic pathways (Fig. 1). To date, most research has focused on the direct effects of pH or associated factors (e.g., metals) on members of aquatic food webs (reviewed by Stokes 1986). Laboratory and field experiments demonstrate that algal growth can decline with pH (e.g., Stokes 1981; Vinebrooke 1996). In contrast, field surveys document that acidification results in species replacements (Turner et al. 1987; Howell et al. 1990; Nichols et al. 1992), although not necessarily a decline in production (Shearer and DeBruyn 1986; *but see* Turner et al. 1987). In principle, trophic interactions within the food web could lead to either increase or decrease phytoplankton and periphyton abundance, depending on whether predators or prey species are more strongly influenced by acidification events (e.g., Schindler et al. 1985; France et al. 1991; Appelberg et al. 1993). Acidification also reduces the availability of dissolved inorganic carbon (DIC) and photosynthesis by periphyton (e.g., Turner et al. 1994, 1995*a,b,c*; Vinebrooke 1996). However, benthic biomass may not decline because severe acidification often leads to the development of loosely attached

[1] Present address: Abisko Scientific Research Center, Box 62, S-981 07, Abisko, Sweden.

Acknowledgments

This research was supported by Natural Sciences and Engineering Research Council of Canada (NSERC) research grants to P.R.L. and J.P.S. Department of Fisheries and Oceans and NSERC also supported P.R.L. with a visiting fellowship. Additional support for R.I.H. from University of Regina.

We thank R. Hesslein, D. W. Schindler and R. Vinebrooke for constructive reviews.

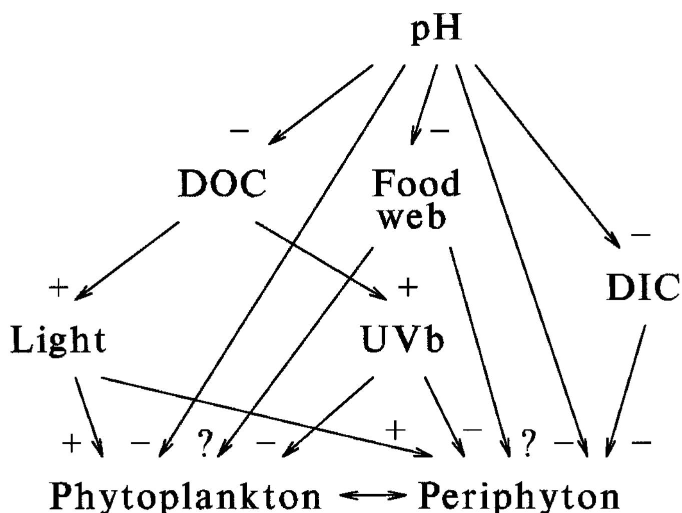

Fig. 1. Main potential direct and indirect effects of lake acidification on algal abundance. Indirect effects of changes in DOC or pH on nutrient or metal availability not shown. Effects of acidification either inhibit (−) or stimulate (+) response variables. Effects of food-web changes on algae depend on complex food-web interactions and are not predictable (?). Further description given in text.

clouds of filamentous green algae (metaphyton) at pH < 5.2 (e.g., Turner et al. 1987; Howell et al. 1990).

Acidification can also reduce concentrations of dissolved organic carbon (DOC; Schindler et al. 1996*a,b*; Yan et al. 1996), one of the main radiation-absorbing agents in the water column (Scully and Lean 1994; Morris et al. 1995). Declines in DOC increase both the penetration of light (Schindler et al. 1996*a*) and the habitable area for deep-water phytoplankton and periphyton (Findlay and Kasian 1990; Findlay et al. 1999) but may also increase penetration of inhibitory ultraviolet radiation (UVR; Schindler et al. 1996*a,b*; Yan et al. 1996; Frost et al. 1999). Changes in DOC content can also alter nutrient and metal availability (Kullberg et al. 1993). Because all factors act simultaneously (Fig. 1), it is difficult to quantify the response of total algal production to lake acidification or the relative importance of potential controls. In particular, little is known of the relative importance of pH- and irradiance-related factors in regulating whole-lake algal abundance and community composition.

Sedimentary pigments may be valuable indicators of algal response to lake acidification because fossil pigments are often well preserved and integrate material from throughout the lake basin (e.g., Carpenter et al. 1988; Leavitt and Carpenter 1990*b*; Leavitt et al. 1994*a*). In particular, carotenoids, chlorophylls (Chls), and their derivatives form a diagnostic group of pigments that can be used to estimate algal standing crop (mass m^{-2} yr^{-1}), gross taxonomic composition, grazing by herbivores, and the vertical zonation of phototrophs (reviewed by Sanger 1988; Leavitt 1993; Millie et al. 1993). Calibrations of fossil pigments against long-term phytoplankton records from freshwater lakes confirm that pigments are as reliable as morphological fossils and can record major changes in algal biomass and gross community composition (Leavitt et al. 1989; Leavitt and Findlay 1994; Leavitt et al. 1994*a*). With improved knowledge of pigment biogeochemistry in freshwater systems (e.g., Hurley and Armstrong 1990, 1991; Leavitt 1993; Steenbergen et al. 1994), it has become possible to use sedimentary pigments to quantitatively reconstruct changes in whole-lake algal communities (e.g., Leavitt and Findlay 1994).

This study used paleoecological reconstructions and historical data (1972–1990) to evaluate the relative importance of pH and irradiance as controls of algal abundance and community composition in two experimentally acidified lake basins. Partial and constrained redundancy analysis was used to partition variance in fossil pigment assemblages from Lake 302S into categories associated with pH, irradiance, and their interactions. Quantification of ubiquitous pigments (β-carotene, Chl *a*, pheophytin *a*) was used to estimate how total algal abundance varied during whole-lake acidification, whereas taxonomically diagnostic carotenoids recorded the responses of most algal groups. Finally, comparison of fossil pigment stratigraphies from Lake 302N (final pH 5.2; HNO_3, HCl added) and Lake 302S (pH 4.5; H_2SO_4) contrasted the effects of moderate and severe acidification on algal communities.

Site description

Natural characteristics—Lake 302 is an oligo-mesotrophic headwater lake in the Experimental Lakes Area (ELA) of northwestern Ontario (49°40.15′N, 93°45.25′W). The lake has two elongate basins (302S, 302N) separated by two narrow, shallow channels (Table 1). Water flows from the south basin into the north basin and out via a single outflow. Regional geology and soils are described by Brunskill and Schindler (1971). Pristine local forests are unaltered by forestry or recent fires and include jack pine (*Pinus banksiana*), red pine (*Pinus resinosa*), and black spruce (*Picea mariana*), with an understory of juniper (*Juniperus communis*) and *Sphagnum* spp. (Rudd et al. 1990).

Before experimental manipulation, Lake 302 was colored, meso-oligotrophic, and strongly stratified, similar to other lakes at the Experimental Lakes Area (Table 1). Deep waters in Lake 302N were seasonally anoxic, cool, and supported zoobenthic communities of Chaoboridae (*Chaoborus flavicans, Chaoborus punctipennis*), chironomids (*Chironomus* spp., *Procladius* spp., *Phaenopsectra coracina*), and oligochaeates (Hamilton 1971). Original zoobenthos of Lake 302 were most similar to those of Lake 227, site of a whole-lake fertilization experiment (Hamilton 1971). Analysis of profundal sediments by Stockner (1971) identified remains of benthic and planktonic diatoms characteristic of unproductive waters (e.g., *Cyclotella stelligera, Cyclotella kützingiana, Fragilaria pinnata, Navicula sphaerocephala, Synedra acus*).

Native phytoplankton communities consisted mainly of chrysophytes throughout the year (Kling and Holmgren 1972). Winter taxa included *Chrysococcus* spp., *Chromulina* spp., and the green-alga *Botryococcus braunii*, whereas several *Mallomonas* and *Dinobryon* species were common in spring along with the cryptophytes *Cryptomonas obovata, Cryptomonas rostratiformis, Cryptomonas pusilla*, and *Rho-*

Table 1. Morphometric characteristics and range of pre-manipulation physico-chemical conditions in Lakes 302 and 227, Experimental Lakes Area, Ontario, 1967–1969. Data from Cleugh and Hauser (1971), Brunskill and Schindler (1971), Armstrong and Schindler (1971), Schindler (1971), and Reid et al. (1975). Pre-manipulation production estimates were not available (na) for Lake 227. All pre-manipulation chemical data from the north basin of Lake 302.

Characteristic	Lake 302		Lake 227
	N	S	
Area (ha)	12.8	10.9	5.0
Volume (10^5 m^3)	7.32	5.54	2.21
Mean depth (Z_{avg}, m)	5.7	5.1	4.4
Max depth (Z_{max}, m)	13.8	10.6	10.0
Shoreline development	1.70	1.82	1.15
Total dissolved P (μg liter^{-1})	4–6		3–7
Total dissolved N (μg liter^{-1})	140–164		144–160
Chl *a* (μg liter^{-1})	1.5–3		2–5
Ice-free production (g C m^{-2})	85*		na
Annual production (g C m^{-2})	100*		na
Color (Hazen Pt units)	15		18
Secchi depth (m)	2.8–4.0		1.2–2.6
Specific conductance (μmhos cm^{-1})	15–19		18–21
Oxygen (mg O_2 liter^{-1} at $Z_{max} - 1$ m)	0.1		0.1
Temp (°C at $Z_{max} - 1$ m)	5.3		4.4
Stratification strength (g cm cal^{-1})†	0.038		0.040
Water renewal (τ, yr)	14		4.2

* Data from 1971.
† Birgean wind work per unit summer heat income (Schindler 1971).

domonas minuta. During summer, loricate, colonial, and scaled chrysophytes were abundant (*Synura* spp., *Chrysosphaerella longispina, Uroglena, Mallomonas* spp., *Dinobryon*), along with lesser densities of dinoflagellates (*Peridinium* spp., *Gymnodinium* spp.), chlorophytes (e.g., *Oocystis, Ankistrodesmus, Gloeococcus, Crucigenia*), and cyanobacteria (*Aphanocapsa, Coelosphaerium, Merismopedia*). Diatoms were comparatively uncommon in the plankton, but included *Cyclotella* and *Synedra* in spring and early summer (Kling and Holmgren 1972). Euglenophyta were virtually absent from algal communities.

The fish community of Lake 302 was simple and composed of planktivorous fishes including fathead minnows (*Pimephales promelas*), pearl dace (*Margariscus margarita*), lake whitefish (*Coregonus clupeaformis*), white sucker (*Catostomus commersoni*), and slimy sculpin (*Cottus cognatus*) (Beamish et al. 1976). Additionally, northern redbelly dace (*Phoxinus eos*) and finescale dace (*Phoxinus neogaeus*) were recorded in both basins of Lake 302 by 1986 (Chalanchuk 1986). Although direct measurements of the original zooplankton community composition are not available, invertebrates most likely consisted of locally common small-bodied crustaceans such as *Bosmina longirostris, Diaptomus minutus*, and *Tropocyclops prasinus mexicanus* or *Mesocyclops edax* (Patalas 1971).

Manipulation history—Lake 302 has been the subject of two whole-lake manipulations. First, the hypolimnion of Lake 302N was experimentally fertilized with P (0.54 g m^{-2} yr^{-1} as H_3PO_4), N (2.79 g m^{-2} yr^{-1} as NH_4Cl), and C (3.73 g m^{-2} yr^{-1} as sucrose) during 1972–1976 and in 1978, while the upstream south basin was isolated by means of an impregnated vinyl curtain (1972–1980) and used as an unaltered reference system. This level of enrichment was chosen to mimic the eutrophication of the Laurentian Great Lakes and to contrast nearby Lake 227, a site whose epilimnion was fertilized with similar levels of P, but with more N (6.3 g m^{-2} yr^{-1}) and no carbon (Schindler 1975; Schindler et al. 1980). The comparison of epi- and hypolimnetic enrichment was intended to test the hypothesis that introduction of nutrients to deep-waters of a stratified lake would result in less eutrophication than a similar discharge into surface waters.

Lake 302 was allowed to circulate freely in 1980 before installation of new curtains in June 1981 to separate the basins for a whole-lake acidification experiment. Following a year of pre-manipulation study, Lake 302S was acidified with H_2SO_4 while Lake 302N received similar amounts of H^+ as HNO_3 (Fig. 2). The pH of Lake 302S declined from pre-acidification levels of ~6.4 to values near 4.5 by 1987, where it was maintained until 1990. The pH of Lake 302N declined more slowly, reaching ~6.0 by 1986, after which HCl was used to reduce pH to ~5.1 by 1990 (Fig. 2). Despite receipt of acidic waters from the south basin, Lake 302N was less acidic than Lake 302S in any given year, partly because nitric acid was neutralized by algal uptake and bacterial denitrification (Rudd et al. 1990).

