

Holocene trophic state history of a subtropical blackwater lake, South Georgia, USA

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Abstract Organic-rich sediment from Lake Louise, a dystrophic sinkhole lake in south Georgia, displays variations in C, N, P, C/N, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, biogenic silica (BSi) and diatom flora that document changes in trophic state over the past $\sim 9,500$ years. The lake initially was oligotrophic and moderately productive, but by the middle Holocene a rising regional water table, driven by eustatic sea level rise, caused expansion of wetlands around the lake and a shift to humic waters. Low rates of sediment accumulation, low C contents, rising C/N, and light $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ indicate this was a time of low productivity, more anoxic bottom waters and extensive recycling of littoral organic matter. These conditions persisted until ~ 1800 AD when a physical disturbance to the watershed, probably the Great Hurricane of 1780, resulted in a dramatic increase in productivity that has continued to the present day. We attribute this shift,

recorded by a $>$ tenfold increase in sediment accumulation rate, higher C, P, and $\delta^{15}\text{N}$, and lower BSi, to establishment of an inflow stream that increased nutrient delivery to the lake, raised water level, and expanded the wetland area around the lake. Since ~ 1930 , logging, farming, and highway construction have impacted the lake, further accelerating biological productivity as well as the delivery of terrigenous sediment. Results of this study illustrate the potential of a single, catastrophic event to permanently alter the hydrology and chemistry of a lacustrine system and confirm that dystrophic lakes can be highly productive and therefore promising targets for paleolimnological study.

Keywords Trophic state · Eutrophication · Dystrophic lake · Holocene · Stable isotopes · Hurricanes

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Introduction

Eutrophication, the increase in biological productivity of a lacustrine system, is a natural trend in the temporal evolution of many lakes as well as an increasingly widespread consequence of anthropogenic disturbance (Smith 1998; Wetzel 2001). Human-induced or cultural eutrophication is ranked among the most serious threats to fresh water bodies today and has been studied extensively with the goals of determining its causes, effects, and mitigation

options (Rohlich 1969; Smol 2002). By comparison, studies of natural eutrophication are less common. In particular, relatively little attention has been paid to eutrophication of dystrophic lakes, which are often assumed to be of low productivity (Wetzel 2001) even though detailed studies have commonly revealed otherwise (Nürnberg and Shaw 1998). Such “blackwater” lakes are widespread throughout the southeastern USA where they are important hydrological, ecological and recreational resources. In this paper we focus on one such lake, Lake Louise, located in south Georgia and the site of an important palynological study of Holocene vegetation history by Watts (1971). At this lake the combination of a long organic-rich sediment record (>9 ka) and high accumulation rates over the past two centuries provides an opportunity to reconstruct a history of both long-term (millennial-scale) and short-term (decadal-scale) shifts in trophic state.

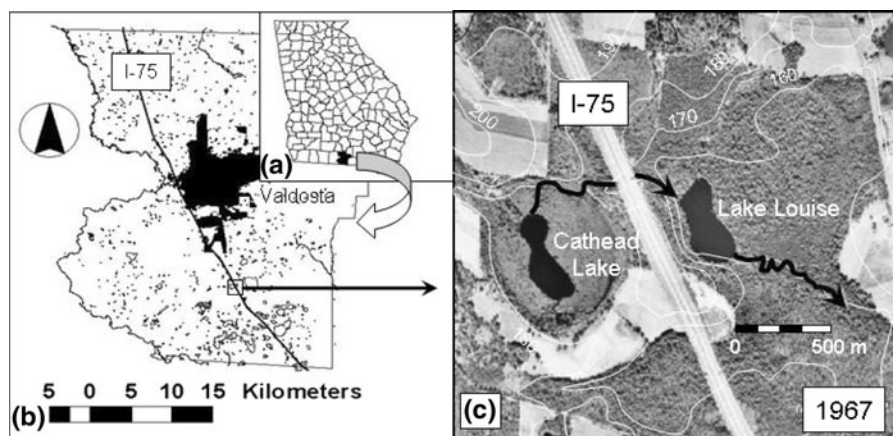
Paleolimnologists utilize a variety of chemical and biological parameters of lake sediment to reconstruct lacustrine trophic state histories. Among the most commonly used are diatom assemblages, total organic content or accumulation rate, total carbon (C) or nitrogen (N) content, C and/or N isotopic composition, and biogenic silica content (Qiu et al. 1993; Meyers and Ishiwatari 1995; Brenner et al. 1996, 1999; Teranes and Bernasconi 2000). However, all of these productivity proxies can also be influenced by other factors including the source(s) of sediment, physicochemical conditions within the water column (e.g. pH, water depth, redox state), and degree of degradation or diagenetic alteration (Meyers 1990; Meyers and Ishiwatari 1995; Moser 2007). For any

particular system, a prerequisite for reconstructing the trophic state history is assessing the extent to which individual sediment parameters correlate with productivity. At Lake Louise our approach to making such an assessment is to focus on sediment deposited since ~1840, an interval during which the sediment accumulation rate, well-constrained by 16 ^{210}Pb dates, increased nearly threefold. By comparing changes in accumulation rate with variations in elemental, isotopic, and floristic data we are able to: (1) identify sediment parameters that correlate with productivity, (2) better understand the underlying causes of the observed trophic state shifts, and (3) reconstruct the trophic state history of the lake as it responded to climatic events, topographically controlled hydrologic changes, and human activity within the watershed.

Lake characteristics and history

Lake Louise (30°43.5'N, 83°15.3'W) is a 5.7-ha “blackwater” lake located near Valdosta in south central Georgia (Fig. 1). Tertiary limestones underlie this portion of the Coastal Plain and the lake occupies two shallow basins ($z_{\text{max}} = 6.4$ m, $z_{\text{mean}} = 4.2$ m) that originated through sinkhole collapse around 9,500 BP (Watts 1971). All ^{14}C ages are reported as calibrated calendar ages. Extensive bay swamp wetlands, underlain by thick accumulations of peat, surround the lake, forming a perimeter that ranges from twenty to several hundred meters in width. The main water sources are diffuse overland flow and shallow interflow from the surrounding wetlands and this accounts for the dark color (Secchi depth <1 m), low pH (5.4–6.0), and high tannin content (2.5 ppm)

Fig. 1 Study site location showing: **a** setting of Lowndes County in Georgia; **b** the location of Lake Louise relative to Valdosta and other lakes in Lowndes County; and **c** aerial photograph of Lake Louise, Cathead Lake, and the stream that connects them. Topography (contours in feet above MSL) taken from USGS 1:24,000 coverage



of the lake waters. The lake also receives inflow from a small intermittent stream that drains Cathead Lake (Fig. 1), but deep groundwater input is believed to be negligible due to the thick accumulation of relatively impermeable gyttja. Water loss is dominated by evapotranspiration during most of the year, supplemented by a small outlet channel that flows during wetter intervals.

