

Inadvertent alkalization of a Florida lake caused by increased ionic and nutrient loading to its watershed

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Abstract We evaluate the effects of land-use change since c.1890 on Little Lake Jackson in south-central Florida, USA. The lake currently is alkaline despite the prevalence of acidic lakes in the region. Watershed soils are acidic and poorly drained, but are underlain by limestone bedrock. Limnetic pH inferences, based on weighted-averaging tolerance regression of sedimented diatoms, indicate that Little Lake Jackson became significantly alkalized during the 1900s. Two driving forces that appear to be responsible for water-quality change are increased ionic loading and increased nutrient loading. Golf courses and residential lawns in the watershed receive substantial applications of lime, fertilizer, and irrigation with alkaline waters from deep wells, some of which reaches the lake in channelized runoff. Stormwater runoff and septic leachate also contribute to nutrient and solute

loading. Sedimentary total P accumulation increased 5-fold and total N accumulation increased 3-fold since c. 1890. $\delta^{15}\text{N}$ values suggest agricultural and septic sources for N loading. Sedimented pigments, inferred limnetic chlorophyll *a* values, and $\delta^{13}\text{C}$ values of organic matter indicate that increased primary productivity occurred. Surface and subsurface inflow is nutrient-rich but low in hardness. Increased cation deposition in sediments indicates that ionic input might have reduced the lake's natural resistance to alkalization. Lake waters remain low in ionic content, which suggests that the addition of base from carbonate sources is not responsible for all of the observed alkalization. Acid neutralization might have been facilitated by phosphate loading that led to increased base generation through greater nitrate assimilation. Inadvertent alkalization might occur commonly in regions where poorly buffered lakes are subject to significant ionic and nutrient loading from agriculture, turfgrass, and septic sources in their watersheds.

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Introduction

Numerous studies have used sedimented diatom and chrysophycean assemblages to assess lake acidification caused by atmospheric loading of sulfate and

nitrate emissions (e.g. Cattaneo et al. 2004). Paleolimnological study of lake acidification in Florida showed that poorly buffered seepage lakes perched in Pleistocene sands of the Central Ridge underwent acidification of 0.5–1.0 pH units during the past 60 years (Sweets et al. 1990). Despite karst basement geology, Florida contains more poorly buffered acid lakes than any other region in the US because of the low edaphic supply of base ions in Plio-Pleistocene sands that mantle many areas of the state (Pollman and Canfield 1991). Most paleolimnological studies that have dealt with changes in limnetic pH have focused on lake acidification, and comparatively less attention has been paid to examples of alkalization.

Examples of human influence on lake alkalization appear to pre-date examples of human-induced acidification. Renberg et al. (1993) studied diatoms in sediment cores from 14 Swedish lakes and concluded that alkalization occurred c. 2500 BP and interrupted natural acidification that was caused by progressive leaching of base cations from watershed soils. Alkalization in these lakes resulted from deforestation, burning, agriculture, and other human activities that increased base saturation and pH of watershed soils. Alkalized soils subsequently led to increased cation and nutrient transport to lakes.

Intentional liming of lakes and streams has been used to neutralize recently acidified waterbodies and to restore affected fisheries (Henrikson and Brodin 1995). In addition to increasing pH and acid-neutralizing capacity (ANC) in lake waters, liming decreases limnetic concentrations of many toxic metals, including aluminum (e.g. Marcus 1988; Fimreite et al. 1996). When lakes are limed directly, low-pH inflow from streams and groundwater tends to return lakes to acidic conditions rather quickly, and acid-neutralizing solutes are lost progressively through outflows (Driscoll et al. 1989). More sustained alkalization effects are achieved when both catchments and waterbodies are limed (Dickson and Brodin 1995) because catchment liming provides base saturation at soil cation exchange sites, which tends to neutralize acidic outputs to receiving waterbodies. Rosseland and Hindar (1988), for example, reported that liming of Tjønnestrand's catchment led to more stable alkalization than could have been accomplished if large lime applications had been restricted to the pond.