Algal responses to acidification—Total phytoplankton biomass within the euphotic zone of Lake 302S was more variable but generally greater than that of Lake 302N following the onset of acidification (Fig. 2). Algal standing crop was particularly elevated in the mid-1980s and again in 1989–1990, relative to Lake 302N and unacidified reference lakes (Findlay and Kasian 1990, 1996; Findlay et al. 1999).

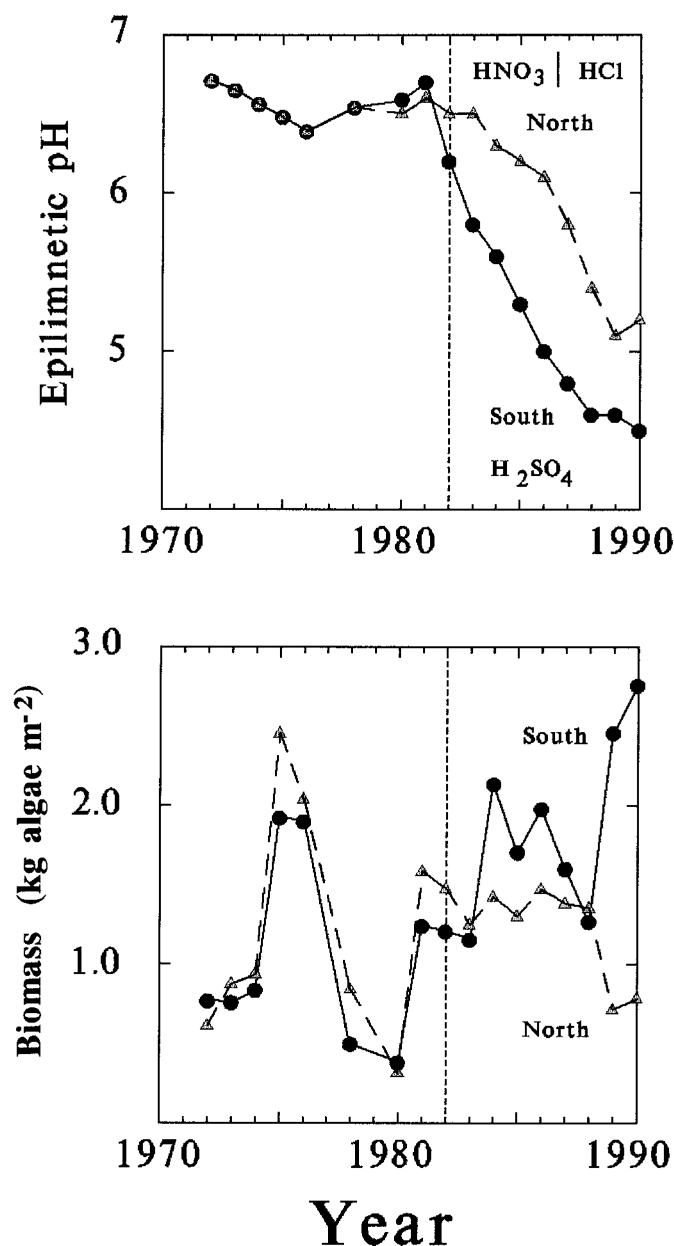

Fig. 2. Changes in epilimnetic pH and total phytoplankton biomass (kg wet wt m^{-2} yr^{-1}) as a result of acidification of Lake 302S (H_2SO_4; 1982–1990—●) and Lake 302N (HNO_3, 1982–1986; HCl, 1986–1990—▲).

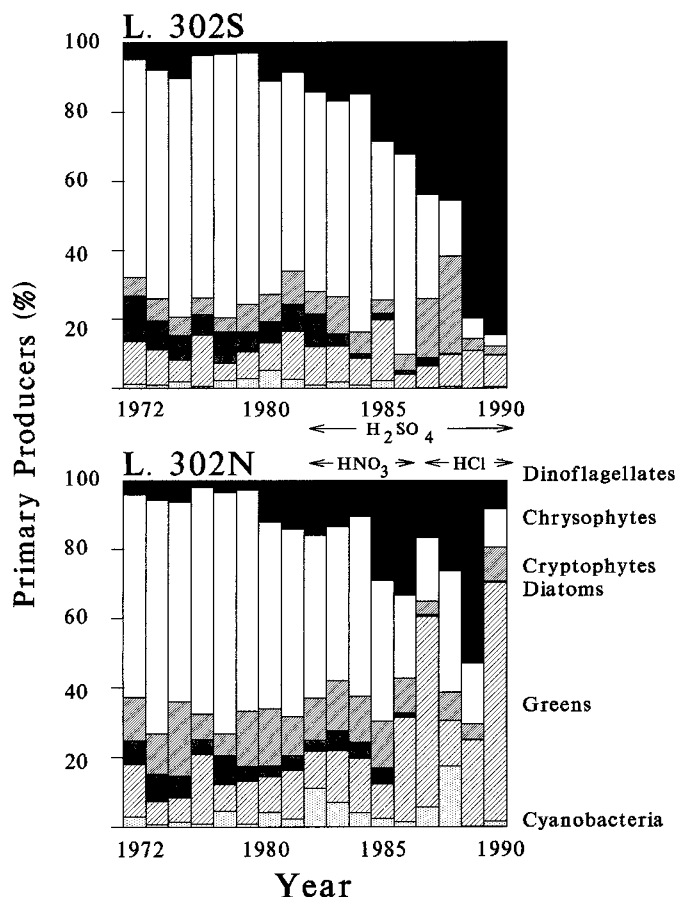

Fig. 3. Change in relative abundance (%) of phytoplankton following acidification of Lake 302S (top) and Lake 302N (bottom). Abundance of dinoflagellates (black), chrysophytes (white), cryptophytes (fine hatch), diatoms (gray), chlorophytes (coarse hatch), and cyanobacteria (stipple) estimated as percent of total time-weighted water-column biomass (kg wet wt algae m^{-2} yr^{-1}). Acidification regime as in Fig. 2.

In contrast, there were few dramatic changes in phytoplankton abundance in the north basin, other than a general decline following acidification to pH 5.1 with HCl. Overall, changes in total biomass were similar to those inferred during the 1970s, although variability in sampling protocols (*see below*) may also contribute to apparent interannual differences during that decade. During the 1970s, algal biomass was usually slightly greater in Lake 302N than in 302S.

In both basins, acidification resulted in an increase in the relative importance (% total mass) of dinoflagellates (*Gymnodinium* sp., *Peridinium inconspicum*) at the expense of chrysophytes and diatoms (Fig. 3). These patterns were not recorded in local reference lakes (Findlay and Kasian 1990; Findlay et al. 1999). Lake 302S also exhibited declines in filamentous and colonial cyanobacteria, especially after pH dropped below 5.0, whereas the relative proportion of chlorophyte phytoplankton increased in Lake 302N following several years of acidification with HNO_3 (Fig. 3).

Benthic communities were also affected by the acidification of L302S (Turner et al. 1987, 1995*a,b,c*; Findlay et al. 1999). In general, net photosynthesis of epilithon declined (Turner et al. 1995*c*) as cyanobacteria were replaced by chlorophytes and dinoflagellates during ice-free seasons (Findlay et al. 1999). Total biomass changed little until pH 4.5 when biomass doubled due to increases in acidobiontic *Mougeotia* and *Tabellaria quadriseptata* (Findlay et al. 1999). At this time, metaphytic *Zygogonium* increased to cover 50–100% of shoreline up to a thickness of 40 cm, although interannual variability in biomass was great (Turner et al. 1995*b,c*). Unfortunately, little is known of periphytic algal growth on other substrates or in Lake 302N where benthic sampling has been infrequent. Consequently, it has been difficult to esti-

mate how whole-lake algal abundance has varied in response to acidification.

Methods

Plankton samples—Samples for phytoplankton and chemical analyses were collected approximately biweekly (1972–1990) during the ice-free period using a variety of intercalibrated techniques (Findlay and Kasian 1996). Between 1972 and 1975, discrete samples were retrieved from five to seven depths within the photic zone using a 2-liter van Dorn water bottle. An integrating sampler was used after 1974 to obtain samples from the epilimnion, metalimnion, or hypolimnion (Shearer 1978). Strata were defined by light and temperature. In 1975–1976 and after 1984, the photic zone was defined by two layers (epilimnetic, hypolimnetic), whereas metalimnetic samples were also collected in other years. Phytoplankton samples were preserved with Lugol's iodine solution, settled, and enumerated using the Utermöhl technique (Nauwerck 1963; Kling and Holmgren 1972; Findlay and Kasian 1990, 1996). Wet weight biomass values (kg m^{-2} yr^{-1}) were estimated from geometric approximations of cell shape and estimated cell density (Vollenweider 1968; Findlay and Kasian 1986). Algal species were grouped according to pigment composition to allow direct comparison of phytoplankton abundance and concentrations of fossil pigments. Because rates of ^{14}C fixation are not accurately recorded in fossil pigment stratigraphies (Leavitt and Findlay 1994), productivity estimates were not compared to fossil stratigraphies.

All chemical analyses followed Stainton et al. (1977). Subsurface light regimes (10% and 1% incident light, extinction coefficient) were measured with a LiCor model 192S sensor (Shearer et al. 1985). Maximum penetration depth of UVR-b was determined as 1% incident levels using measured DOC levels and the empirical formula of Schindler et al. (1996*b*). Solute concentrations were time- and lake volume-weighted for the ice-free season.

Sediment samples—Sediments were obtained from the deepest point of each basin of Lake 302 in January 1990 using a high-resolution freeze-coring technique (Swain 1973). Frozen cores were sectioned lengthwise into four quarters and the outermost 5 mm of sediment removed using a wood plane (Leavitt and Findlay 1994). Cleaned cores were freeze-dried 24 h at 0.01 Pa before sectioning at 3-mm intervals (Leavitt et al. 1989). Visible sedimentary laminae were absent from both basins. Isolated intervals were dried a further 2 h at 0.01 Pa and stored under a N_2 atmosphere (dark, −20°C) for 24 h before further analysis (Leavitt et al. 1989).

Sediment age was estimated from mean annual accumulation rates of bulk sediments published previously for both Lake 302S (28 mg cm^{-2} yr^{-1}; 3.8 mm yr^{-1}) and Lake 302N (23 mg cm^{-2} yr^{-1}; 3.1 mm yr^{-1})(Anderson et al. 1987). In addition, changes in fossil chrysophyte assemblages were used to verify whether fossil chronologies constructed with bulk rates were reliable. Scaled chrysophytes are sensitive indicators of changes in lake water pH (Dixit et al. 1989*a,b*, 1992). If fossil chronologies based on linear accumulation rates (mm yr^{-1}) were accurate, then changes in the chrysophyte community composition should occur concomitant with documented acidification of Lake 302. Direct estimation of sediment age from the vertical distribution of radioisotopes was not attempted because fine-interval sampling leads to low total ^{210}Pb and ^{137}Cs activities and artifacts in radiometric dating in these lakes (e.g., Wolfe et al. 1994).

Sediments were prepared for analysis of siliceous scales from chrysophytes following standard procedures (Smol 1983; Zeeb et al. 1994). Freeze-dried sediments were digested with a mixture of 1 g of $K_2Cr_2O_7$ in 20 ml of H_2SO_4 for 3–5 d at room temperature, boiled to complete digestion, and rinsed with distilled water to completely remove traces of acid. Aqueous suspensions of siliceous remains were evaporated onto glass coverslips and mounted in Naphrax medium on glass microscope slides. Chrysophyte scale taxonomy and ecological inferences followed Asmund and Kristiansen (1986) and Silver (1991). Past changes in pH in Lake 302S were quantitatively reconstructed from the relative abundances of fossil chrysophyte scales using a pH transfer function developed for acidified and circumneutral lakes of Ontario (Dixit et al. 1989*a,b*, 1992) and the computer program WACALIB v. 3.3 (Line et al. 1994). Reconstructions were not attempted for Lake 302N because its complex manipulation history (*see above*) prevented establishment of a stable baseline community against which pH-related changes could be evaluated.