Although lacking the “pea-soup” appearance commonly associated with eutrophic lakes, Lake Louise does meet numerous criteria for eutrophic classification (Lampert and Sommer 1997; Nürnberg and Shaw 1998) including: (1) high primary production (960 mg C/m²-day for 1999–2000 based on sediment trap data), (2) high algal biomass (up to 270 µg Chl/L in the epilimnion during summer), (3) high nutrient levels ($P_{\text{total}} > 80$ µg/L during mixing), (4) an anoxic hypolimnion (D.O. < 0.2 ppm), and (5) cyanobacteria blooms (J Nienow, in litt.). Duckweed blooms (*Spirodela* and *Wolffia*) have occurred in recent years and may be a significant component of near-surface sediment. Average atomic N:P > 20 for the water column indicates that the system is P-limited. Lake Louise is monomictic, developing pronounced stratification by mid-spring. As a result of the large volume of oxygen-poor water that builds up in the lake by late fall (80% of lake volume has <1.0 ppm D.O.) and the high levels of dissolved organic carbon, the bottom waters at Lake Louise remain poorly oxygenated (D.O. < 3 ppm) even during winter months.

The recorded history of human activity around Lake Louise extends back only about 150 years. Indigenous peoples undoubtedly visited the lake but there is no indication of established settlements and archaeological evidence indicates that this region of south Georgia was largely unpopulated during the interval between the departure of the Spanish in the late 1650s and the arrival of European settlers beginning in the early 1820s (Daughters of the American Revolution 1944). Clearing of land for farming within the watershed probably began in the 1840s and logging of old-growth pines around the lake occurred during the 1910s–1920s. A major disruption of the catchment occurred in 1961–1963 with the construction of Interstate Highway 75 (I-75), which passes a few hundred meters to the west (Fig. 1). The lake has been maintained as an

ecological research station by Valdosta State University for the past several decades.

Methods

Core collection

Our study is based on a 9.2-m core obtained with a Wright piston corer from the center of the north basin in May 1996. Individual cores were extruded and securely wrapped in the field and then stored at 5°C in a cold room. Each drive was split lengthwise and subsamples for chemical analysis were taken from the center of the working half at intervals of 1–10 cm, care being taken to avoid including any macroscopic fragments of organic debris, which were very rare. All samples were then dried at 105°C and pulverized in a ceramic mortar.

Sediment trap studies

At the coring site a sediment trap suspended at 4 m depth (2.4 m above the bottom) was used to monitor the accumulation rate and composition of sediment in the water column over an 11-month interval from July 1999–June 2000. The trap was retrieved at approximately 6-week intervals and the collected sediment was dried and weighed. Calculated average trap collection rates varied systematically over the year (0.58–9.44 g/m²-day), being highest in the late summer and fall. Combining data for the individual sampling intervals with interpolated rates for 2 months of missing data yielded an annual trap collection rate of 1,260 g/m²-year.

CHN analyses

A total of 139 core samples plus 19 sediment trap and vegetation samples were analyzed for C, H, and N on a Perkin-Elmer 2400 CHNS/O analyzer at Valdosta State University using acetanilide and cystine as standards. Analytical precision (2σ) was calculated from 19 replicate analyses of the 7.50 m sample, which yielded C = 35.39 ± 1.30 wt% (3.6% relative), H = 4.28 ± 0.18 wt% (4.4% relative), and N = 2.00 ± 0.30 wt% (15.5% relative). Based on these values the 2σ uncertainty in atomic C/N is 3.18 (15.4% relative).

Inorganic elemental analyses

A subset of 29 samples was fused with LiBO_2 and analyzed for inorganic major elements by ICP-AES at the University of New Mexico. Five natural rock standards were used; only the Al data are included here for which analytical precision (1σ) based on replicate analyses of three samples is better than 0.04 wt. % Al_2O_3 . Labile P was measured by ICP-AES at the University of Puget Sound on 14 samples that were leached for 48 h with 20% HNO_3 and run against standards made from a 1,000 ppm P solution. Analytical precision (1σ) is within 2 ppm P.

Biogenic silica

Biogenic silica (BSi) was determined by spectrophotometry on 31 samples extracted with a wet alkaline digestion (0.2 N NaOH) at 90–95°C. A correction for partial dissolution of silicate minerals was made using a timed extraction procedure (DeMaster 1981). Relative analytical uncertainty (1σ) is 7.7%, based on three replicate analyses of the 3.0 m sample.

Isotopic analyses

Carbon and nitrogen isotopic analyses of 63 core samples and 10 sediment trap and vegetation samples were performed at the University of New Mexico on a Finnigan DeltaPlus XL. A lab graphite standard was used for C analyses; a USGS standard and ATO were used for N. Analytical precision (1σ) is 0.15‰ for both $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ and the results are reported relative to PDB (for C) and air (for N).

Diatom analysis

Diatom analysis was performed on 18 samples. For each sample a freeze-dried split weighing 200 mg was oxidized with 30% hydrogen peroxide to remove organic matter and then rinsed repeatedly with distilled water until neutral pH was achieved. Oxidized sediment slurries were spiked with a known quantity of *Eucalyptus* pollen in order to estimate sediment diatom concentrations (Wolfe 1997). Diluted aliquots from the slurries were dried onto coverslips at room temperature and mounted to slides using Naphrax[®] medium. A minimum of 300 valves was identified and enumerated from each interval;

these were reported as relative abundances and also as total diatom concentrations estimated from counting introduced *Eucalyptus* markers.

Age control

The top 200 cm of sediment was dated by ^{210}Pb utilizing a separate 3 m core collected adjacent to the main core site in January 2000. Carbon analyses were used to correlate the two cores (Electronic Supplemental Fig. 1); depth agreement between them is estimated at better than 5 cm (<5 years) within the upper 65 cm and better than 10 cm (<10 years) below that. The ^{210}Pb core was divided into 1-cm intervals (from 0 to 65 cm) and 2-cm intervals (from 65 to 244 cm), each of which was dried and weighed to determine the dry mass. Sixteen samples were analyzed for ^{210}Pb by MyCore, Inc. using the ^{210}Po counting method; ages and sedimentation rates for each depth interval (Electronic Supplemental Table 1) were calculated using the constant rate of supply model (CRS; Appleby and Oldfield 1983). This model assumes constant fallout of unsupported ^{210}Pb from the atmosphere and is appropriate for lakes such as this one where the sedimentation rate has varied through time. Because ^{210}Pb dates are sensitive to several potential sources of error, independent confirmation of the results is important. Three such confirmations corroborate our ^{210}Pb results. First, the date obtained at the base of a silt layer at 0.23 m depth ($1,965 \pm 2$) follows closely the date of construction of I-75 (1961–1963), which is the presumed cause of the silt influx. Second, the CRS sedimentation rate calculated for the top 9 cm (~ 8 years) of the core is within 10% of the rate measured for 1999–2000 using sediment traps. Rapid accumulation of organic sediment, ~ 15 cm in last 25 years, is also indicated by comparing the thickness of gyttja we measured atop the I-75 silt layer in our core from 1996 versus the thickness reported by Watts (1971). Third, over the longer term, the high sedimentation rate calculated from the ^{210}Pb dates (1.2 ± 0.2 m/century) matches within error the rate obtained using the AMS ^{14}C date (AD 1785 ± 50) we obtained from a sedge blade at 2.53 m. This ^{14}C date was measured at the University of Arizona AMS Facility (AA#27946) and calibrated using the University of Washington CALIB (2.0) program.