Garrison et al. (1995) intentionally alkalized Max Lake, a small acidic (pH = 5.16, ANC = $-4.9 \mu\text{eq l}^{-1}$) seepage lake in northern Wisconsin, to study the chemical and biological responses of the lake to decreasing acidity. They accomplished alkalization by pumping groundwater (pH = 8.27, ANC = $1213 \mu\text{eq l}^{-1}$) into the lake as needed to reach pH target goals. pH of the lake increased from 5.16 to 5.62 over a 3-year period when 5–9% of the lake's hydrologic budget was introduced as groundwater, and pH reached 6.69 in the 5th year when 22% of the input was groundwater. Resistance to alkalization occurred initially because of adsorption of cations by sediment particles, although less additional groundwater was needed over time to change pH because sediment cation exchange sites became progressively saturated. Limnetic total P also increased slightly in Max Lake because of groundwater inputs.

Several studies have examined water chemistry in poorly buffered Florida lakes that received groundwater augmentation to maintain falling lake stage, but for which alkalization was not an intended outcome. Martin et al. (1976) showed that six augmented Florida lakes demonstrated greater hardness, inorganic carbon concentrations, and pH than unaugmented lakes in the vicinity. Dooris and Martin (1979) assessed chemical conditions in augmented lakes before and after groundwater addition. Groundwater augmentation of Lake Starvation converted it from a waterbody dominated by Na^+ , SO_4^{2-} and Cl^- , to one dominated by Ca^{2+} and HCO_3^- . Pfishner (1968) demonstrated that land-use practices, such as agriculture, also exert strong influence on the ionic content of poorly buffered Florida lakes in homogeneous terrain. Stauffer (1991) documented significant enrichment of K^+ , Na^+ , Mg^{2+} , Ca^{2+} , Cl^- , and SO_4^{2-} in Florida's Central Ridge lakes that had been subject to fertilization from citrus agriculture, but not subject to groundwater irrigation.

Alkalization can be effected by the addition of nutrients to a waterbody, and the resulting change in pH can be more pronounced than if an equivalent mass of CaCO_3 was added. Davison et al. (1995) showed that phosphate fertilizers increase primary productivity and lead to base generation from increased assimilation of nitrates, and they proposed the use of phosphate fertilizer rather than CaCO_3 to treat lake acidification. Addition of phosphorus is more efficacious than the addition of CaCO_3 be-

cause 16 mol of base are generated for every mole of phosphate that is utilized. When phosphate addition leads to greater organic matter deposition and anoxic decomposition of sediments, more base is generated by anoxic dissimilative processes. Davison et al. (1995) showed that phosphate loading to acidic, unproductive Seathwaite Tarn resulted in significantly higher limnetic pH. Addition of 5.9 m³ of phosphate fertilizer to Seathwaite had the same acid-neutralizing effect on pH as would have been produced by the addition of 34 metric tons of CaCO₃.

Recent paleolimnological studies in Florida have documented the inadvertent alkalization of lakes caused by the addition of groundwater to maintain lake-water levels. Brenner et al. (2000) examined ²²⁶Ra introduction caused by groundwater augmentation of Round Lake, a small, poorly buffered lake in south-central Florida. Augmentation waters were significantly higher than lake waters in specific conductance and total P content (Brenner and Whitmore 1998), and they represented approximately 3.5 times the amount of rainwater that entered the lake on an annual basis (Brenner et al. 2000). Recent sediments displayed increases in concentrations of calcium and carbonate-carbon, and sedimented diatoms indicated that pH and specific conductance had increased over time (Brenner and Whitmore 1998). Groundwater augmentation for lake-stage maintenance led to alkalization of four other Florida lakes (Brenner et al. 2006), and a paleolimnological comparison of 12 augmented and 12 non-augmented lakes has shown significantly more alkalization in groundwater-augmented lakes (Whitmore 2004).

The present study uses paleolimnological methods to examine the inadvertent alkalization of Little Lake Jackson. Previous paleolimnological studies have documented intentional alkalization caused by the application of lime to lakes or watersheds, by the application of P to lakes, or by the direct addition of groundwater to lakes to counteract acidic precipitation, whereas other studies have documented inadvertent alkalization caused by the direct addition of groundwater to lakes to maintain lake-stage levels. The present study differs from these because it investigates recent, inadvertent alkalization caused by ionic and nutrient loading to a lake's watershed because of multiple factors that are related to urbanization and turfgrass maintenance.