Carotenoids, chlorophylls, and their derivatives were extracted (18 h, 4°C, dark, under N_2) from freeze-dried sediments using a standard mixture of acetone : methanol : water (80 : 15 : 5 by vol.; Leavitt et al. 1989). Sediment residues were exhaustively extracted with three aliquots of solvent mixture, extracts filtered (0.22-μm Acropore membrane), and solvents evaporated in the dark using N_2 gas. Dried extracts were stored at −20°C under N_2 in the dark until pigment analysis. Just prior to quantification, pigments were brought to room temperature in the dark and dissolved in a precisely known volume of injection solvent (acetone : ion-pairing reagent : methanol; 70 : 25 : 5 by vol.) containing 3.2 mg $liter^{-1}$ Sudan II (Sigma). This chromatographic dye is an internal standard that has carotenoid-like absorption characteristics (λ_{max} = 485, 442.5 nm in acetone), runs at a unique position on the chromatogram (7.3 min) between aphanizophyll (7.0 min) and myxoxanthophyll (7.6 min), and is used to correct for dilution, injection, and chromatographic errors (Leavitt and Findlay 1994). Ion-pairing reagent (IPR) consists of 0.75 g of tetrabutyl ammonium acetate and 7.7 g of ammonium acetate in 100 ml of water.

Concentrations of fossil pigments were quantified using a Waters HPLC system with fixed wavelength absorbance (435 nm) and fluorescence detectors following the reversed-phase liquid chromatography procedure of Mantoura and Llewelyn (1983) as modified by Leavitt et al. (1989). Briefly, analytical separation was achieved by isocratic delivery (1.5 ml min^{-1}; 21,000 kPa) of a mobile phase A (10% IPR in methanol) for 1.5 min, a linear succession to 100% solution B (27% acetone in methanol) over 7 min, and isocratic hold for 12.5 min. Rainin C-18 columns (10 cm, 5-μm particles) were re-equilibrated by continued isocratic delivery for 3

min, a linear return to 100% A over 3 min, and isocratic supply for a final 4 min.

Pigments isolated from sediments were compared to those from unialgal cultures of known pigment composition (Leavitt et al. 1989; Leavitt and Findlay 1994). Spectral characteristics, chromatographic mobility, and functional group assays (Liaaen-Jensen 1971) were used to tentatively identify pigments from all sources (Leavitt et al. 1989). Acid and methyl derivatives of chlorophyllous pigments were created either by aqueous-alcohol extraction (chlorophyllides) or by acidification following the procedures of Leavitt et al. (1989). Pyropheophytin *a* and a compound tentatively identified as pyropheophorbide *a* were collected by HPLC isolation from sediments of several lakes.

Analysis of fossil pigments was restricted to carotenoids characteristic of cryptophytes (alloxanthin), mainly diatoms (diatoxanthin), diatoms with chrysophytes and some dinoflagellates (fucoxanthin), dinoflagellates (peridinin), chlorophytes and cyanobacteria (lutein-zeaxanthin), cyanobacteria (echinenone), filamentous or colonial cyanobacteria (myxoxanthophyll), and N_2-fixing cyanobacteria (aphanizophyll), as well as the major *a-, b-*, and *c-* phorbins. Goodwin (1980) further reviews the distribution of carotenoids among algae. Chl *b* and pheopigment derivatives (mainly pheophytin *b*) were used to distinguish green algae from cyanobacteria, whose carotenoid zeaxanthin was not separated from the chlorophyte pigment lutein on our HPLC system. Similarly, chromatographic peaks from aphanizophyll (*Aphanizomenon*), oscillaxanthin (Oscillatoriaceae), and 4-keto-myxoxanthophyll (*Anabaena*) were incompletely resolved and were reported as aphanizophyll. Pigment concentrations were expressed as nmol pigment g^{-1} organic matter following determination of organic content by combustion for 1 h at 500°C (Dean 1974), as recommended by Leavitt (1993) and Leavitt and Findlay (1994). Comparison of 20 yr of phytoplankton data with annual fossil records in nearby Lake 227 demonstrates that organic matter-specific concentrations are linearly correlated to algal biomass for a wide variety of fossil carotenoids, particularly for algae that are abundant during the ice-free season (Leavitt and Findlay 1994).

Sediments from Lake 302S also contained two pigments characteristic of environments with high UV irradiance (Leavitt et al. 1994*b*; Leavitt et al. 1997). One compound (C_a) exhibited a symmetrical absorbance spectrum with a maximum at 381 nm in acetone, whereas the second compound (C_b) absorbed strongly at 440 nm in acetone. Both non-fluorescent pigments were compared with similar pigments from transparent alpine lake sediments that had been isolated by HPLC, purified using a Sep-Pak C-18 cartridge, rechromatogrammed and isolated, and dried under N_2 before further analysis. Pigments Ca and Cb exhibited unique retention times (5.7 and 6.1 min, respectively) intermediate to those of fucoxanthin (5.0 min) violaxanthin (6.4 min), aphanizophyll (7.0 min), and Sudan II (7.3 min). These compounds are found commonly in sediments of shallow, UVR-transparent lakes within alpine (Leavitt et al. 1994*b*, 1997), prairie (Vinebrooke et al. 1998), and high arctic regions (Leavitt et al. unpub. data) and are believed to be derived from benthic algae (Leavitt et al. 1997). Because the molecular weight and light extinction coefficients of these pigments are unknown, we assumed that their light-attenuating characteristics were similar to those of carotenoids (following Davies 1976). This procedure allowed estimation of its relative stratigraphic abundance based on approximate concentrations of pigments. Further characterization of these pigments is on-going and will be presented elsewhere.

Numerical procedures—Constrained and partial canonical ordinations (ter Braak 1988*a,b*) were used to quantify the relationship between changes in the chemical and optical characteristics in Lake 302S and the fossil pigment record of algal community change. This method of variance partitioning uses direct gradient analysis to measure the fraction of variance in fossil composition explained by measured environmental variables and their interactions (Borcard et al. 1992). Four steps were required to partition the variance in fossil pigment data. First, constrained ordinations were used to measure the total amount of variation (sum of canonical eigenvalues) in the pigment stratigraphy that could be explained by measured historical data. In our case, we ran independent ordinations constrained by factors related to pH and irradiance (*see below*). Second, partial canonical ordinations were used to measure the portion of variation that remains after removing the effects of selected environmental covariables by multiple linear regression (ter Braak 1988*a*). Third, the importance of interactions between variables was determined by difference between eigenvalues derived from constrained and partial canonical ordinations. Here this procedure measured variance which was attributable to pH and irradiance, but which could not be assigned uniquely to either factor. Finally, unexplained variance was calculated as the difference between unity and the total variance captured by the ordinations. Borcard et al. (1992), Legendre (1993), and Lotter and Birks (1993) have provided further details of variance-partitioning procedures.

Ordinations were performed using $\ln(x + 1)$-transformed concentrations of the main algal indicator pigments in Lake 302S; β-carotene, alloxanthin, fucoxanthin, diatoxanthin, lutein-zeaxanthin, Chl *a,* Chl *b,* and Chl *c*. Redundancy analysis (RDA) was used to partition variance because exploratory detrended correspondence analysis (DCA) suggested that pigment responses to environmental change were best explained by linear rather than unimodal relationships (ter Braak 1986). Computations were performed using the computer program CANOCO v. 3.12 (ter Braak 1990). The statistical significance of each block of partitioned variance was assessed using Monte Carlo simulations with 99 random permutations.

Historical data relating to irradiance within Lake 302S during 1972–1990 included time-weighted annual estimates of extinction coefficient (m^{-1}), total phytoplankton standing crop (kg wet wt m^{-2}), Chl *a* (μg liter^{-1}), dissolved organic carbon (mg liter^{-1}), Secchi depth (m), depth of 10% incident light (m), depth of 1% incident light (m), and maximum depth of UVR-b penetration (m; estimated from Schindler et al. 1996*b*). Factors related to the changes in lake chemistry included pH, DIC (μM), conductivity (μS cm^{-1}), and mass of H_2SO_4 added (kg). Optical records of DOC content and UVR-b depth were extrapolated 4 yr to 1972 using mean values for 1976–1980. This procedure allowed us to match

the length of fossil and historical records as required for the ordination (Borcard et al. 1992). However, use of long-term averages will slightly underestimate actual historical variability for 1972–1990, as well as the amount of fossil pigment variability that can be explained by changes in irradiance.

Explanatory variables were retained in ordinations only if they independently explained a significant amount of fossil variance ($P < 0.05$) and were not redundant with other variables within each category as estimated from variance inflation factors (ter Braak 1988*b*). Hall et al. (1999) have provided further information on objective criteria for selection of explanatory variables.

Results

Sediment description and chronology—Sediments from Lakes 302N lacked visible laminae and were finely divided, uniform, and tan in appearance below a depth of 4 cm. Surficial sediments also exhibited black inclusions similar to charcoal deposits reported for other local lakes (Wolfe et al. 1994). In Lake 302S, sediments additionally included chironomid tubes down to a depth of 20 cm, although these were avoided during sediment sampling. High densities of chironomids (*Chironomus*) and chaoborids (*C. punctipennis, C. flavicans*) were evident during core collection in Lake 302S, but not in Lake 302N.

Analyses of fossil chrysophyte scales in Lake 302S were used to determine whether the ^{210}Pb-inferred sediment chronology of Anderson et al. (1987) could be applied to these freeze cores. We hypothesized that if the sediment chronology was reliable, then changes in fossil community composition should occur concomitant with acidification, such as occurs in other regions (e.g. Dixit et al. 1989*a*, 1992). Scales from 22 taxa of chrysophytes were recovered from sediments of Lake 302S, including 16 species of *Mallomonas*. Together, mean (± SD) abundance of *Mallomonas duerrschmidtiae* ($pH_{optimum}$ = 6.9; Dixit et al. 1989*b*) and *Synura echinulata* ($pH_{optimum}$ = 5.6) accounted for 71.9 ± 8.7% of all scales in the upper 8 cm of sediment (ca. 1968–1990). When plotted as a function of inferred sediment age, changes in fossil chrysophyte assemblage composition occurred concomitant with lake acidification in 1982, with *S. echinulata* increasing mainly at the expense of *M. duerrschmidiae* (Fig. 4). Further, estimates of lake pH based on chrysophyte inference models were highly correlated (r^2 = 0.85, $P < 0.0001$; 1978–1989) with observed pH, although the range of inferred values (5.0–5.7) was less than that for air-equilibrated measurements during the ice-free season (4.5–6.6; Fig. 4).

Sediments of Lake 302S had a slightly greater mean (±SD) organic content (39.3 ± 3.0%) than did those of Lake 302N (35.9 ± 2.1%). In both south and north basins, organic content was greatest in the 0–1-cm depth interval, declined ~8% by 5-cm depth, and was uniform in sediments to 30-cm depth (38.3 ± 2.0%, 35.2 ± 1.4%, respectively). Values for deep sediments were somewhat greater than the 31.7% reported for Lake 302N in 1969 (Brunskill et al. 1971).

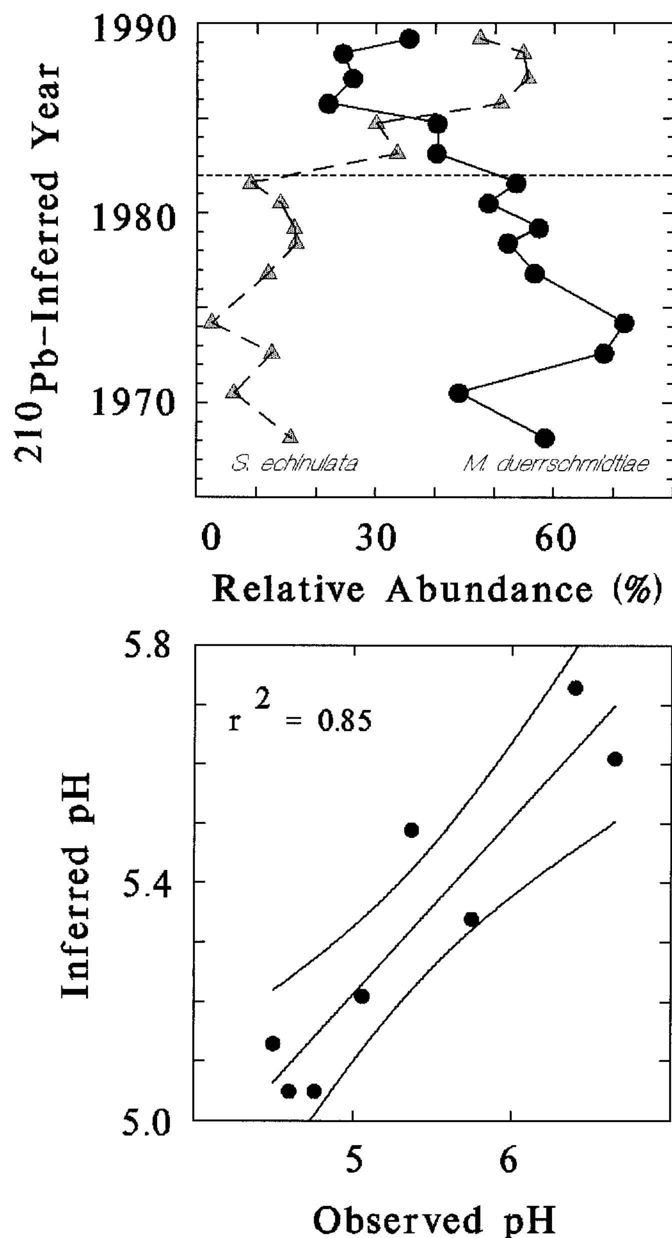

Fig. 4. Change in the relative abundance (%) of the main fossil chrysophytes in the sediments of Lake 302S (top). Sediment age inferred from ^{210}Pb-derived accumulation rates of Anderson et al. (1987). Horizontal line represents the start of lake acidification with H_2SO_4 in 1982. Linear regression between chrysophyte-inferred pH (Dixit et al. 1989*a,b*) and measured, air-equilibrated pH is statistically significant (r^2 = 0.85) at $P < 0.0001$ (bottom).