For the deeper portion of the core, radiocarbon dating was hampered by the paucity of macroscopic organic matter. The only suitable sample recovered, a wood fragment from 8.22 m, yielded an AMS age of >45,000 BP. However, Watt's (1971) ^{14}C dates, recalculated as calibrated ages of $9,502 \pm 83$ BP at 1,160 cm (the base of the organic section) and $7,589 \pm 114$ BP at 1,007 cm, provide general age constraints on our core.

Calculation of sedimentation rates

The CRS model (Appleby and Oldfield 1983) was used to calculate sedimentation rates over the past ~ 160 years. The results are discussed in a later section and summarized in Electronic Supplemental Table 1. Rates prior to that were estimated using the above ages from Watts (1971) at 1,160 and 1,007 cm. Assuming a constant rate and accounting for the fact that the organic section of our core is 18% longer, attributable to sediment focusing, the calculated rate over the first $\sim 2,000$ years is $0.09 \text{ cm year}^{-1}$. Extrapolating this rate to the top of Interval 1 (6.90 m; defined below) implies a significantly lower rate of $0.02 \text{ cm year}^{-1}$ during Interval 2 (6.90–2.51 m). Alternatively, if we use only Watt's (1971) date of 9,502 BP for the base of the organic section and our AMS date of 1785 AD at 2.53 m, the average rate over both intervals is $0.05 \text{ cm year}^{-1}$. In summary, although rates for Intervals 1 and 2 are less well constrained, it is clear that sedimentation increased dramatically, by more than tenfold, after ~ 1790 AD, i.e. in Interval 3.

Results

For the purpose of discussion we divided the core into four intervals, each representing a different chapter in the history of the lake. Boundaries between intervals correspond to abrupt changes in chemistry and/or diatom assemblages. Two are also marked by silt-rich layers indicative of enhanced terrigenous input. In this section we summarize the characteristics of each interval that are important for reconstructing the trophic state history. Complete tables of chemical and isotopic data are available as Electronic Supplemental Table 2.

Interval 0 (9.15–6.90 m), the oldest material, consists of highly decomposed peat containing wood and charcoal fragments overlain by ~ 130 cm of rubble, silt, and sand. The age of the peat ($>45,000$ BP), combined with its high C/N (>28 , indicative of terrestrial plant matter) and low Al content (indicative of low terrigenous sediment influx), is consistent with Watts's (1971) interpretation that the basal peat in his core accumulated in a shallow marsh during the last interglacial. We infer the rubble layer to record sinkhole collapse that formed the lake. Interval 0 thus predates the establishment of the lake and will not be discussed further in this paper.

Interval 1 (6.90–3.72 m) extends from the lowermost lacustrine sediment up to a depth at which C and N contents, $\delta^{13}\text{C}$, and the diatom flora all change abruptly. Within this interval the sediment consists of massive dark brown to black algal gyttja containing short hair-like organic fibers. Carbon contents fluctuate between 28 and 36 wt%, displaying meter-scale increases and decreases, but no consistent upsection trend (Fig. 2a). Nitrogen levels (2.0–2.7 wt%) are among the highest in the lake's history and show the same meter-scale fluctuations as C, but with a general trend toward higher values upsection (Fig. 2b). Atomic C/N is low, declining from ~ 18 –20 when the lake formed to ~ 14 at 5 m depth, and then rising to ~ 16 at the top of the interval (Fig. 2c). The values suggest a mix of algae (C/N < 10) and vascular plant matter (C/N > 20 ; Meyers and Lallier-Vargas 1999). Carbon isotope ratios range between -30.3 and -24.5‰ and tend to parallel variations in C content. There is a general trend toward heavier $\delta^{13}\text{C}$ over the upper ~ 2 m of Interval 1, the largest jump being a $+3\text{‰}$ shift between 4.52 and 4.34 m (Fig. 3a). A different pattern is seen in the N isotope data: below 5.0 m $\delta^{15}\text{N}$ variations ($+1.5$ to $+3.5\text{‰}$) mimic the $\delta^{13}\text{C}$ data, however above this depth, where C isotopes get heavier, $\delta^{15}\text{N}$ values drop precipitously from $+2.5$ to -2.2‰ (Fig. 3b). Biogenic silica increases over the bottom 70 cm of Interval 1 and then remains relatively constant at ~ 10 wt% before rising sharply over the upper ~ 50 cm (Fig. 4a). Al contents (Fig. 4b) decline, aside from a spike at 4.8 m, and indicate gradually diminishing delivery of terrigenous sediment. The diatom assemblage of this interval (Fig. 5) is dominated by *Aulacoseira ambigua* (50–80% of total) accompanied by up to $\sim 25\%$ each of *Discostella* (*Cyclotella*) *stelligera* (only in

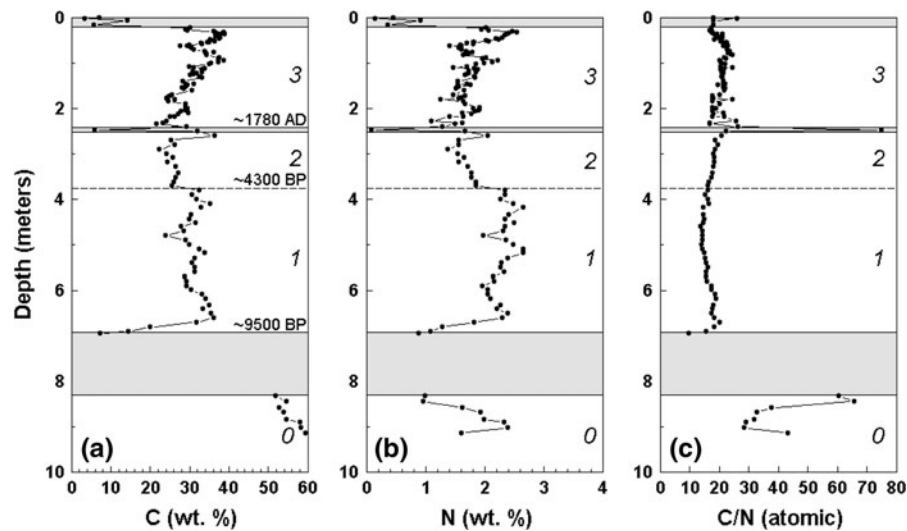


Fig. 2 Stratigraphic variation in **a** C content, **b** N content, and **c** atomic C/N. Silt-rich layers are indicated by gray shading. Intervals 0–3 are labeled at the right edge; the dashed line marks the boundary between Intervals 1 and 2. Approximate boundary ages are indicated; see text for discussion of age

constraints. Features to note are the low C and N contents that characterize Interval 2, the steady rise in C and N contents within Interval 3, and the gradual increase in C/N that occurs between ~5 and ~1 m depth

lowest samples), *Cymbella minuta*, *Cymbella gracilis*, and various species of *Eunotia* and alkalifilous *Fragilaria*. These species are indicative of clear waters, with $\text{pH} > 7$ in the early stages, and sufficient light penetration to support benthic species (A Wolfe in litt.).