Study site

Little Lake Jackson lies at 27°28'02" N, 81°27'46" W in Highlands County, south-central Florida. The lake has a surface area of approximately 63 ha, a watershed area of 425 ha, and a maximum depth of 6.9 m. The lake is located on the Intraridge Valley of the Central Lake District in peat and mucky peat deposits that overlie the calcareous Fort Preston Formation (Canfield 1981). Watershed soils tend to be acidic and poorly drained (Carter et al. 1989). Intraridge Valley lakes generally are acidic (pH range = 5.3–6.7), oligo-mesotrophic or mesotrophic lakes that are low in ionic content (Canfield 1981). Little Lake Jackson currently is meso-eutrophic and alkaline (Table 1). The lake lies near the city of Sebring, which was settled in 1913 and currently has a population of around 35,000. Sixty-three percent of the watershed is residential, and 21% is recreational, including two golf courses and a baseball park.

Several changes that are associated with urbanization have occurred in Little Lake Jackson's watershed since the 1920s (Table 2). The Sebring Municipal Golf Course was constructed on the western shore of Little Lake Jackson around 1926 (Fig. 1). The golf course was irrigated until the 1960s with lake-water withdrawn from the lake via a canal. This canal became a source of hard water input to the lake from the 1960s to 1989 when the golf course was irrigated from a 390-m-deep well that supplied water from the basement limestone aquifer. After 1989, a deeper (490 m) well with a pH of 8.2 (SWFWMD, unpublished data) was used to irrigate the golf course. The canal currently serves as a site for stormwater drainage and it is the principal source of surface-water inflow to the lake.

Harder Hall Hotel is a large, 134-room facility that was built on the western lake shore around 1928. Dredge spoil from the lake was used to fill low areas on the hotel property. The hotel used septic tanks that discharged to drainage fields from the 1930s through the early 1950s. In 1952–1954, the hotel was connected to a sewage treatment facility that is outside of the watershed. Harder Hall Golf Course was built on the southwestern shore in the 1950s. A 2.9-km-long canal system was dug on the southeastern shore between 1969 and 1971 to permit construction of high density housing with lake access. Residential

Table 1 Water quality measures for Little Lake Jackson calculated from monthly averages

Water quality variable	Annual mean	Range
Limnetic total P ^a	52 $\mu\text{g l}^{-1}$	23–110 $\mu\text{g l}^{-1}$
Total N ^a	970 $\mu\text{g l}^{-1}$	620–2240 $\mu\text{g l}^{-1}$
Chlorophyll <i>a</i> ^a	12 $\mu\text{g l}^{-1}$	39–175 $\mu\text{g l}^{-1}$
Secchi depth ^a	1.1 m	0.3–1.7
Mean pH (averaged from H ⁺ conc.) ^b	8.05	6.70–9.04
Mean pH ^c	7.2	–
Total alkalinity ^b	17 mg l^{-1} as CaCO_3	–
Hardness ^b	38 mg l^{-1} as CaCO_3	–
Calcium ^b	10 mg l^{-1}	–
Magnesium ^b	3 mg l^{-1}	–
Potassium ^c	4 mg l^{-1}	–
Sodium ^c	9 mg l^{-1}	–
Chloride ^c	18 mg l^{-1}	–
Specific conductance ^c	147 $\mu\text{S cm}^{-1}$	–
Color ^c	28 Pt–Co units	–

^a Source: Florida Lakewatch (1999), monthly data for 1991–1999

^b Southwest Florida Water Management District, unpub. report. Monthly data for 1995–1996

^c Source: Florida Lakewatch (1999), monthly data for 2 months between 1991 and 1999

Table 2 Summary of recent changes in Little Lake Jackson's watershed

City of Sebring established	1913
Sebring Municipal Golf Course constructed	1926
Harder Hall Hotel constructed on western shore	1928
Hotel used septic tanks	1930–1950
Hotel connected to sewage treatment facility	1952–1954
Harder Hall Golf Course constructed	1950
Residential development expands on southern shore	1960
Sebring Municipal Golf Course irrigated from deep (390-m) well	1960–1989
Canal dug for residential boat access on southeastern shore	1969–1971
Sebring Municipal Golf Course irrigated from deeper (490-m) well	After 1989