Fossil pigment record of acidification—Fossil pigments exhibited three main stratigraphic patterns following acidification of Lake 302S (Fig. 5). Concentrations of fucoxanthin (diatoms, chrysophytes, some dinoflagellates), undegraded Chl *b* (chlorophytes), and lutein-zeaxanthin (chlorophytes, cyanobacteria; not shown) increased 2–4 fold immediately upon acidification of Lake 302S. Peak concentrations of fucoxanthin were recorded ~1985, but declined to near baseline levels again by 1988, whereas Chl *b* and lutein-zeaxan-

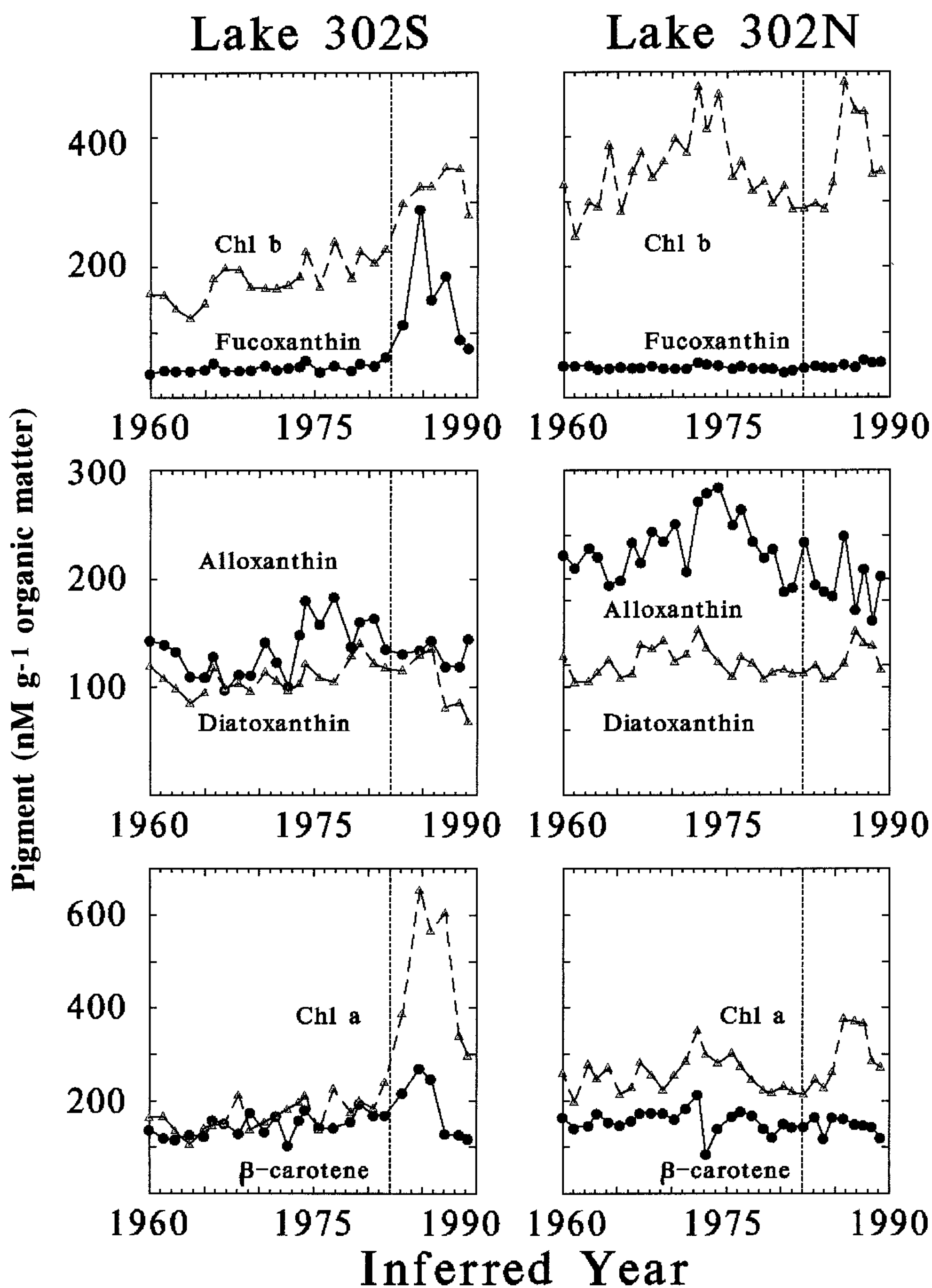

Fig. 5. Change in fossil pigment concentration in Lakes 302S and 302N, 1960–1990. Top row—fucoxanthin (diatoms, chrysophytes, some dinoflagellates) and Chl *b* (chlorophytes); middle row—alloxanthin (cryptophytes) and diatoxanthin (mainly diatoms); bottom row—β-carotene and undegraded Chl *a* (all algae). Onset of acidification indicated with vertical lines. Sediment age as in Fig. 4.

thin were elevated until 1990. In contrast, concentrations of fossil alloxanthin (cryptophytes) changed little following acidification, while diatoxanthin (mainly diatoms) declined 50% after 1985 (pH 5.0). Peridinin from dinoflagellates (not shown) was only detected in one sample in Lake 302S, whereas aphanizophyll was completely absent and myxoxanthophyll was near the limits of detection (<5 nmol g^{-1} organic matter) throughout the core. Overall, concentrations of ubiquitous β-carotene, undegraded Chl *a*, and its derivative pheophytin *a* (not shown) increased 2–4 fold to peak values in the mid-1980s, then declined to near-baseline by 1990.

Sedimentary fucoxanthin was significantly correlated to the biomass of planktonic chrysophytes ($r^2 = 0.72$, $P < 0.005$) or chrysophytes and diatoms ($r^2 = 0.67$, $P < 0.01$) between 1978 and 1989. Similarly, fossil concentrations of

undegraded Chl *a* were directly related to the standing crop of total algae ($r^2 = 0.60$, $P < 0.05$) and of chrysophytes ($r^2 = 0.54$, $P < 0.05$), whereas its derivative pheophytin *a* was uncorrelated with either group. Unexpectedly, β-carotene was correlated to the biomass of planktonic chrysophytes ($r^2 = 0.68$, $P < 0.01$) but not to total phytoplankton biomass ($r^2 = 0.08$, $P > 0.4$). Standing crops of planktonic chlorophytes were only weakly correlated to fossil Chl *b* ($r^2 = 0.22$, $P = 0.2$) and lutein-zeaxanthin ($r^2 = 0.29$, $P = 0.13$), as were diatoms and the carotenoid diatoxanthin ($r^2 = 0.29$, $P = 0.13$). Total abundances of cryptophytes and fossil alloxanthin varied little through the historical record and were not reliably related.

Stratigraphic patterns of fossil pigment change were less marked in moderately-acidified Lake 302N than in 302S (Fig. 5). As in the south basin, concentrations of undegraded Chl *b* and lutein-zeaxanthin (not shown) increased ~2-fold following acidification of Lake 302N with HNO_3 but declined to near-baseline values by 1988 during acidification with HCl (Fig. 2). Increases of <100% of background were recorded for diatoxanthin and Chl *a* but not for alloxanthin, β-carotene, or fucoxanthin. Elevated concentrations of Chl *b*, lutein-zeaxanthin, alloxanthin, and Chl *a* were also recorded for the period ca. 1971–1976, similar to the period of hypolimnetic nutrient injection (Schindler et al. 1980).

Sediments of Lake 302S contained significant concentrations of pigments characteristic of UVR-transparent environments (Fig. 6). Concentrations of C_a and C_b were highly correlated ~1960–1990 ($r^2 = 0.79$, $P < 0.0001$) and increased ~400% following acidification of Lake 302S. In general, concentrations of C_b appeared to rise then decline earlier than those of C_a. When expressed as a proportion (%) of the sum of indicator carotenoids (alloxanthin, diatoxanthin, lutein-zeaxanthin), relative concentrations of C_a were significantly correlated ($r^2 = 0.70$, $P < 0.0001$; 1978–1988) with the depth of 1% surface irradiance of UVR-b. Neither compound was recovered from sediments of Lake 302N. C_a and C_b are commonly >100% of the indicator carotenoid sum in shallow ($Z_{avg} < 5$ m) transparent lakes in which concentrations of UVR-absorbing DOC are <2 mg liter^{-1} (e.g. Leavitt et al. 1994*b*, 1997).

Relative importance of pH and irradiance—Variance partitioning suggested that 80–83% of total variation in fossil pigment composition was explained by historical changes in environmental factors related to pH and irradiance (Table 2). When RDA was performed on all pigments or on Chls alone, pH (12%) and irradiance (7–9%) accounted for comparatively small amounts of variance. Instead, ~61% of total variance in fossil pigments was attributable to joint influences of pH- and irradiance-related factors. In contrast, analysis of carotenoids alone suggested that pH-related factors accounted for 51.4% of total variance and that irradiance alone (12.5%) and the combined effects of pH and irradiance (19.2%) also explained significant variation in fossil pigments ($P < 0.05$). In all analyses significant explanatory variables included conductivity, DIC, mass of H_2SO_4 added, DOC, and depth of 10% incident light (Table 2). The depths of UVR-b penetration, 1% incident irradiance, and Secchi measurements were also significant variables in analyses that included chlorophylls. pH was not included as a predictor variable because of high colinearity with H_2SO_4. Similarly, planktonic Chl *a* (μg liter^{-1}) and algal abundance (kg wet wt m^{-2}) were not included in the irradiance category because these factors are often correlated with fossil pigment concentration (Leavitt 1993; Leavitt and Findlay 1994), independent of their effects on subsurface light regimes. Variance

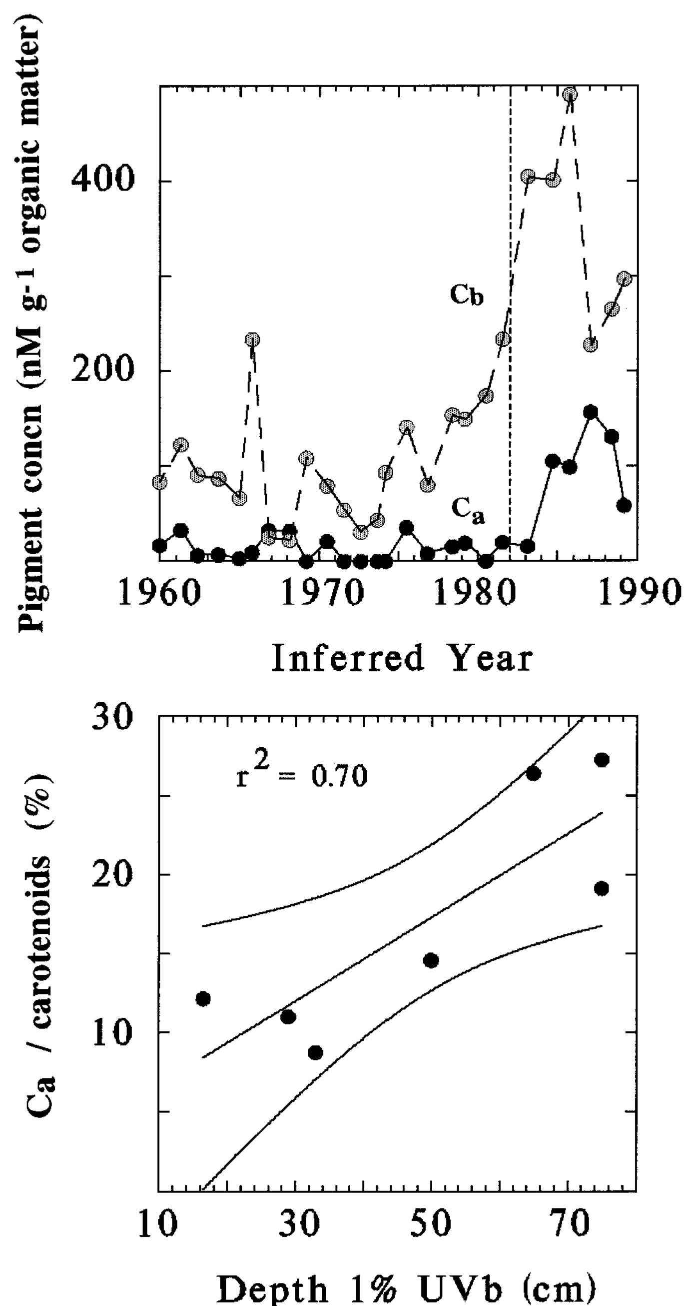

Fig. 6. Estimated concentrations (nmol g^{-1} organic matter) of UVR-absorbing compounds C_a and C_b in Lake 302S (1960–1990, top) and the relationship between relative abundance of C_a (as % carotenoid sum) and depth of 1% incident UVb radiation (m) 1978–1987 (bottom). Carotenoid sum composed of alloxanthin, diatoxanthin, and lutein-zeaxanthin. Sediment age as Fig. 4. (Modified from Leavitt et al. 1997.)