Interval 2 (3.72–2.51 m) is relatively homogenous compared to those above and below. It consists of massive black-brown algal gyttja similar to that of Interval 1, but without the organic fibers. It is characterized by low C contents (22–27 wt%) and low N contents that decline upsection (1.8–1.5 wt%; Fig. 2a, b). As a result of the N variation, C/N ratios show a steady rise (16.1–22.4; Fig. 2c), indicative of an increasing contribution of terrigenous plant matter. Carbon isotopic ratios ($\delta^{13}\text{C} = -32.8$ to -32.1‰) are markedly lighter than in Interval 1 and fluctuate in tandem with C content (Fig. 3a). Delta ^{15}N values reach their lightest state (-2.2 to -1.5‰) before climbing to values around 0‰ at the top of the interval, and for the most part variations in $\delta^{15}\text{N}$ mimic those seen in $\delta^{13}\text{C}$ and C content (Fig. 3b). This interval also has the highest BSi levels (~ 20 wt%; Fig. 4a), uniformly low Al (Fig. 4b), and a markedly different diatom assemblage from Interval 1, being dominated (75–80%) by *Aulacoseira granulata* var. *angustissima* and *Asterionella formosa*

(Fig. 5). These are species characteristic of dystrophic lakes and humic waters (A Wolfe in litt.).

Interval 3 (2.51–0.0 m) is bounded at top and bottom by silt-rich horizons and shows systematic chemical and isotopic trends over both meter (\sim century) and decimeter (\sim decade) scales. The top 0.23 m consists of laminated gray silt and clay that grades upward into darker, more organic-rich material, whereas the basal silt (2.51–2.42 m) is massive and contains wood debris. In between these clastic-rich layers, Interval 3 is comprised of massive, black-brown algal gyttja, locally with lighter colored mottling. Within this organic material, C content (21–39 wt%) and N content (1.1–2.5 wt%) vary in tandem: both show a general upsection increase upon which smaller fluctuations are superimposed (Fig. 6a, f). Carbon content is the highest in the lake's history near the top of this interval. Variation in C/N is more erratic, but shows a general rise from 17 to 18, to an all time high of ~ 24 , before declining to ~ 17 at the top of the interval (Fig. 6f). Carbon isotopic values become lighter upsection, reaching an all-time low $\delta^{13}\text{C} \sim -35\text{‰}$ at ~ 50 cm depth before rising to $\sim -32\text{‰}$ at the top (Fig. 6c). Nitrogen isotope values rise upsection ($\delta^{15}\text{N} = -1.7$ to $+2.5\text{‰}$; Fig. 6b), following C content. Phosphorus content (Fig. 6e) shows a gradual increase upsection that

Fig. 3 Stratigraphic trends in **a** C and **b** N isotopic composition. *Shading and labeling* are the same as in Fig. 2. *Open circles* represent sediment trap samples. Note the shift to lighter isotopic composition that occurs within Interval 2, the trend toward heavier $\delta^{15}\text{N}$ within Interval 3, and the general lack of correlation between the two isotopic systems

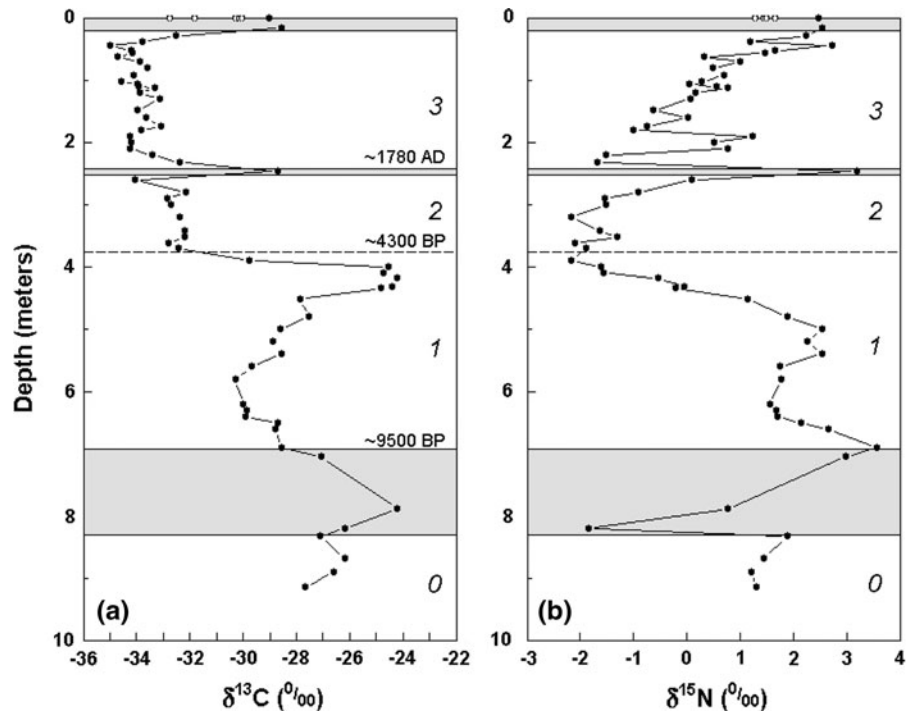
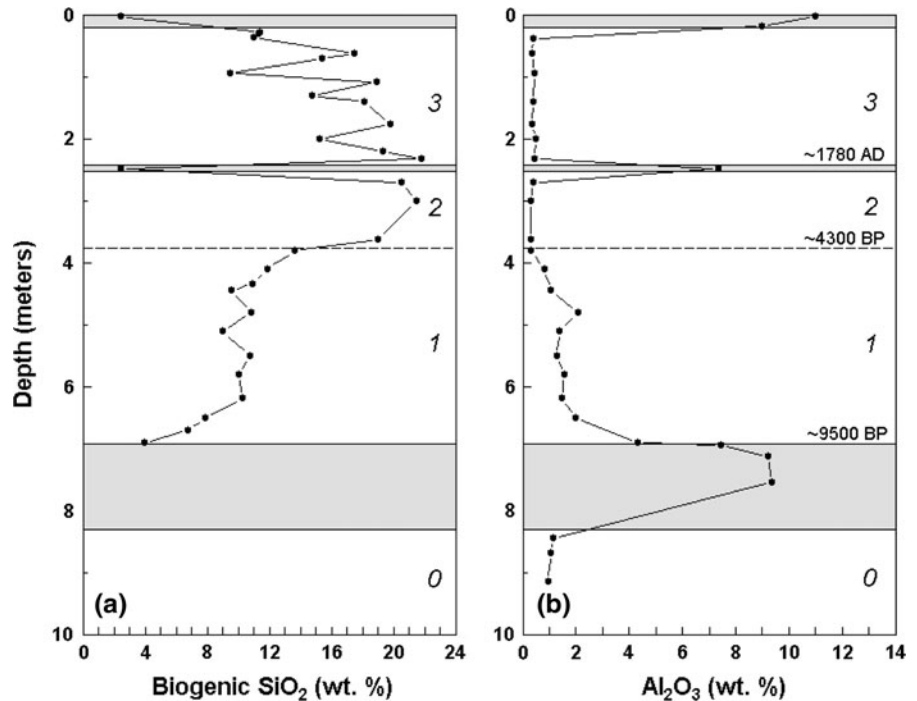