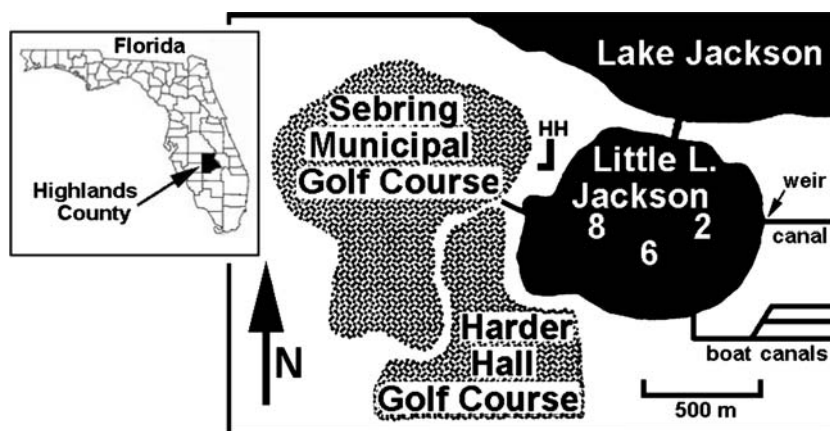


Fig. 1 Little Lake Jackson and its watershed in Highlands County Florida. HH denotes the Harder Hall Hotel. The

principal input is the canal on the west side, and outflow is intermittent over the weir to the canal on the east. The canal

development occurred on the southern and southwestern shores during the 1960s.

Soils in the southwestern and southern portions of Little Lake Jackson's watershed are poorly drained and subject to saturation during the seasonally high water table (Carter et al. 1989). To counteract soil acidity, the Sebring Municipal Golf Course, one of two golf courses in the drainage basin, currently applies 11.2 metric tons ha^{-1} of lime per year, 4.5 metric tons of which are slow-release dolomite. Sebring Municipal and Harder Hall Golf Courses probably contributed acid-neutralizing solutes and nutrients to Little Lake Jackson in recent decades through liming and fertilization.

In the past, wetlands surrounding Little Lake Jackson influenced lake-water quality, but their influence subsequently has been reduced. 1952 aerial photographs show that a large wet prairie connected the south side of Little Lake Jackson with Lake Huckleberry (limnetic $\text{pH} = 5.3$). Aerial photographs from 1974 and 1993 indicate that this wetland became increasingly forested. Survey maps from 1856 show that Little Lake Jackson was connected by a meandering creek to a large wetland outside of the watershed but adjacent to the eastern shore. 1952 aerial photographs show that this wetland was reduced to approximately 650 ha and that water flowed out of Little Lake Jackson through channelized Josephine Creek to the swamp. Between 1970 and 1975, the Jackson–Josephine Canal was constructed to carry the outflow through Josephine Creek all the way to Lake Josephine. A weir installed during canal construction precluded overland outflow into the canal between 1973 and 1995.

Little Lake Jackson is connected by a shallow canal on its north side to Lake Jackson, a larger waterbody (1381 ha) that is more acidic ($\text{pH} = 6.3$) and has lower limnetic nutrient concentrations (mean total $\text{P} = 16 \mu\text{g l}^{-1}$, total $\text{N} = 400 \mu\text{g l}^{-1}$; Florida Lakewatch 1999). Lake Jackson demonstrates somewhat lower specific conductance ($97 \mu\text{S cm}^{-1}$) and total alkalinity values (5 mg l^{-1} as CaCO_3) than Little Lake Jackson does (Table 1). Limnetic concentrations of cations such as calcium (4 mg l^{-1}), magnesium (9 mg l^{-1}), potassium (2 mg l^{-1}), and sodium (8 mg l^{-1} ; Florida Lakewatch 1999) are low in Lake Jackson, and they are comparable with cation values in Little Lake Jackson (Table 1). Since the early 1900s, a series of bridges have spanned the

canal that joins the lakes, and a ferry service between the lakes operated from the 1920s until the 1940s. The canal bridge was expanded in the 1960s to accommodate the joined US Highways 27 and 98 and State Highways 25 and 700. Infilling of the canal occurred during this construction, which together with low-water levels stopped outflow from Little Lake Jackson to Lake Jackson from the 1960s until 1982 (SWFWMD, unpub. data).

Methods

We retrieved sediment cores in November 1996 from nine evenly spaced sites throughout the limnetic zone of Little Lake Jackson to assess the spatial distribution of organic deposits and to identify appropriate coring sites for paleolimnological study. Sediment cores were collected for paleolimnological study from Stations 2 and 6 (Fig. 1) using a 1.6-m long sediment/water interface corer (Fisher et al. 1992). During continuing study in January 2005, a sediment core was collected from Station 2 for pigment analyses and a core was collected from Station 8 for cation analyses with a 4-cm diameter, 1.83-m long cellulose acetate butyrate piston corer (Fig. 1). All cores were extruded vertically and sectioned at 5-cm intervals.