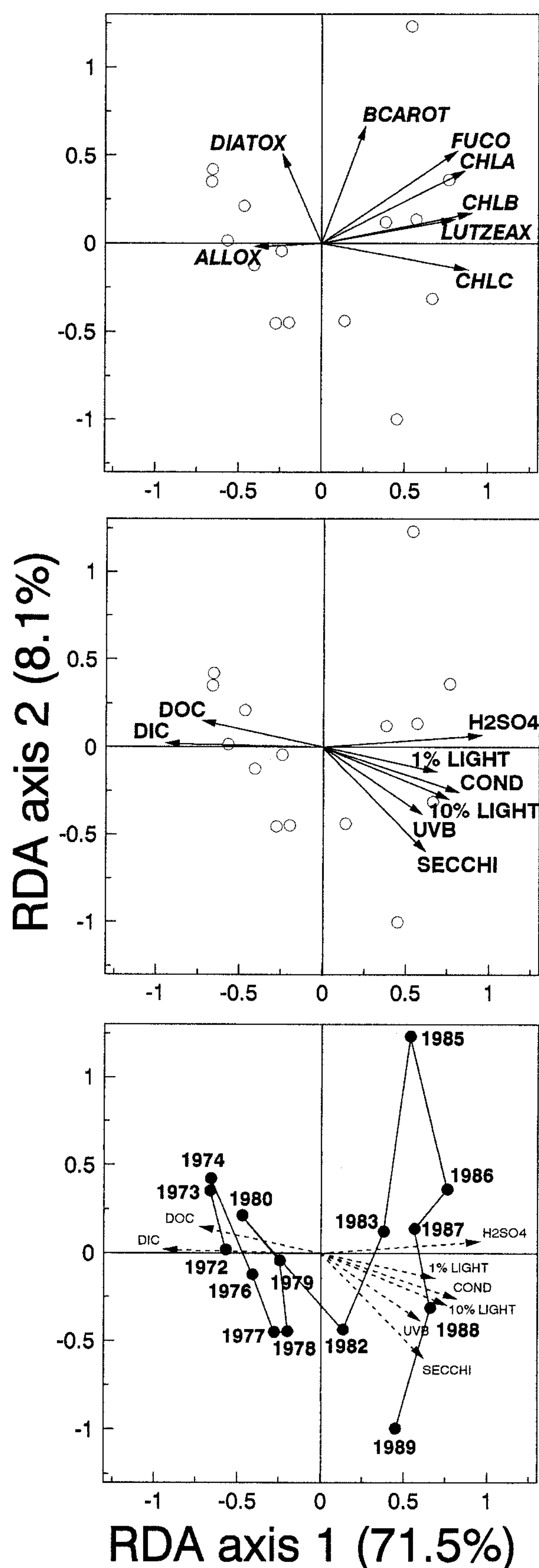

Fig. 7. Redundancy analysis (RDA) covariance biplot showing relationships among ln $(x + 1)$-transformed pigment concentrations (arrows; upper), pH- and irradiance-related environmental variables (arrows; middle, lower), and fossil pigment samples (circles; all) in sediments from Lake 302S (1972–1990). Sample scores are 0.5 times actual values. Explanatory environmental variables include dissolved inorganic (DIC) and organic carbon (DOC), mass of acid added (H_2SO_4), conductivity at 25°C (cond), and depths of 1% incident light (1% light), 10% incident light (10% light), 1% UVR-b (UVb), and Secchi measurements (Secchi). Pigments include β-carotene (bcarot), alloxanthin (allox), diatoxanthin (diatox), fucoxanthin (fuco), lutein-zeaxanthin (lutzeax), and Chl *a, b,* and *c*.

Table 2. Variance in fossil pigment composition (%) explained by historical variation in environmental variables related to pH and irradiance in Lake 302S, 1972–1990. Ordinations conducted with total pigments, Chls alone, or carotenoids alone. Total pigments include undegraded Chls *a, b* and *c,* and carotenoids β-carotene, diatoxanthin, fucoxanthin, alloxanthin, and lutein-zeaxanthin. Significant explanatory variables are listed below variance analyses and include conductivity (cond; μS cm^{-1}), dissolved inorganic carbon (DIC; μM), mass of H_2SO_4 added (H_2SO_4; kg), Secchi depth (Secchi; m), depth of 10% surface irradiance (10% light; m), depth of 1% surface irradiance (1% light; m), depth of 1% UVR-b (UVR-b; m), and dissolved organic carbon (DOC; mg DOC $liter^{-1}$).

	Total pigments	Chls	Carotenoids
Total explained	82.4	80.6	83.1
pH-related	12.0	12.3	51.4
Irradiance related	9.0	6.6	12.5
pH × irradiance	61.4	61.7	19.2
Unexplained	17.6	19.4	16.9
pH related	cond DIC H_2SO_4	cond DIC H_2SO_4	cond DIC H_2SO_4
Irradiance related	10% light DOC 1% light UVR-B Secchi	10% light DOC 1% light UVR-B Secchi	10% light DOC

partitioning that included Chl *a* and phytoplankton biomass explained ~5% more variance than did procedures without these algal variables (data not shown).

RDA ordinations separated fossil pigments from Lake 302S along gradients related to pH and irradiance (Fig. 7). RDA axis 1 was significant ($P < 0.05$), explained 71.5% of fossil variance, and was positively correlated with H_2SO_4 and the maximum depth of light penetration and inversely related to DIC and DOC contents. In general, this axis separated pigments from chlorophytes (Chl *b,* lutein-zeaxanthin), siliceous algae (fucoxanthin), and sedimentary Chl *a* in clear acidic waters from the cryptophyte carotenoid alloxanthin which was common when carbon content was great. The second RDA axis was only marginally significant ($P = 0.07$), explained 8.1% of total variance, and was negatively correlated with secchi depth and UVR-b penetration (Fig. 7). Diatoxanthin from diatoms was characteristic of waters with low transparency and UVR-b. Ubiquitous β-carotene was not clearly related to either RDA axis.

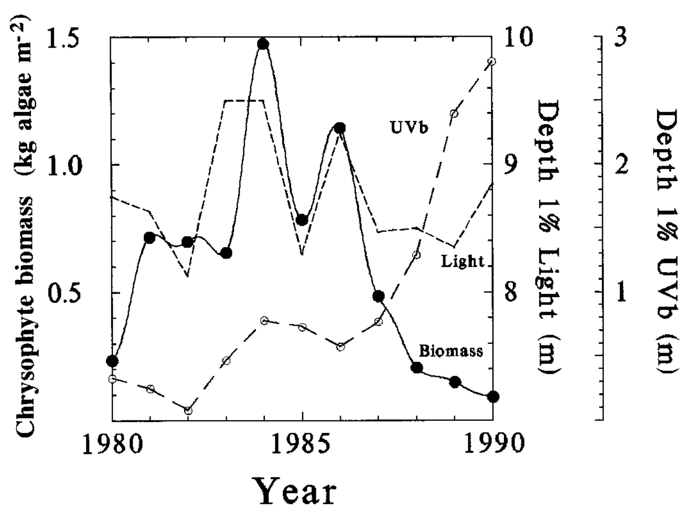

Fig. 8. Historical change in euphotic, planktonic chrysophyte biomass (kg wet wt m^{-2}; ●), photic zone depth (1% incident light, m; – – –), and depth of 1% incident UVR-b (m; ○) in Lake 302S (1980–1990).

Ordinations of fossil pigment samples separated pre-manipulation assemblages from those occurring after the onset of acidification (Fig. 7). Before 1982, total fossil pigment composition was characteristic of colored waters with relatively large DIC and DOC content. During this period, most of the variance in fossil composition was parallel to axes associated with Secchi depth or UVR penetration. Following the onset of acidification in 1982, assemblages moved into the ordination space characterized by low pH (high H_2SO_4) and low carbon content. Unexpectedly, subsequent variation appeared to be in a direction not clearly associated with either pH or irradiance, but which appeared to record mainly changes in fossil β-carotene and fucoxanthin content (Fig. 7).

Complex interactions between pH and irradiance were also evident in historical records of phytoplankton and limnological conditions (Fig. 8). Deep-water populations were common in Lake 302 and were composed mainly of chrysophytes between 1973 and 1987 (Fee 1976; Findlay and Kasian 1990; Findlay et al. 1999). Although chrysophyte standing crop was weakly correlated ($r^2 = 0.23$, $P = 0.13$) with photic zone depth between 1980 and 1990, correlations were particularly poor following an 8-fold increase in the depth to which UVR penetrated (post-1987; Fig. 8).

Discussion

Fossil chronology—Several lines of evidence suggest that the fossil chronology of Lake 302S derived from previous ^{210}Pb analyses (Anderson et al. 1987) was reliable despite high densities of burrowing and epipelic zoobenthos. First, changes in the community composition of acid-sensitive chrysophytes occurred concomitant with the start of acidification in Lake 302S, when acidophilic *S. echinulata* ($pH_{optimum} = 5.6$; Dixit et al. 1989*b*) increased mainly at the expense of *M. duerrschmidtiae* ($pH_{optimum} = 6.9$; Fig. 4). Additionally, chrysophyte-inferred pH was highly correlated ($r^2 = 0.85$; $P < 0.0001$) with the epilimnetic pH measured during the ice-free season in Lake 302S (Fig. 4). The reduced range of inferred pH (5.0–5.7) relative to aerated surface water values (4.5–6.6) is consistent with the observation that a large portion of the chrysophyte biomass was associated with metalimnetic blooms (Fee 1976; Findlay and Kasian 1990; Findlay et al. 1999) and that the pH of these deep waters was up to 1 unit greater than epilimnetic values during acidification (Rudd et al. 1990). Additionally, small populations of chrysophytes were also present under ice (*see above*; Kling and Holmgren 1972) when average pH was either lower (pre-acidification) or higher (during acidification) than mean summer pH (Rudd et al. 1988). Finally, correlations between fossil and algal abundance were significant for comparisons of fucoxanthin–chrysophytes ($r^2 = 0.72$, $P < 0.05$) or fucoxanthin–siliceous algae ($r^2 = 0.67$, $P < 0.05$), as expected because chrysophytes were the main algal group until 1988 (Fig. 3) and because their predominantly planktonic populations were well-sampled by routine methods (Findlay and Kasian 1990).

The reliability of the Lake 302N chronology was not evaluated using fossil chrysophytes. However, Anderson et al. (1987) suggested that accumulation rates in the north basin are as predictable and reliable as those in Lake 302S. This hypothesis was supported by the observation that concentrations of several fossil pigments increased 25–85% between 1972 and 1976 when N and P were added to the hypolimnion of Lake 302N and euphotic Chl and algal biomass increased 113% and 25% respectively (Schindler et al. 1980).