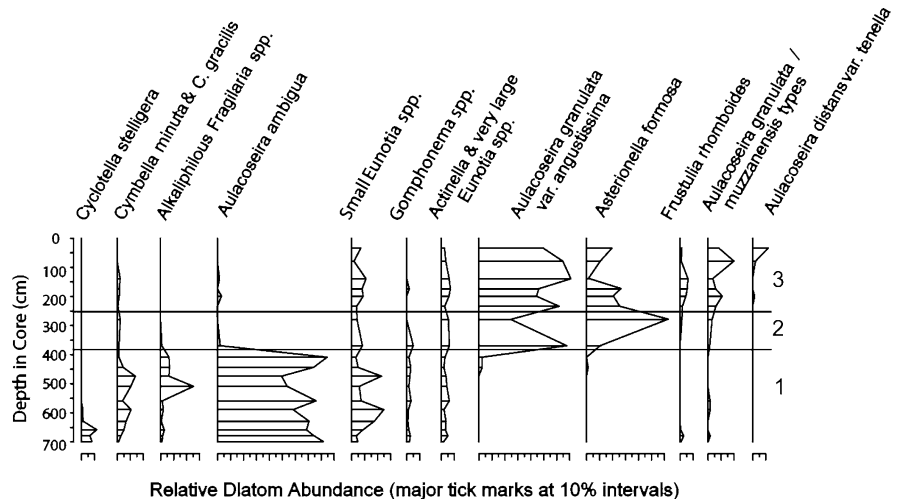
Fig. 4 Stratigraphic variation in **a** BSi and **b** Al content. *Shading and labeling* are the same as in Fig. 2



mimics trends seen in C and N, but then jumps to threefold higher levels in the top 50 cm. Al content is uniformly very low except within the silt-rich horizons (Fig. 6e). Biogenic silica shows a strong inverse

correlation with C content, declining from ~22 to ~11 wt% and displays wide fluctuations not seen in lower intervals (Fig. 6d). The dystrophic species *Aulacoseira granulata* var. *angustissima* and

Fig. 5 Stratigraphic variations in diatom flora. Horizontal lines indicate boundaries between intervals, which are numbered at the right. Note the disappearance of *Aulacoseira ambigua* and the appearance of *Aulacoseira granulata* at the boundary between intervals 1 and 2



Asterionella formosa continue to dominate the diatom flora, joined by *Aulacoseira granulata* var. *muzzanensis*, *Aulacoseira distans* var. *tenella*, and *Frustulia rhomboides* (Fig. 5).