Samples for diatom analyses were collected from a thin layer at the top of each 5-cm sediment core section in the 1996 Station 2 and 6 cores. Diatom samples were digested in 35% H_2O_2 and $\text{K}_2\text{Cr}_2\text{O}_7$ according to Van der Werff (1955), and slides were prepared with Naphrax[®] mounting medium. At least 500 valves were counted and identified at each level at 1500 \times magnification using dark-phase microscopy. Diatoms in core samples were classified with respect to pH preferences using autecological information compiled from many sources (e.g., Hustedt 1930–1966; Lowe 1974; Patrick and Reimer 1966–1975; Whitmore 1989; Van Dam et al. 1994; Krammer and Lange-Bertalot 1986–1991). Percentages of diatoms in pH preference categories were summed for each sample. Percentages of taxa that spanned more than one ecological category were divided equally among the pH categories involved.

Past limnetic water-quality conditions were inferred using sedimented diatom assemblages and weighted-averaging tolerance regression (WACALIB: Line

et al. 1994). Past limnetic pH values were inferred using a calibration set of 74 Florida lakes (r^2 adj. = 0.83, standard error of the prediction = 0.519). Past limnetic chlorophyll *a* concentrations were inferred using log-transformed chlorophyll *a* values for a calibration set of 75 Florida lakes (r^2 adj. = 0.77, s.e. pred. = 0.282), then de-transforming the inferences to yield chlorophyll *a* estimates.

Sediment subsamples for geochemical analyses were dried in a Virtis Unitrap II freeze drier. Dried samples were ground in a mortar and pestle and assessed for organic matter content by loss-on-ignition at 550°C (Boyle 2004). Total C and total N were determined using a Carlo-Erba NA 1500 C/N/S analyzer. Total P was measured using a Technicon Autoanalyzer II with a single-channel colorimeter following digestion with H₂SO₄ and K₂S₂O₈ (Schelske et al. 1986). NTA-P, which assesses cation-bound (Al, Fe, Mg, Ca) P, was measured after adding 0.01 M nitrilotriacetic acid to dry sediment and shaking for 20 h (Golterman 1977; Kenney et al. 2001). Biogenic silica was analyzed following Conley and Schelske (1993), which separates diatoms and sponge silica with a time-series digestion process. This procedure was modified to account for variability in silica dissolution among samples. Cation concentrations in sediments were analyzed with a Perkin-Elmer 4300 DV ICP-OES after digestion with concentrated HNO₃ and H₂O₂.

Radioisotopic activities for ²¹⁰Pb dating were obtained by direct gamma counting (Appleby et al. 1986) using an intrinsic germanium detector connected to a 4096-channel, multichannel analyzer (Schelske et al. 1994). Unsupported ²¹⁰Pb activity was calculated by subtracting ²²⁶Ra from total ²¹⁰Pb activity in each sample. Sediment ages and bulk sediment accumulation rates were calculated using the constant rate of supply (CRS) model (Appleby and Oldfield 1983). ²¹⁰Pb dates correspond to the base of each 5-cm section. Nutrient accumulation rates were calculated by multiplying the bulk sediment accumulation rate by nutrient concentrations for each stratigraphic interval.

Stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) signatures of sedimented organic matter were examined for evidence of changes in past primary productivity and nitrate sources to the lake (Brenner et al. 1999). Stable isotope values were obtained by combusting samples in a Carlo Erba NA 1500 C/N/S analyzer. Combustion gases (CO₂ and N₂) were analyzed with a VG PRISM

II series mass spectrometer. CO₂ values were standardized to CM-UF REF (Carrara Marble-University of Florida Reference Gas) and N₂ values were standardized to UF-N₂ REF, both in-house reference standards. $\delta^{13}\text{C}$ is expressed as the per mil (‰) deviation from the Vienna PeeDee Belemnite (VPDB) limestone standard, and $\delta^{15}\text{N}$ is expressed as the per mil (‰) deviation from the atmosphere.

Myxoxanthophyll, oscillaxanthin, total carotenoids, and chlorophyll pigments were extracted from wet sediment samples using acetone and were analyzed according to Swain (1985) and Waters et al. (2005). Spectrophotometry was used to measure total chlorophyll (665 nm), percent native chlorophyll (at 665 nm before and after acidification), total carotenoids (448 nm), oscillaxanthin (529 nm), and myxoxanthophyll (504 nm) concentrations. Total carotenoid, total chlorophyll, oscillaxanthin, and myxoxanthophyll values were expressed per unit organic matter to reduce variance caused by changes in inorganic sediment supply.