Strong correlations between fossil pigment concentrations and algal standing crop during ice-free season are expected when phytoplankton are quantitatively more important than other sources of pigment and when under-ice algal production is relatively unimportant (Leavitt and Findlay 1994; Leavitt et al. 1994*a*). In Lake 302S, significant correlations between planktonic chrysophytes and fucoxanthin ($r^2 = 0.72$, $P < 0.001$) or undegraded Chl *a* are consistent with the observations that this taxon bloomed mainly in summer (Kling and Holmgren 1972), was the predominant phytoplankton group until 1987 (Fig. 3; Findlay and Kasian 1990), and lacked significant benthic populations (e.g., Leavitt et al. 1994*a*). Significant correlation between total phytoplankton standing crop and chemically labile Chl *a* ($r^2 = 0.60$, $P < 0.05$), but not chemically stable β-carotene (Leavitt and Carpenter 1990*a*; Hurley and Armstrong 1990; Hurley and Armstrong 1991; $r^2 = 0.08$, $P < 0.46$), probably reflects the observations that chrysophytes were located deep in the water column (Fee 1976; Findlay and Kasian 1990; Findlay et al. 1999) above anoxic waters (Schindler et al. 1980, 1996*b*) where oxidative losses are low and labile pigments are deposited before degradation (Leavitt and Carpenter 1990*b*; Leavitt 1993). In contrast, concentrations of chemically stable β-carotene are less influenced by oxidation and better record lake-wide algal biomass, including non-planktonic sources (Leavitt and Carpenter 1990*a*; Hurley and Armstrong 1990).

Correlations between fossil Chl *b* ($r^2 = 0.22$, $P < 0.2$) or lutein-zeaxanthin ($r^2 = 0.29$, $P = 0.13$) and planktonic chlorophytes were likely weakened by benthic production of filamentous green metaphyton (Turner et al. 1995*a,b,c*) or by

contributions from zeaxanthin-containing cyanobacteria (Findlay and Kasian 1990; Findlay et al. 1999). Similarly, cryptophytes commonly bloom under-ice prior to the onset of regular planktonic sampling (Kling and Holmgren 1972; Findlay and Kasian 1990; Leavitt and Findlay 1994). Overall, correlations between planktonic populations and their respective algal indicator pigments were stronger than those recorded for nearby Lake 227, a site with annually laminated sediments, persistent deep-water anoxia, and few benthic invertebrates compared to Lake 302S (Leavitt and Findlay 1994; Leavitt et al. 1994*a*).

Algal response to lake acidification—Comparison of fossil records from the south and north basins of Lake 302 suggested that moderate acidification with H_2SO_4 resulted in transient increases in total algal abundance (as Chl *a*, β-carotene, pheophytin *a*) due to deep-water blooms of chrysophytes (fucoxanthin) and benthic green algae (Chl *b*; Fig. 5). Concentrations of most pigments increased shortly after acidification commenced, peaked during the mid-1980s, then declined following 1987 when pH was reduced to <4.8. We infer that fossil fucoxanthin recorded mainly changes in planktonic chrysophytes because fucoxanthin levels were more highly correlated with chrysophyte biomass alone ($r^2 = 0.72$, $P < 0.05$) than with chrysophytes and diatoms together ($r^2 = 0.67$, $P < 0.05$), because diatoms were rare in the phytoplankton and declined following acidification (Fig. 3; Findlay and Kasian 1990) and because the diatom-specific carotenoid diatoxanthin also declined after 1985 (Fig. 5).

Increased concentrations of Chl *b* (Fig. 5) and associated pigments (pheophytin *b*, lutein-zeaxanthin; not shown) were consistent with elevated abundance of filamentous green metaphyton following 1983 (Turner et al. 1995*c*). These fossil patterns are unlikely to have arisen from increased inputs from macrophytes or terrestrial plants because aquatic plants are rare in Lake 302 (D. W. Schindler unpubl. data) because the local forest has been undisturbed for over 25 yr and because pigments from terrestrial sources are usually degraded prior to permanent deposition (Gorham and Sanger 1975; Leavitt 1993). Instead, increases in Chl *b*, pheophytin *b*, and lutein-zeaxanthin were most consistent with elevated biomass of metaphytic *Zygogonium*, a chlorophyte taxon with efficient DIC uptake and low sensitivity to benthic grazers (Turner et al. 1995*a,b,c*).

Differences between fossil concentrations of fucoxanthin in the north and south basins suggested that the degree of acidification was the key to triggering chrysophyte blooms. For example, fossil fucoxanthin increased in Lake 302S during 1984–1987 (Fig. 5) when pH was 4.7–5.2 (Fig. 2), but not in Lake 302N (Fig. 5) where chrysophytes were common also (Fee 1976) although pH remained >5.2. Although equimolar quantities of H^+ were added as HNO_3, pH declined less in the north basin because HNO_3 was more efficiently neutralized by algal uptake and bacterial denitrification (Rudd et al. 1990). Overall, these deep-water blooms resulted in 2–4 fold increases in total algal biomass (Chl *a*, β-carotene, pheophytin *a*) in Lake 302S relative to both preacidification conditions and algal abundance in Lake 302N (Fig. 5).

Algal community changes inferred from fossil pigments in Lake 302S were similar to those recorded in both experimentally (Findlay and Kasian 1996) and atmospherically acidified lakes (Schindler et al. 1991). Moderate acidification to pH ~5.0 commonly increases the abundance of chrysophytes and dinoflagellates, often at the expense of planktonic diatoms (Yan and Stokes 1978; Nichols et al. 1982; Schindler et al. 1991; Findlay and Kasian 1996). These studies also often show that continued acidification to pH<5.0 results in predominance by dinoflagellates and loss of chrysophytes, such as occurred in Lake 302S when deep-water chrysophyte populations collapsed (Findlay and Kasian 1990; Findlay et al. 1999).

Acidification of Lake 302N with HNO_3 apparently increased the abundance of chlorophytes as recorded by fossil Chl *b* (Fig. 5) and lutein-zeaxanthin (not shown). Historical records confirm that planktonic green algae (containing *b*-phorbins, lutein) and unicellular cyanobacteria (zeaxanthin) increased during the later stages of HNO_3 addition (Fig. 3; Findlay and Kasian 1990), although filamentous green metaphyton remained rare in comparison to Lake 302S (Turner et al. 1987). The magnitude of fossil increase during the mid-1980s was similar to that observed during fertilization of the hypolimnion of Lake 302N with N, P, and C (1972–1976, 1978; Schindler et al. 1980), consistent with the suggestion that added HNO_3 was rapidly taken up by algae and deposited at the lake bottom (Rudd et al. 1990). Overall, fossil analyses suggest that the total abundance of chlorophyte algae declined during initial acidification with HCl during 1987–1989 (Fig. 5), similar to observed decreases in green phytoplankton (Fig. 3). Since 1990, planktonic chlorophytes have been variable but generally abundant due to further manipulations (Findlay et al. unpubl. data). The observation that concentrations of fossil Chl *a* and β-carotene varied little between 1960 and 1989 suggests that neither hypolimnetic enrichment nor moderate acidification (pH > 5.1) greatly stimulated whole-lake algal production, consistent with conclusions of Schindler et al. (1980) and Findlay and Kasian (1990), respectively, based on phytoplankton alone.

Not all aspects of algal community change following acidification were accurately recorded by sedimentary pigments. For example, peridinin is a highly labile carotenoid produced by dinoflagellates (Hurley and Armstrong 1990; Leavitt and Carpenter 1990*a*) that was completely degraded before burial. Consequently, it was not possible to reconstruct changes in dinoflagellate abundance, despite their importance in the plankton following 1987 (Findlay and Kasian 1990; Findlay et al. 1999). Similarly, specific pigments from filamentous cyanobacteria (e.g., myxoxanthophyll, aphanizophyll) were rare in sediments from both basins. The relationship between cryptophyte abundance and fossil alloxanthin was also untested in this study because cryptophytes commonly bloom under ice in spring, usually before the onset of routine summer sampling (Findlay and Kasian 1990; Leavitt and Findlay 1994) and because planktonic populations varied little through the experiment (Fig. 3). Low correlations commonly result from insufficient variation in explanatory variables (e.g., Leavitt and Findlay 1994). Fortunately, fossil estimates of total algal abundance were unlikely to be biased by loss of peridinin or cyanobacterial carotenoids or by the unknown

reliability of alloxanthin, because all taxa also contain both β-carotene and Chl *a* (Goodwin 1980; Leavitt 1993).

Relative importance of pH and irradiance—Variance partitioning analysis and ordinations suggested that pH was the main control of fossil carotenoid composition (Table 2, Fig. 7). Over 50% of variance in indicator carotenoids was explained by historical changes in the mass of H_2SO_4 added, DIC, and conductivity. In particular, ordinations of fossil pigments suggested that alloxanthin (cryptophytes) and secondarily diatoxanthin (mainly diatoms) declined with DIC during acidification, whereas pigments from green algae (Chl *b*, lutein-zeaxanthin) and chrysophytes (fucoxanthin, Chl *c*, Chl *a* in part) were more common in acidic waters (Fig. 7). Turner et al. (1987) also demonstrated that benthic photosynthesis could be limited by the supply of DIC, whereas Vinebrooke (1996) and Vinebrooke and Graham (1997) used multivariate analyses to determine that DIC and DOC were the main controls of periphyton composition and recovery in acidified lakes on the Canadian Shield. In our analyses, the influence of DIC cannot be easily distinguished from those of other chemical factors because the effects of DIC were strongly and negatively correlated with that of H_2SO_4 and positively correlated with DOC and pH (Fig. 7).

Irradiance and its combined effects with pH accounted for 12–32% of historical variation in fossil carotenoid assemblages (Table 2). Examination of ordination biplots showed that most variation in fossil assemblages prior to acidification was correlated to variation in Secchi depth (Fig. 7), whereas both pH and irradiance were important following 1982. In contrast, comparisons of ordinations with and without chlorophylls (Table 2) suggested that total algal abundance may have been controlled mainly by the joint influence of pH- and irradiance-related factors. For example, ordinations that included ubiquitous Chl *a* always exhibited ~60% of total fossil variance in the interaction term between pH and irradiance (Table 2). Similarly, historical changes in equally widespread β-carotene were not clearly related to either pH or irradiance alone (Fig. 7). We speculate that these patterns arise because regulation of total algal biomass is under multifactorial control (e.g., Kitchell 1992; Carpenter and Kitchell 1993), whereas individual algal groups exhibit more restricted environmental preferences, even at comparatively coarse taxonomic levels (Fig. 7). Hall et al. (1999) also demonstrate that the amount of variance explained by higher order interaction among environmental factors varies inversely with the taxonomic resolution of the fossil group (pigments > chironomids > diatoms).

Limnological records also suggested that acidification of Lake 302S altered the subsurface light regime and intensified deep-water blooms of chrysophytes, dinoflagellates, and benthic green metaphyton (e.g., Findlay and Kasian 1990). Frequently, deep-water populations in small lakes are limited by light rather than by nutrient supply or grazing invertebrates (Pick et al. 1984; St. Amand and Carpenter 1993). Because moderate acidification of lakes commonly reduces DOC content and increases light penetration (Schindler et al. 1996*a*; Yan et al. 1996; Williamson et al. 1996), we hypothesize that increased whole-lake algal abundance may have resulted from improved subsurface light regimes and increased deep-water habitat. Because most of the phytoplankton biomass was associated with deep-water blooms of chrysophytes until 1987 (Findlay and Kasian 1990), changes in light penetration might be expected to alter total algal biomass without greatly changing relative phytoplankton composition.

Changes in penetration of ultraviolet radiation may have contributed to algal community change in Lake 302S. Schindler et al. (1996*b*) demonstrated that severe acidification of the south basin reduced DOC to <1.5 mg $liter^{-1}$ and resulted in an 8-fold increase in penetration of UVR-b, as has been shown in other acidified lakes (Yan et al. 1996; Williamson et al. 1996; Frost et al. 1999). In Lake 302S, the greatest increases in UVR penetration occurred following acidification to pH ~4.5 (Fig. 8). By 1990, UVR-b was detectable at 2.8 m (Fig. 8) and UVR-a should have penetrated 2.5-fold deeper (Williamson et al. 1996), encompassing much of the water column (Table 1). UVR-a is known to inhibit growth of many eucaryotic algae in transparent freshwaters (Bothwell et al. 1993, 1994; Vinebrooke and Leavitt 1996), although little is known of the specific sensitivity of planktonic chrysophytes to UVR. Recent research has demonstrated that the most UVR-resistant algal taxa tend to be those that contain high contents of sporopollenin, have thick cell walls, or are large cells (diameters >100 μm; Xiong et al. 1996, 1997; Garcia-Pichel 1994), all features that are absent from the chrysophytes of Lake 302S (*see* Lee 1989; Findlay and Kasian 1990). In contrast, the abundance of armored dinoflagellates (*Peridinium* spp.) was more strongly correlated with the depth of UVR penetration ($r^2 = 0.90$, $P < 0.0001$; 1972–1990) than with epilimnetic pH ($r^2 = 0.68$, $P < 0.001$) in Lake 302 (Findlay et al. unpubl. data), suggesting that these taxa were less inhibited by UVR than were the chrysophytes.