Discussion

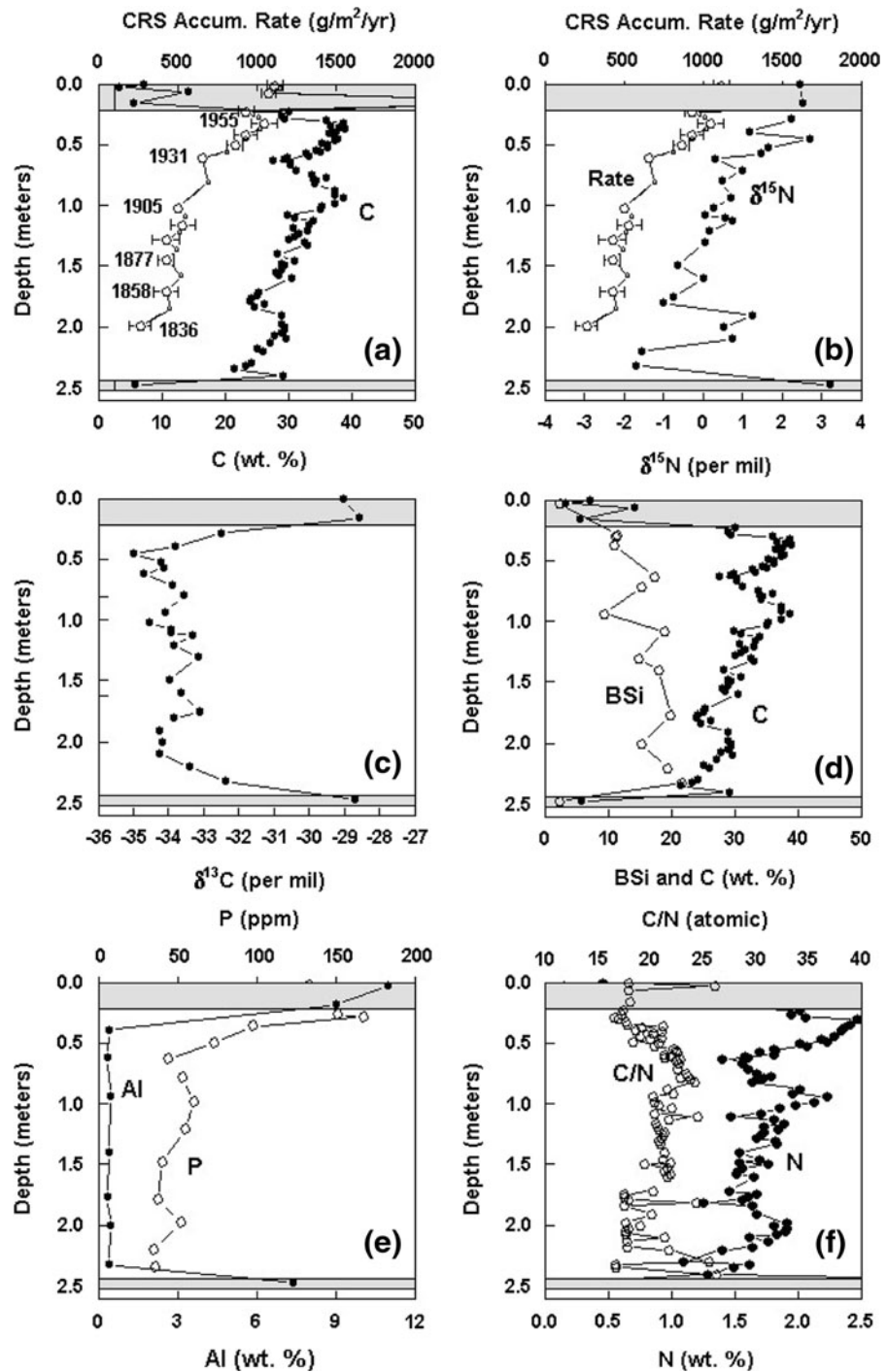
Impact of decomposition and diagenesis

Decomposition and diagenetic processes can significantly alter the abundance and composition of lacustrine organic matter. Carbon content in particular can be dramatically lower in bottom sediments than in surface particulate matter (Meyers and Ishiwatari 1995). At Lake Louise however, three lines of evidence indicate that variations in the C content dominantly reflect changes in productivity rather than changes in preservation. (1) There is good agreement between the sedimentation rate determined with sediment traps ($1.2 \times 10^3 \text{ g m}^{-2} \text{ year}^{-1}$) and the CRS sedimentation rate ($1.1 \times 10^3 \text{ g m}^{-2} \text{ year}^{-1}$) calculated for the top 9 cm (~ 8 years) of the core. Both of these rates are also consistent with autotrophic production rates inferred from Chl data (up to $270 \mu\text{g/L}$ or $\sim 1,000 \text{ mg/m}^2\text{-year}$) if phytoplankton mortality (3–25% per day; Wetzel 2001) is included. Because rates of phytoplankton mortality/respiration are poorly known it is difficult to quantify the allochthonous contribution to the sediment at Lake Louise, but mass balance and geochemical constraints, e.g. low C/N in both trap and core sediment, suggest it is minimal at

the coring site. (2) Carbon contents of trap samples (27.6–33.3 wt%) are comparable to those of core samples that pre-date highway construction (avg. = 29.5 wt% at 23–29 cm depth). Conversely, C contents of core samples that postdate I-75 are lower and more variable because bioturbation and gas release caused mixing with the underlying silt layer. Observations (1) and (2) suggest that, for at least the past ~ 50 years, close to 90% of the organic matter settling below the epilimnion has become part of the sediment record with less than $\sim 10\%$ loss of C. These low rates of decomposition are consistent with the small size, shallow depth, oxygen-poor bottom waters, and rapid sedimentation rate in the lake. For older sediment, a third argument against decomposition having a major control on C content is that shifts in C content are synchronous with shifts in other proxies for environmental change that are not sensitive to decomposition, including diatom assemblages, isotopic composition, and pollen record (Figs. 2, 3, 4, 5 and 6).

C/N ratios are also subject to modification during early diagenesis, but in most cases the magnitude of this effect is small enough that information about the source of the organic matter is retained (Meyers and Ishiwatari 1995). To assess the impact of diagenesis on Lake Louise C/N, we compared analyses of trap samples with analyses of recent sediment from different depths. Trap samples contain higher N (2.7–3.3 wt%) than surface sediment (2.1 wt%) or ~ 40 -year-old sediment (1.9–2.1 wt% at 23–29 cm). As a result, there is a progressive increase in C/N from the trap samples (avg. = 12.2) to the surface

Fig. 6 Variations in accumulation rate and sediment chemistry within Interval 3. *Shaded* portions indicate silt-rich horizons. **a** CRS accumulation rate and C content; note the close correlation between these two parameters. **b** CRS accumulation rate and $\delta^{15}\text{N}$; again note the similarity of their trends. **c** Carbon isotopic composition. **d** BSi and C contents; note the strong inverse correlation between these two sediment components. **e** Aluminum and phosphorus contents. **f** Atomic C/N and N content. N variations parallel those seen in C (a); C/N shows a slight upsection increase until ~ 0.7 m, above which it declines. This decline, which correlates with highest productivity, is attributed to anthropogenic nutrient loading



sample (13.7) to the deeper samples (avg. = 17.1). This shift may reflect preferential degradation of nitrogenous (algal) matter, which is generally more reactive than other components of organic sediment (Meyers 1990). Our data are consistent with previous

work (Meyers and Ishiwatari 1995) that indicates most diagenetic C/N change occurs before or soon after the sediment reaches the bottom, i.e. before permanent burial. Because C/N variations within our core include both increases and decreases, occur over

both meter and decimeter lengths, and vary independently from C content or accumulation rate, we infer that diagenetic change after deposition was minimal. Therefore, although some diagenetic shift in C/N has probably occurred, most likely an increase on the order of ~ 5 , information about changing organic matter sources appears to be preserved.

For C and N isotopic ratios, previous studies concluded that diagenetic effects are generally minimal. Meyers and Ishiwatari (1995) reported that diagenetic $\delta^{13}\text{C}$ shifts over thousands of years are $<2\text{‰}$ in organic-rich sediments, while Meyers and Lallier-Vargas (1999) concluded that diagenetic $\delta^{15}\text{N}$ shifts are negligible, even in cases where significant post-depositional degradation of nitrogenous matter has occurred. At Lake Louise, surface sediment is isotopically heavier than trap sediment by $\sim 1\text{‰}$ for $\delta^{15}\text{N}$ and $\sim 1\text{--}3\text{‰}$ for $\delta^{13}\text{C}$ (Fig. 3). This difference may reflect mixing with terrigenous sediment and/or diagenesis, but regardless of cause, the magnitude of the effect is small compared to the isotopic variations observed in the core.

Evaluation of paleoproductivity proxies

To evaluate individual chemical and isotopic parameters as proxies for productivity at Lake Louise, we focused on the organic-rich portion of Interval 3 (0.23–2.40 m), a ~ 175 -year span during which the CRS sedimentation rate increased threefold to $>1,000\text{ g/m}^2\text{-year}$. This high rate of accumulation, up to 2 cm/year, allows us to gauge the sensitivity of individual proxies to both short-term (decade or less) and long-term productivity fluctuations. Within this depth interval, sedimentation rate correlates directly with C content ($r^2 = 0.71$) and P content ($r^2 = 0.72$), inversely with BSi, and not at all with Al content, which remains uniformly low (Fig. 6a, d, e). This, together with previously mentioned evidence that loss of organic matter during settling is minimal, leads us to infer that changes in sedimentation rate and C content record changes in productivity, not changes in organic matter preservation or terrigenous sediment delivery, both of which would impact Al content. Similar correlations between primary productivity and sedimentation rate, P accumulation rate, and/or organic content have been documented at many other lakes (Birch et al. 1980; Schelske et al. 1988; Hollander et al. 1992).

Nitrogen content (Fig. 6f) correlates closely with both sedimentation rate ($r^2 = 0.70$) and C content ($r^2 = 0.73$), as does nitrogen isotopic composition, which shifts toward heavier $\delta^{15}\text{N}$ during intervals of greater productivity (Fig. 6b). The latter relationship is attributable to depletion of the biologically-favored ^{14}N in situations where a significant portion of the available N has been utilized, which leads to higher $\delta^{15}\text{N}$ in subsequently produced organic matter (Teranes and Bernasconi 2000).