Most paleolimnological analyses were performed on cores taken from Stations 2 and 6 in 1996. The sediment core used for pigment analyses was retrieved from Station 2 in 2005, and the sediment core used for cation analyses was retrieved from Station 8 in 2005. Additional sedimentation in the 2005 cores makes direct stratigraphic correlation with the 1996 cores less accurate, although historic trends within cores still are comparable.

Results

Total ²¹⁰Pb profiles for all four sediment cores show curves that are typical for the exponential decay process, and they show no evidence of significant sediment mixing (Fig. 2). Total ²¹⁰Pb inventories are somewhat high in all sediment cores (~40 dpm/cm⁻²) and suggest that sediment focusing is occurring at these coring sites. This is consistent with the observation that thick organic deposits are present in the deep (>4 m) central portion of Little Lake Jackson whereas organic deposits are thin or absent in shallower areas. ²²⁶Ra values are elevated slightly in the upper 40 cm of these sediment cores, which suggests that dissolved radium is reaching the lake from radium-rich groundwaters that are

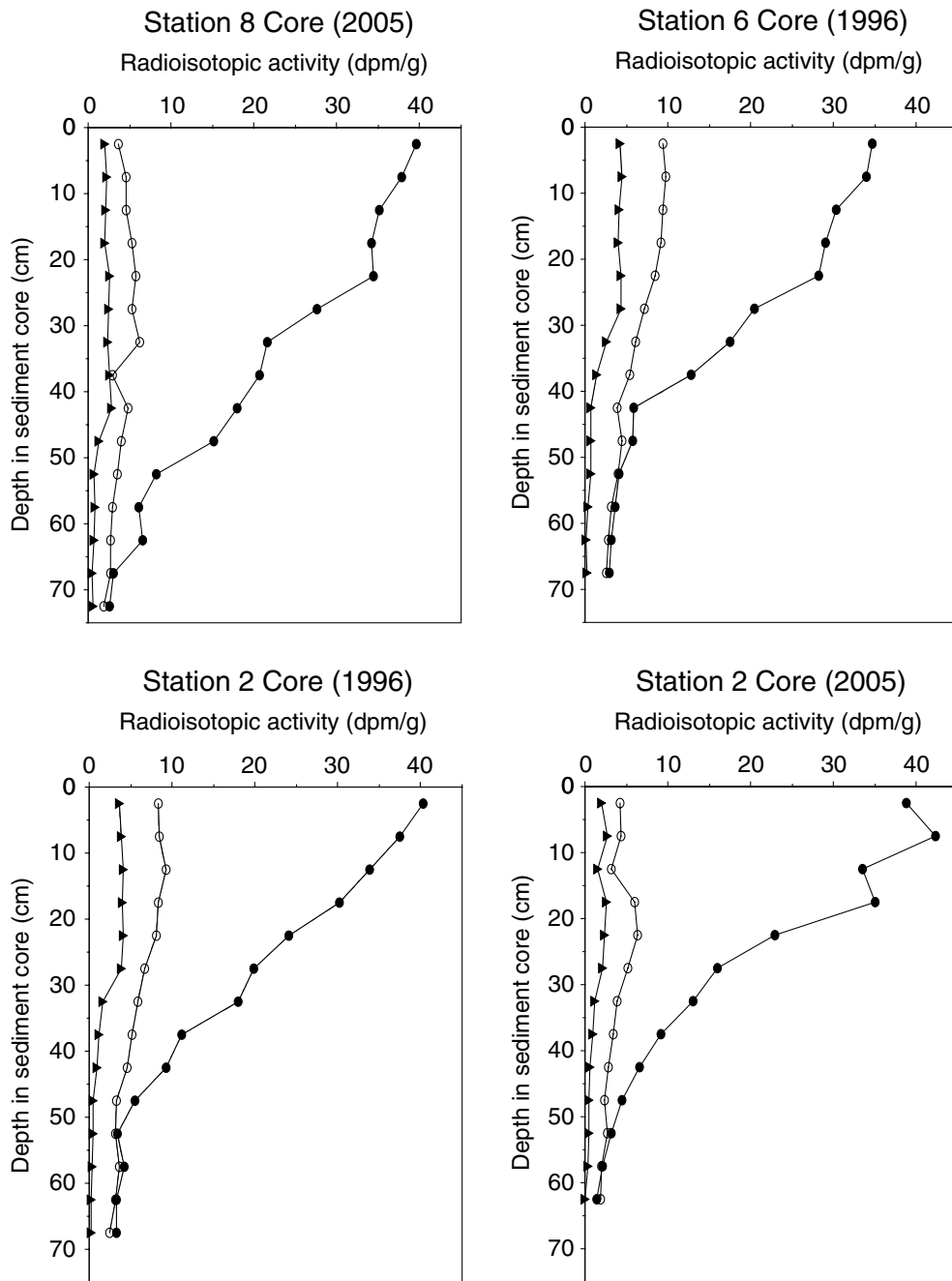


Fig. 2 Radioisotopic activity for the four ^{210}Pb -dated cores. ^{137}Cs is denoted by triangles to the left in each figure, ^{226}Ra activity is denoted by open circles in the center, and total ^{210}Pb is denoted by closed circles to the right