Increased penetration of UVR was also recorded by changes in fossil pigments characteristic of highly transparent lakes (Fig. 6). These pigments are common in many alpine (Leavitt et al. 1994*b*), prairie (Vinebrooke et al. 1998), and arctic lakes (Leavitt et al. unpubl. data). Typically, fossil concentrations are greatest in lakes with low integral attenuation of UVR (Leavitt et al. 1997), such as those which are both shallow ($Z_{avg} < 5$ m) and contain low concentrations of DOC (<2 mg $liter^{-1}$), the main factor absorbing UVR in water (Scully and Lean 1994; Morris et al. 1995; Williamson et al. 1996). Carotenoid-normalized concentrations of UVR-absorbing C_a ($\lambda_{max} = 381$ nm) were linearly correlated ($r^2 = 0.70$, $P < 0.05$, 1977–1988) with the maximum depth of UVR penetration (Fig. 6), consistent with a proposed photoprotective function of this compound. Survey of 62 alpine lakes demonstrates that these compounds occur only on soft substrates and presumably arise from benthic algae (Leavitt et al. 1997). Linear correspondence between relative pigment abundance and UVR penetration suggests that these compounds may be promising paleolimnological indicators of past UVR environments.

Some variance in fossil records may be due to unmeasured regulatory processes. For example, changes in food-web composition arising from acidification (e.g., Schindler 1988; Schindler et al. 1985, 1991) or UVR (Williamson et al. 1999; Frost et al. 1999) may have altered algal community com-

position before 1990 (e.g., Fig. 1). Elsewhere we have demonstrated that changes in food-web structure can alter both light penetration and the abundance of metalimnetic phototrophs in lakes (Leavitt et al. 1989), as well as the mechanism by which fossil records are formed (Leavitt and Carpenter 1990*b*; Leavitt 1993). In addition, unpublished analyses show that some common grazers (e.g., *Daphnia galeata mendotae, Diaphanosoma birgeii*) declined during acidification of Lake 302S (D. F. Malley et al. pers. comm.) and that populations of zooplanktivorous fishes collapsed during summer 1989 (Mills et al. 1992). However, the observation that changes in crustacean zooplankton biomass were not marked until after 1987 (D. F. Malley pers. comm.), yet algal communities were already substantially altered by that time (Fig. 5; Findlay and Kasian 1990), suggests that most changes in the fossil record were independent of food-web alterations. Because partitioning analyses explained more than 80% of variation in fossil pigments (Table 2), it appears that most of the important explanatory variables were measured.

Conclusions

Comparison of fossil records from the north and south basins of Lake 302 suggested that inferred lake-wide algal abundance increased more than 2-fold during acidification to pH ~5.0 but that biomass declined upon further acidification to pH 4.5. Variance partitioning analysis suggested that ~50% of variation in past algal composition could be directly attributed to changes in pH and related factors, whereas total algal abundance was more responsive to the combined effects of pH and irradiance. In particular, historical and fossil records showed that deep-water populations of chrysophytes initially increased, possibly because of moderate DOC loss and increased penetration of light. However, continued severe acidification of Lake 302S further reduced DOC to <1.5 mg liter^{-1}, increased penetration of inhibitory UVR, and may have led to loss of deep-water chrysophytes in favor of armored dinoflagellates.

Taken together, fossil and historical records suggest that algal response to acidification will depend on complex interactions between pH and DOC-regulated irradiance. Under conditions of high DOC content (e.g., >5 mg DOC liter^{-1}), moderate acidification to pH ~5.0 may reduce DOC levels, increase light penetration, and stimulate production of deep-water or benthic algae. Alternately, if DOC levels are initially low (e.g., ~2 mg liter^{-1}), or if acidification is severe and prolonged (pH $<$ 4.5), the main effect of acidification may be to increase the penetration of damaging UV radiation and to nullify increases in production that would otherwise arise from an improved light regime. Further tests of this hypothesis are required and should include use of fossil pigments to reconstruct past changes in algal communities and UVR environments.

References

ANDERSON, R. F., S. L. SCHIFF, AND R. H. HESSLEIN. 1987. Determining sediment accumulation and mixing rates using ^{210}Pb, ^{137}Cs, and other tracers: Problems due to postdepositional mobility or coring artifacts. Can. J. Fish. Aquat. Sci. **44** (suppl. 1)**:** 231–250.

APPELBERG, M., B.-I. HENRIKSON, L. HENRIKSON, AND M. SVEDANG. 1993. Biotic interactions within the littoral community of Swedish forest lakes during acidification. Ambio **22:** 290–297.

ARMSTRONG, F. A. J., AND D. W. SCHINDLER. 1971. Preliminary chemical characterization of waters in the Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Bd. Can. **28:** 171–187.

ASMUND, B., AND J. KRISTIANSEN. 1986. The genus *Mallomonas* (Chrysophyceae). Opera Bot. **85:** 128 p.

BEAMISH, R. J., L. M. BLOUW, AND G. A. MCFARLANE. 1976. A fish and chemical study of 109 lakes in the Experimental Lakes Area, northwestern Ontario, with appended reports on lake whitefish ageing errors and northwestern Ontario baitfish industry. Can. Fish. Mar. Serv. Tech. Rep. 607.

BORCARD, D., P. LEGENDRE, AND P. DRAPEAU. 1992. Partialling out the spatial component of ecological variation. Ecology **73:** 1045–1055.

BOTHWELL, M. L., D. SHERBOT, AND C. M. POLLOCK. 1994. Ecosystem response to solar Ultraviolet-B radiation: Influence of trophic-level interactions. Science **265:** 97–100.

———, ———, A. C. ROBERGE, AND R. J. DALEY. 1993. Influence of natural ultraviolet radiation on lotic periphytic diatom community growth, biomass accrual, and species composition: Short-term versus long-term effects. J. Phycol. **29:** 24–35.

BRUNSKILL, G. J., D. POVOLEDO, B. W. GRAHAM, AND M. P. STAINTON. 1971. Chemistry of surface sediments of sixteen lakes in the Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Bd. Can. **28:** 277–294.

———, AND D. W. SCHINDLER. 1971. Geography and bathymetry of selected lake basins, Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Bd. Can. **28:** 139–155.

CARPENTER, S. R., AND J. F. KITCHELL [eds.] 1993. The trophic cascade in lake ecosystems. Cambridge.

———, P. R. LEAVITT, J. J. ELSER, AND M. M. ELSER. 1988. Chlorophyll budgets: Response to food web manipulations. Biogeochemistry **6:** 79–90.

CHALANCHUK, S. M. 1986. Condition and growth of white suckers, *Catostomus commersoni*, in Lake 302, a double-basin acidified lake in the Experimental Lakes Area. Can. Tech. Rep. Fish. Aquat. Sci. 1476.

CLEUGH, T. R., AND B. W. HAUSER. 1971. Results of the initial survey of the Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Bd. Can. **28:** 129–137.

DAVIES, B. H. 1976. Carotenoids, p. 38–165. *In* T. W. Goodwin [ed.], Chemistry and biochemistry of plant pigments. V. 2. Academic.

DEAN, W. E. 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: Comparison with other methods. J. Sediment. Petrol. **44:** 242–248.

DIXIT, S. S., A. S. DIXIT, AND J. P. SMOL. 1989*a*. Lake acidification recovery can be monitored using chrysophycean microfossils. Can. J. Fish. Aquat. Sci. **46:** 1309–1312.

———, ———, AND ———. 1989*b*. 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.

———, ———, AND ———. 1992. Algal microfossils provide high temporal resolution of environmental trends. Water Air Soil Pollut. **62:** 75–87.

FEE, E. J. 1976. The vertical and seasonal distribution of chlorophyll in lakes of the Experimental Lakes Area, northwestern Ontario:

Implications for primary production estimates. Limnol. Oceanogr. **21:** 767–783.

FINDLAY, D. L., AND S. E. M. KASIAN. 1990. Phytoplankton communities of lakes experimentally acidified with sulfuric and nitric acids. Can. J. Fish. Aquat. Sci. **47:** 1378–1386.

———, AND ———. 1996. The effect of incremental pH recovery on the Lake 223 phytoplankton community. Can. J. Fish. Aquat. Sci. **53:** 856–864.

———, ———, M. T. TURNER, AND M. P. STAINTON. 1999. Comparison of responses of phytoplankton and epilithon during acidification and early recovery. Freshwater Biol. **38:** In press.

FRANCE, R. L., E. T. HOWELL, M. J. PATTERSON, AND P. M. WELBOURN. 1991. Relationship between littoral grazers and metaphytic filamentous algae in five softwater Ontario lakes. Hydrobiologia **220:** 9–27.

FROST, T. M. AND OTHERS. 1999. Multiple stresses from a single agent: Diverse responses to the experimental acidification of Little Rock Lake, Wisconsin. Limnol. Oceanogr. **44:** 784–794.

GARCIA-PICHEL, F. 1994. A model for internal self-shading in planktonic microorganisms and its implications for the usefulness of sunscreens. Limnol. Oceanogr. **39:** 1704–1717.

GOODWIN, T. W. 1980. The biochemistry of the carotenoids. V. 1. Chapman and Hall.

GORHAM, E., AND J. SANGER. 1975. Fossil pigments in Minnesota lake sediments and their bearing upon the balance between terrestrial and aquatic inputs to sedimentary organic matter. Int. Ver. Theor. Angew. Limnol. Verh. **19:** 2267–2273.

HALL, R. I., P. R. LEAVITT, R. QUINLAN, A. S. DIXIT, AND J. P. SMOL. 1999. Effects of agriculture, urbanization, and climate on water quality in the northern Great Plains. Limnol. Oceanogr. **44:** 739–756.

HAMILTON, A. L. 1971. Zoobenthos of fifteen lakes in the Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Bd. Can. **28:** 257–263.

HOWELL, E. T., M. A. TURNER, R. L. FRANCE, M. B. JACKSON, AND P. M. STOKES. 1990. Comparison of zygnematacean (Chlorophyta) algae in the metaphyton of two acidic lakes. Can. J. Fish. Aquat. Sci. **47:** 1085–1092.

HURLEY, J. P., AND D. E. ARMSTRONG. 1990. Fluxes and transformations of aquatic pigments in Lake Mendota, Wisconsin. Limnol. Oceanogr. **35:** 384–398.

———, AND ———. 1991. Pigment preservation in lake sediments: A comparison of sedimentary environments in Trout Lake, Wisconsin. Can. J. Fish. Aquat. Sci. **48:** 472–486.

KITCHELL, J. F. [ed.] 1992. Food web management: A case study of Lake Mendota. Springer.

KLING, H. J. AND S. K. HOLMGREN. 1972. Species composition and seasonal distribution of phytoplankton in the Experimental Lakes Area, northwestern Ontario. Can. Fish. Mar. Serv. Tech. Rep. 337.

KULLBERG, A., K. A. BISHOP, A. HARGEBY, M. JANSSON, AND R. C. PETERSEN. 1993. The ecological significance of dissolved organic carbon in acidified lakes. Ambio **22:** 331–337.

LEAVITT, P. R. 1993. A review of factors that regulate carotenoid and chlorophyll deposition and fossil pigment abundance. J. Paleolimnol. **9:** 109–127.

———, AND S. R. CARPENTER. 1990*a*. Aphotic pigment degradation in the hypolimnion: Implications for sedimentation studies and paleolimnology. Limnol. Oceanogr. **35:** 520–535.

———, AND ———. 1990*b*. Regulation of pigment sedimentation by photo-oxidation and herbivore grazing. Can. J. Fish. Aquat. Sci. **47:** 1166–1176.

———, ———, AND J. F. KITCHELL. 1989. Whole-lake experiments: The annual record of fossil pigments and zooplankton. Limnol. Oceanogr. **34:** 700–717.

———, AND D. L. FINDLAY. 1994. Comparison of fossil pigments with 20 years of phytoplankton data from eutrophic Lake 227, Experimental Lakes Area, Ontario. Can. J. Fish. Aquat. Sci. **51:** 2286–2299.

———, B. J. HANN, AND OTHERS. 1994*a*. Paleolimnological analysis of whole-lake experiments: An overview of results from Experimental Lakes Area Lake 227. Can. J. Fish. Aquat. Sci. **51:** 2322–2332.

———, D. E. SCHINDLER, A. J. PAUL, A. K. HARDIE, AND D. W. SCHINDLER. 1994*b*. Fossil pigment records of phytoplankton in trout-stocked alpine lakes. Can. J. Fish. Aquat. Sci. **51:** 2411–2423.