The relationship between $\delta^{13}\text{C}$ and productivity at Lake Louise is more complex. Over most of Interval 3, $\delta^{13}\text{C}$ shows limited variability (-33.1 to -35.2‰), with some hint of an upsection trend toward lighter values (Fig. 6c). Below ~ 1.5 m depth, small decreases in $\delta^{13}\text{C}$ appear to correlate with increases in C content, the opposite of what would be expected if $^{13}\text{C}/^{12}\text{C}$ fractionation were a consequence of productivity-driven ^{12}C depletion (Brenner et al. 1999). An inverse correlation between $\delta^{13}\text{C}$ and accumulation rate is also observed in our sediment trap data and may reflect a greater amount of duckweed (-27.8‰) relative to plankton (-29.2‰) during duckweed blooms. Only at the top of Interval 3 is there any suggestion of a positive correlation with $\delta^{13}\text{C}$, but this lone data point more likely reflects mixing with the overlying silt layer (Fig. 6c). Teranes and Bernasconi (2005) have shown that the relationship between $\delta^{13}\text{C}$ of organic sediment and primary productivity can be obscured if the sediment is a mixture of phytoplankton, which gets isotopically heavier if productivity is the dominant control, and microbial biomass produced under anoxic conditions, which is very light. The latter situation likely exists at Lake Louise, with its large anoxic hypolimnion, and may be augmented by the large reservoir of available C that prevents appreciable ^{12}C depletion even during times of high productivity.

Biogenic silica content has been observed to correlate with productivity in large oligotrophic lakes where Si limitation is not a factor (Qiu et al. 1993; Schelske et al. 2006), but in smaller eutrophic systems Si depletion within the water column may confound this relationship (Conley and Schelske 2001). At Lake Louise BSi contents in Interval 3 show a strong inverse correlation with both C content and accumulation rate (Fig. 6d). However, BSi accumulation rates, obtained by multiplying CRS rate by BSi content, are relatively uniform ($100 \pm 20\text{ g/m}^2\text{-year}$),

indicating that the fluctuations in BSi content are largely, if not entirely controlled, by changes in C content. Thus, BSi is diluted during intervals of rapid organic matter production and the result is an inverse correlation between BSi and productivity.

In summary, trends that correlate with increased productivity at Lake Louise within Interval 3 are: (1) higher accumulation rate, (2) higher C content, (3) higher P content, (4) higher N content, (5) heavier $\delta^{15}\text{N}$, and (6) lower BSi. Variations in $\delta^{13}\text{C}$ appear to be controlled dominantly by the relative proportions of algal versus microbial biomass. Applying these findings to the earlier history of Lake Louise, we suggest that correlated variations involving several of these trophic state proxies likely reflect productivity shifts. Conversely, non-correlated excursions (e.g. a change only in $\delta^{15}\text{N}$) are more likely responses to other chemical or physical factors.

Reconstruction of Lake Louise history

Interval 1

Elevated Al and C/N point to a significant allochthonous component in the earliest Lake Louise sediments, a situation that may have been facilitated by enhanced local relief following sinkhole collapse and the absence of surrounding wetlands. Pollen studies (Watts 1971) indicate the local landscape was drier than today, consisting of a mix of oak savannah and small prairies. The diatom flora is indicative of clear, somewhat alkaline waters, while the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values are in the normal range for modern lakes ($\delta^{13}\text{C} = -24$ to -30% , $\delta^{15}\text{N} = 1$ – 5%), indicating that lacustrine organic matter was utilizing atmospheric CO_2 and NO_3 (Meyers and Lallier-Vargas 1999). High C and N contents, high $\delta^{15}\text{N}$, and low BSi at the beginning of Interval 1 suggest moderately high productivity; preservation of this organic sediment suggests rapid accumulation and/or anoxic bottom waters. The lake may also have been deeper at that time, prior to accumulation of >6 m of sediment, and this would have facilitated development of an oxygen-poor hypolimnion.

Proceeding upsection within Interval 1, the allochthonous sediment flux diminishes (lower Al and C/N) and there are signs of declining productivity (C content drops, BSi rises). The first clear indications of a major change in lake conditions are a -4%

shift in $\delta^{15}\text{N}$ and rise in C/N that begin at ~ 5 m depth, approximately 6,300 BP. These changes are coincident with vegetation changes (decrease in oak/increase in pine) that Watts (1971) ascribed to a rising water table. We attribute the $\delta^{15}\text{N}$ and C/N trends to increased delivery of humic matter as wetlands began to develop around the lake, and increased recycling of light N derived from this material. Alternatively, the direction and magnitude of the $\delta^{15}\text{N}$ shift could be explained by a rise in NH_4 (vs. NO_3), as anoxic bottom waters expanded (Teranes and Bernasconi 2000), but this would not explain the rise in C/N values.

Continuing upsection, the drop in $\delta^{15}\text{N}$ is followed by an abrupt $\sim 4\%$ increase in $\delta^{13}\text{C}$ that probably reflects a change in C speciation and could be explained either by increased CH_4 production, with its concomitant increase in $\delta^{13}\text{C}$ of CO_2 , or by enhanced biological utilization of HCO_3^- (Brenner et al. 1999). Because there is no evidence for an increase in pH or in productivity over this interval, we attribute the $\delta^{13}\text{C}$ increase to enhanced CH_4 production, as delivery of organic matter from adjacent wetlands increased and bottom waters became more anoxic. In summary, Interval 1 records a lake with clear water and moderate productivity that over time received increasing amounts of organic matter from its surrounding wetlands. In response, the lake appears to have experienced a general decrease in productivity and an expansion of anoxic bottom waters. These events coincide in time with the final stages of eustatic sea level rise that followed the last glacial maximum, when sea level rose from -24 m at 9,500 BP to around -3 m at 6,500 BP (Fleming et al. 1998). A result of sea level rise was an increase in water table elevations throughout the Southeastern coastal plain (Booth and Rich 1998). Hyatt and Gilbert (2004) document 7–10 m of water level rise since 9,120–9,020 cal BP in two other sinkhole lakes located less than 6 km from Lake Louise. Expansion of the wetlands around Lake Louise and the resulting shift in water chemistry during Interval 1 are thus responses to global warming and eustatic sea level rise after the last glacial maximum.

Interval 2

The low sedimentation rate, low C content, and high BSi of this interval suggest it was a time of low

productivity. Expansion of the wetlands around the lake and increased delivery of humic waters from these bogs is reflected by low levels of terrigenous sediment input, a dramatic shift in diatom flora, a rise in C/N, continued low $\delta^{15}\text{N}$, and a rise in cypress (*Taxodium*) pollen (Watts 1971). The abrupt -8% shift in $\delta^{13}\text{C}$ that coincides with the start of this interval probably reflects utilization of CO_2 liberated from breakdown of DOC in the humic waters (Rau 1978), as well as increased microbial biomass that produced anoxic conditions (Teranes and Bernasconi 2005). Taken together, these data paint Interval 2 as a time when the lake had acquired its dystrophic character, but was far less productive than it is today. Low productivity was probably a consequence of low nutrient supply resulting from lower lake levels and smaller wetland area compared to today, and the absence of the inflow stream.