being pumped on the watershed for irrigation (Brenner et al. 2004). The ^{137}Cs profile is blurred in all four sediment cores, which is a common presentation for ^{137}Cs profiles in Florida lakes (Brenner et al. 2006).

Bulk sediment accumulation rates remained remarkably constant throughout the datable portion of the sediment cores from Stations 2 to 6. In the 1996 sediment core from Station 2, the bulk sediment accumulation rate in c. 1894 (50-cm level) was

55.7 mg cm⁻² yr⁻¹ and in 1994 it was 56.9 mg cm⁻² yr⁻¹, with a mean of 58.8 mg cm⁻² yr⁻¹ for the 100-yr period. The bulk sediment accumulation rate at the top of the Station 2 core from 2005 was 66.4 mg cm⁻² yr⁻¹. At Station 6, the bulk sediment accumulation rate in c. 1884 (50-cm level) was 66.2 mg cm⁻² yr⁻¹ and in 1995 it was 75.3 mg cm⁻² yr⁻¹, with a mean of 63 mg cm⁻² yr⁻¹ for the 111-yr period. The bulk sedimentation rates in the Station 8 core, which was retrieved nearest to the Harder Hall Hotel property, showed higher

sedimentation rates in the early 1900s than during recent decades. From 1932 to 1950 (50–60-cm levels), bulk sediment accumulation rates at Station 8 averaged 117 mg cm⁻² yr⁻¹, they decreased in c. 1959 (45-cm level) to 66 mg cm⁻² yr⁻¹, and they remained near this value until c. 2003 (0-cm level) when the bulk accumulation rate was 59.5 mg cm⁻² yr⁻¹.

Pronounced stratigraphic changes in the atomic C/N ratio of sediments occurred at Stations 2 and 6 (Fig. 3). Below the 50-cm level, sediments have C/N ratios >24, which suggests that macrophytes were