———, R. D. VINEBROOKE, D. B. DONALD, J. P. SMOL, AND D. W. SCHINDLER. 1997. Past ultraviolet radiation environments in lakes derived from fossil pigments. Nature **388:** 457–459.

LEE, R. E. 1989. Phycology, 2nd ed. Cambridge.

LEGENDRE, P. 1993. Spatial autocorrelation: Trouble or new paradigm? Ecology **74:** 1659–1673.

LIAAEN-JENSEN, S. 1971. Isolation, reactions, p. 61–188. *In* O. Isler [ed.], Carotenoids. Birkhauser.

LINE, J. M., C. J. F. TER BRAAK, AND H. J. B. BIRKS. 1994. WACALIB version 3.3: A computer program to reconstruct environmental variables from fossil assemblages by weighted-averaging and to derive sample-specific errors of prediction. J. Paleolimnol. **10:** 147–152.

LOTTER, A. F., AND H. J. B. BIRKS. 1993. The impact of the Laacher See Tephra on terrestrial and aquatic ecosystems in the Black Forest (southern Germany). J. Quat. Sci. **8:** 263–276.

MANTOURA, R. F. C., AND C. A. LLEWELLYN. 1983. The rapid determination of algal chlorophyll and carotenoid pigments and their breakdown products in natural waters by reverse phase high-performance liquid chromatography. Anal. Chim. Acta **151:** 297–314.

MILLIE, D. F., H. W. PAERL, AND J. P. HURLEY. 1993. Microalgal pigment assessments using high-performance liquid chromatography: A synopsis of organismal and ecological applications. Can. J. Fish. Aquat. Sci. **50:** 2513–2527.

MILLS, K. H., S. M. CHALANCHUK, AND D. J. ALLAN. 1992. Effects of acidification on lake whitefish (*Coregonus clupeaformis*). Pol. Arch. Hydrobiol. **39:** 423–430.

MORRIS, D. P., AND OTHERS. 1995. The attenuation of UVR radiation in lakes and the role of dissolved organic carbon. Limnol. Oceanogr. **40:** 1381–1391.

NAUWERCK, A. 1963. Die Beziehungen zwischen Zooplankton und Phytoplankton im See Erken. Symb. Bot. Ups. **17:** 163 p.

NICHOLS, K. H., J. L. BEAVER, AND R. H. ESTABROOK. 1982. Lake wide odours in Ontario and New Hampshire caused by *Chrysochromulina breviturrita* Nich. (Prymensiophyceae). Hydrobiologia **96:** 91–95.

———, L. NAKAMOTO, AND W. KELLER. 1992. Phytoplankton of the Sudbury area lakes (Ontario) and relationships with acidification status. Can. J. Fish. Aquat. Sci. **49** (suppl. 1): 40–57.

PATALAS, K. 1971. Crustacean plankton communities in forty-five lakes in the Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Bd. Can. **28:** 231–244.

PICK, F. R., C. NALEWAJKO, AND D. R. S. LEAN. 1984. The origin of a metalimnetic chrysophyte bloom. Limnol. Oceanogr. **29:** 125–134.

REID, R. A., D. W. SCHINDLER, AND R. V. SCHMIDT. 1975. Phytoplankton production in the Experimental Lakes Area, 1969–1973. Can. Fish. Mar. Serv. Tech. Rep. 560.

RUDD, J. W. M., C. A. KELLY, D. W. SCHINDLER, AND M. A. TURNER. 1988. Disruption of the nitrogen cycle in acidified lakes. Science **240:** 1515–1517.

———, ———, ———, AND ———. 1990. A comparison of the acidification efficiencies of nitric and sulfuric acids by two

whole-lake addition experiments. Limnol. Oceanogr. **35:** 663–679.

ST. AMAND, A., AND S. R. CARPENTER. 1993. Metalimnetic phytoplankton dynamics, p. 210–224. *In* S.R. Carpenter and J. F. Kitchell [eds.], The trophic cascade in lakes. Cambridge.

SANGER, J. E. 1988. Fossil pigments in paleoecology and paleolimnology. Palaeogeogr. Palaeoclim. Palaeoecol. **62:** 343–359.

SCHINDLER, D. W. 1971. Light, temperature and oxygen regimes of selected lakes in the Experimental Lakes Area (ELA), northwestern Ontario. J. Fish. Res. Bd. Can. **28:** 295–301.

———. 1975. Whole-lake eutrophication experiments with phosphorus, nitrogen, and carbon. Int. Ver. Theor. Angew. Limnol. Verh. **19:** 3221–3231.

———. 1988. Effects of acid rain on freshwater ecosystems. Science **239:** 149–157.

———, S. E. BAILEY, AND OTHERS. 1996*a*. The effects of climatic warming on the properties of boreal lakes and streams at the Experimental Lakes Area, northwestern Ontario. Limnol. Oceanogr. **41:** 1004–1017.

———, P. J. CURTIS, B. R. PARKER, AND M. P. STAINTON. 1996*b*. Consequences of climate warming and lake acidification for UV-B penetration in North American boreal lakes. Nature **379:** 705–706.

———, T. M. FROST, AND OTHERS. 1991. Comparison between experimentally- and atmospherically-acidified lakes during stress and recovery, p. 193–226. *In* Acidic deposition: Its nature and impacts. Proc. R. Soc. Edinb. **97.**

———, K. W. MILLS, AND OTHERS. 1985. Long-term ecosystem stress: The effects of years of acidification of a small lake. Science **228:** 1395–1401.

———, T. RUSZCZYNSKI, AND E. J. FEE. 1980. Hypolimnion injection of nutrient effluents as a method for reducing eutrophication. Can. J. Fish. Aquat. Sci. **37:** 320–327.

SCULLY, N. M. AND D. R. S. LEAN. 1994. The attenuation of ultraviolet radiation in temperate lakes. Arch. Hydrobiol. **43:** 135–144.

SHEARER, J. A. 1978. Two devices for obtaining water samples integrated over depth. Can. Fish. Mar. Serv. Tech. Rep. 772.

———, AND E. R. DEBRUYN. 1986. Phytoplankton productivity responses to direct addition of sulfuric and nitric acids to the waters of a double-basin lake. Water, Air, Soil Pollut. **30:** 695–702.

———, ———, D. R. DECLERQ, D. W. SCHINDLER, AND E. J. FEE. 1985. Manual of phytoplankton primary production methodology. Can. Fish. Aquat. Sci. Tech. Rep. 1341.

SIVER, P. A. 1991. The biology of *Mallomonas*: Morphology, taxonomy and ecology. Kluwer.

SMOL, J. P. 1983. Paleophycology of a high arctic lake near Cape Herschel, Ellesmere Island. Can. J. Bot. **61:** 2195–2204.

STAINTON, M. P., M. L. CAPEL, AND F. A. J. ARMSTRONG. 1977. The chemical analysis of fresh water, 2nd ed. Can. Fish. Mar. Serv. Misc. Spec. Publ. 25.

STEENBERGEN, C. L. M., H. J. KORTHALS, AND E. G. DOBRYNIN. 1994. Algal and bacterial pigments in non-laminated lacustrine sediment: Studies of their sedimentation, degradation and stratigraphy. FEMS Microbiol. Ecol. **13:** 335–352.

STOCKNER, J. G. 1971. Preliminary characterization of lakes in the Experimental Lakes Area, northwestern Ontario, using diatom occurrences in sediments. J. Fish. Res. Bd. Can. **28:** 265–275.

STOKES, P. M. 1981. Benthic algal communities in acidic lakes, p. 119–138. *In* R. Singer [ed.], Effects of acidic precipitation on benthos. N. Am. Benthol. Soc.

———. 1986. Ecological effects of acidification on primary producers in aquatic systems. Water, Air Soil Pollut. **30:** 421–438.

SWAIN, A. M. 1973. A history of fire and vegetation in northeastern Minnesota as recorded in lake sediments. Quat. Res. **3:** 383–396.

TER BRAAK, C. J. F. 1986. Canonical correspondence analysis: A new eigenvector technique for multivariate direct gradient analysis. Ecology **67:** 1167–1179.

———. 1988*a*. CANOCO—A FORTRAN program for canonical community ordination by (partial) (detrended) (canonical) correspondence analysis, principal components analysis, and redundancy analysis (version 2.1). Wageningen Inst. Appl. Computer Sci. Tech. Rep. LWA-88-02.

———. 1988*b*. Partial canonical correspondence analysis, p. 551–558. *In* H. H. Brock [ed.], Classification and related methods of data analysis. North Holland.

———. 1990. CANOCO: A FORTRAN program for canonical community ordination. Microcomputer Power.

TURNER, M. A., E. T. HOWELL, AND OTHERS. 1995*a*. Growth characteristics of bloom-forming filamentous green algae in the littoral zone of an experimentally acidified lake. Can. J. Fish. Aquat. Sci. **52:** 2251–2263.

———, ———, AND OTHERS. 1994. Roles of nutrients in controlling growth of epilithon in oligotrophic lakes of low alkalinity. Can. J. Fish. Aquat. Sci. **51:** 2784–2793.

———, M. D. JACKSON, AND OTHERS. 1987. Early responses of periphyton to experimental lake acidification. Can. J. Fish. Aquat. Sci. **44** (suppl. 1)**:** 133–149.

———, G. G. C. ROBINSON, B. E. TOWNSEND, B. J. HANN, AND J. A. AMARAL. 1995*b*. Ecological effects of blooms of filamentous green algae in the littoral zone of an acid lake. Can. J. Fish. Aquat. Sci. **52:** 2264–2275.

———, D. W. SCHINDLER, D. L. FINDLAY, M. B. JACKSON, AND G. G. C. ROBINSON. 1995*c*. Disruption of littoral algal associations by experimental lake acidification. Can. J. Fish. Aquat. Sci. **52:** 2238–2250.

VINEBROOKE, R. D. 1996. Abiotic and biotic regulation of periphyton in recovering acidified lakes. J. N. Am. Benthol. Soc. **15:** 318–331.

———, AND M. D. GRAHAM. 1997. Periphyton assemblages as indicators of recovery in acidified Canadian Shield lakes. Can. J. Fish. Aquat. Sci. **53:** 1557–1568.

———, R. I. HALL, P. R. LEAVITT, AND B. F. CUMMING. 1998. Fossil pigments as indicators of phototrophic response to salinity and climatic change in lakes of western Canada. Can. J. Fish. Aquat. Sci. **55:** 668–681.

———, AND P. R. LEAVITT. 1996. Effects of ultraviolet radiation on periphyton in an alpine lake. Limnol. Oceanogr. **41:** 1035–1040.

VOLLENWEIDER, R. A. 1968. Water management research. OECD Paris. DAS/CSI/68.27.

WILLIAMSON, C. E., B. R. HARGREAVES, P. S. ORR, AND P. A. LOVERA. 1999. Does UV radiation play a role in changes in predation and zooplankton community structure in acidified lakes? Limnol. Oceanogr. **44:** 774–783.

———, R. S. STEMBERGER, D. P. MORRIS, T. M. FROST, AND S. G. PAULSEN. 1996. Ultraviolet radiation in North American lakes: Attenuation estimates from DOC measurements and implications for plankton communities. Limnol. Oceanogr. **41:** 1024–1034.

WOLFE, B., H. J. KLING, G. J. BRUNSKILL, AND P. WILKINSON. 1994. Multiple dating of a freeze core from Lake 227, an experimentally fertilized lake with varved sediments. Can. J. Fish. Aquat. Sci. **51:** 2274–2285.

XIONG, F., J. KOMENDA, J. KOPECKY, AND L. NEDBAL. 1997. Strategies of ultraviolet-B protection in microscopic algae. Physiol. Plant. **96:** 254–265.

———, F. LEDERER, J. LUKAVSKY, AND L. NEDBAL. 1996. Screen-

ing of freshwater algae (Chlorophyta, Chromophyta) for ultraviolet-B sensitivity of the photosynthetic apparatus. J. Plant Physiol. **148:** 42–48.

YAN, N. D., W. KELLER, N. M. SCULLY, D. R. S. LEAN, AND P. J. DILLON. 1996. Increased UV-B penetration in a lake owing to drought-induced acidification. Nature **381:** 141–143.

———, AND P. M. STOKES. 1978. Phytoplankton of an acidic lake, and its responses to experimental alterations of pH. Environ. Conserv. **5:** 93–100.

ZEEB, B. A., AND OTHERS. 1994. Responses of diatom- and chrysophyte-assemblages in Lake 227 sediments to experimental eutrophication. Can. J. Fish. Aquat. Sci. **51:** 2300–2311.