Interval 3

Around 1800 AD the lake underwent a profound change, after which CRS sedimentation rates began a steady climb from <300 to $>1,000$ $\text{g}/\text{m}^2\text{-year}$ (Fig. 6a). As noted above, the correlated increases in sedimentation rate, C and P content, and $\delta^{15}\text{N}$, with no Al variation, strongly suggest that the rise in sedimentation rate resulted from increased productivity and not from changes in preservation efficiency or the influx of terrigenous matter. In seeking an explanation for these changes, there are two important observations to note. First, there is the 9-cm layer of silt and plant debris at the bottom of Interval 3, which indicates the changes began after a physical disturbance of the watershed. Second, most of the subsequent chemical and isotopic changes occurred gradually over the next 150+ years. This implies that the triggering event caused a permanent shift in the physical and chemical behavior of the system. The date of the triggering event is too early to attribute to European settlement (~ 1840), but correlates well with the devastating hurricane season of 1780, which featured three major storms, one of them the deadliest Atlantic hurricane on record (http://en.wikipedia.org/wiki/Great_Hurricane_of_1780). The low $\delta^{18}\text{O}$ isotopic signature of precipitation from this hurricane season has been identified in tree rings from longleaf pine stumps at Lake Louise, indicating that the impact of the storm(s) was felt in this watershed

(Miller et al. 2006). We propose therefore, that heavy rainfall associated with one or more hurricanes in 1780 resulted in establishment of the inflow channel that now links Lake Louise with Cathead Lake (Fig. 1). Based on current topography, a water level rise of <1 m would have been sufficient for Cathead Lake to overtop the ridge separating the two lakes, and after this ridge was overtopped the combination of a relatively steep topographic gradient and easily eroded loamy soils would have led to rapid channel incision and significant delivery of silt and clay to Lake Louise. Longer-term effects of the new inflow stream would include delivery of nutrients from a larger drainage area, higher lake level, and expansion of the surrounding wetlands. Evidence for the latter is provided by the abrupt rise in cypress pollen (*Taxodium*) that occurred around the same time (Watts 1971). Our digital elevation modeling indicates that a 1 m rise in lake level would have resulted in a threefold increase in wetland area around Lake Louise. This expansion and the attendant inundation of standing litter would have enhanced PO_4 mobility and further facilitated the delivery of nutrients to the lake (Howard-Williams 1985).

Within Interval 3, the general trend toward higher productivity is interrupted by two lower-C excursions, one between 1.71 and 1.84 m (\sim AD 1849–1858) and one between 0.61 and 0.82 m (\sim AD 1913–1928; Fig. 6a). In addition to a 5–11 wt% drop in C content, each excursion is associated with a decrease in $\delta^{15}\text{N}$ (Fig. 6b). The earlier event corresponds to a series of dry years in the tree ring record from 1851 to 1865 (HD Grissino-Mayer in litt.) and may reflect decreased productivity brought about by a drop in lake level and/or decreased runoff. The more recent episode coincides with logging around the lake, which occurred during the 1910s–1920s (HD Grissino-Mayer, in litt.). Although there is no evidence from Al data for enhanced erosion during this time (Fig. 6e), there is an abrupt increase in C/N (Fig. 6f) that points to greater delivery of terrestrial organic matter and may be a consequence of logging in the surrounding wetlands. Beginning ~ 1930 (0.60 m) P content, C content, sedimentation rate, and $\delta^{15}\text{N}$ all increase markedly, reaching the highest values in the lake's history to that point during the mid-1950s (Fig. 6a,b,e). These increases are accompanied by a steady decline in C/N (Fig. 6f). We attribute these changes to an expansion of farming close to the lake,

and in particular to increased application of manure-based fertilizers having $\delta^{15}\text{N} > +5\text{‰}$ (Kendall et al. 2007). A consequence of increased nutrient delivery was enhanced algal production, which drove C/N to lower values.

Sediment deposited in Lake Louise since the early 1960s contains higher amounts of silt and clay as a result of Interstate 75 construction. Although much of this material was probably deposited around the time of construction, bioturbation and gas release continue to mix it into the younger, biogenic sediment, thereby obscuring the relationship between C content and lake productivity during the past 50 years.

Conclusions

Lake Louise is a small, blackwater lake in which conditions favorable for the preservation of organic matter have resulted in the accumulation of ~ 7 m of organic-rich sediment over the past $\sim 9,500$ years. Preserved within this sediment are variations in C, N and P contents, C/N, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, BSi, and the diatom flora that record changes in productivity, water chemistry, and organic matter sources. Two events in particular had major and lasting impacts on the geochemistry and trophic state of Lake Louise: (1) an early Holocene rise in the regional water table in response to eustatic sea-level rise, which led to an expansion of wetlands around the lake and a transition from oligotrophic to dystrophic conditions, and (2) a late Eighteenth Century event, probably a hurricane, that altered the surface hydrology of the watershed, increased the wetland area and nutrient supply, and dramatically accelerated the productivity of the lake. Anthropogenic contributions to eutrophication are apparent only after ~ 1930 and consist mainly of agricultural activity that further accelerated productivity within the water column.

Carbon content, N content, and $\delta^{15}\text{N}$ correlate with sedimentation rate and appear to be reliable indicators of trophic state shifts at Lake Louise, whereas $\delta^{13}\text{C}$ and C/N do not. In contrast, Brenner et al. (1999), in a study of anthropogenic eutrophication at four Florida lakes, determined that $\delta^{13}\text{C}$, C/N, and to a lesser extent $\delta^{15}\text{N}$, accurately recorded changes in trophic state as inferred from diatoms. Several factors may account for the different results of the two studies. First, at Lake Louise the proportionally large

anoxic hypolimnion and high DOC water provides for higher microbial biomass production and a large C reservoir that is less susceptible to photosynthetically driven ^{12}C depletion. Second, in the lakes studied by Brenner et al. (1999), enhanced algal production, which resulted in lower C/N of sediment, was linked to anthropogenic P loading. At Lake Louise, at least up until ~ 1930 , most nutrients were derived from the littoral zone, which meant that P was accompanied by dissolved and particulate organic matter, both of which have high C/N (Wetzel 2001). Deposition of this material would tend to obscure any trend toward lower sediment C/N caused by increased algal growth in the water column. Lastly, the variable $\delta^{15}\text{N}$ behavior observed by Brenner et al. (1999) may be a consequence of lake-to-lake differences in N loading and extent of N-limitation. Lake Louise, being significantly smaller than any of those studied in Florida, is more prone to ^{14}N depletion and as a result displays more coherent $\delta^{15}\text{N}$ behavior during trophic state shifts.

The results of this study illustrate the potential of a single catastrophic event, such as a hurricane, to permanently alter the hydrology and trophic state of a lake, and also confirm that dystrophic (blackwater) lakes can be highly productive. Such lakes, which are widespread in the southeastern U.S. and have the potential for excellent preservation of organic sediment, are attractive targets for paleolimnological investigations.

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