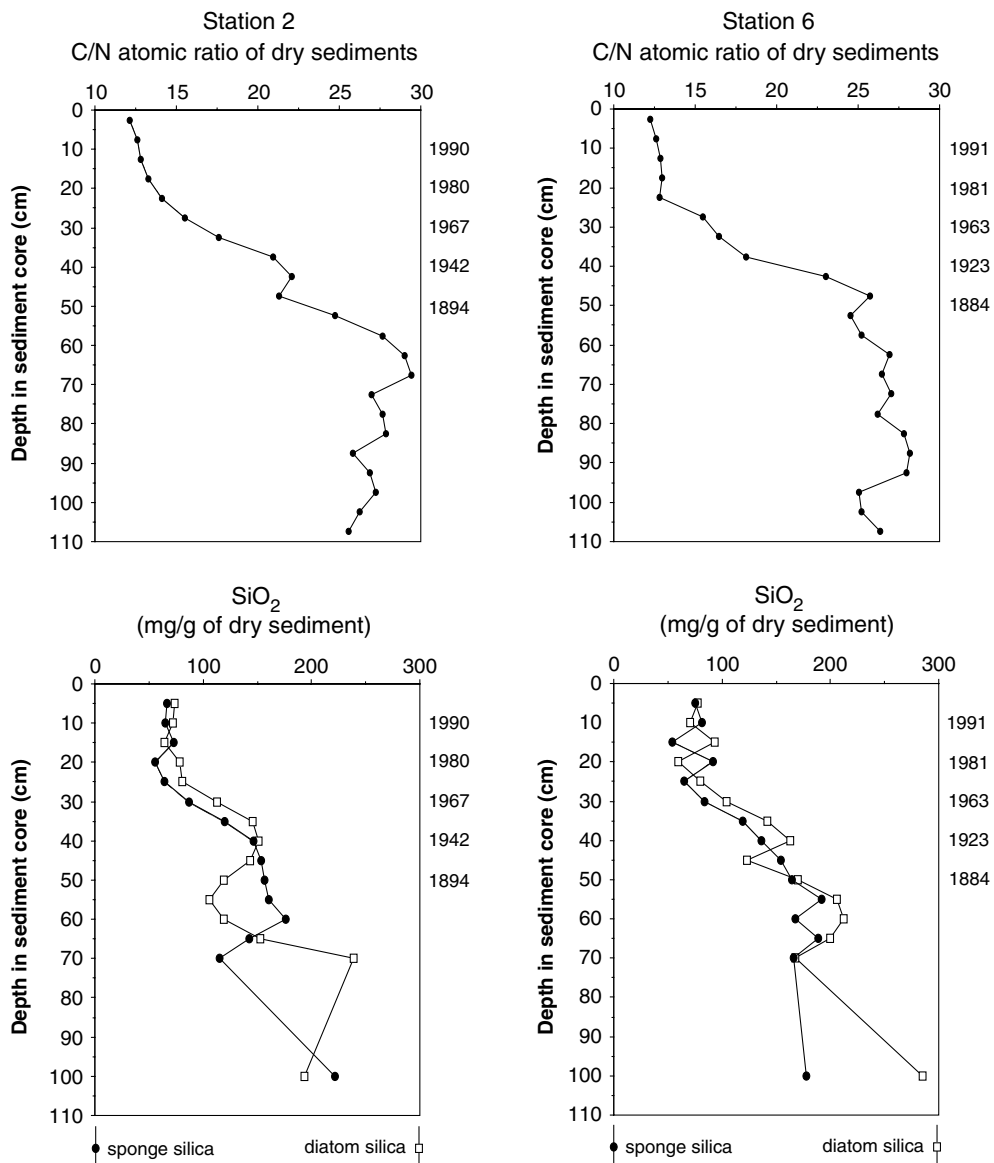


Fig. 3 C/N atomic ratios and biogenic silica content from the Stations 2 and 6 sediment cores

abundant, but C/N ratios decline to about 12 in the topmost core samples suggesting a shift to algal dominance (Brenner et al. 2006). Sponge spicules are evident with microscopy below the 45-cm level at Station 2 and beneath the 40-cm level at Station 6. Sponge silica concentrations decline by about 50% from the bottoms to the tops of the sediment cores (Fig. 3).

Sediment cores from Stations 2 and 6 show nearly identical stratigraphies with respect to physical and chemical variables. Total C concentrations averaged 196 mg g^{-1} at the base of these cores and increased to approximately 246 mg g^{-1} in the upper portion of the cores, with the period of change occurring c. 1922 at Station 2 and c. 1884 at Station 6. Organic matter accumulation rate increased 1.6–2-fold since the c. 1890 levels in the Stations 2 and 6 sediment cores retrieved in 1996 and in the station 8 core retrieved in 2005. Organic matter accumulation rate at the top of the 2005 sediment core from Station 2 was 25% higher than it was in 1994 ($40 \text{ vs. } 32 \text{ mg cm}^{-2} \text{ yr}^{-1}$), and it appeared to be lower at the datable base of this core as well ($11.7 \text{ vs. } 15.6 \text{ mg cm}^{-2} \text{ yr}^{-1}$). Organic matter accumulation rate, therefore, increased approximately 3.4-fold in the Station 2 sediment core that was retrieved in 2005.

Sediment P and N concentrations show pronounced increases from the base to the tops of the cores at Stations 2 and 6. Total N concentrations increase >3-fold and total P concentrations increase about 13-fold, with the period of most rapid increase occurring between the 1920s and the 1960s (Fig. 4). Since c. 1890 (~50-cm level) in both cores, total N accumulation rates increased 3-fold and total P accumulation rates increased about 5-fold. NTA-P (cation-bound P) at the base of the Station 2 and 6 cores shows values of 0.077 mg g^{-1} and 0.101 mg g^{-1} , respectively. NTA-P concentrations in both cores increase to approximately 1.7 mg g^{-1} near the 20-cm level (1974–1980), then values decline to approximately 1.3 mg g^{-1} at the top of the cores (Fig. 4).

Diatoms show distinctive changes in community composition throughout the cores from Stations 2 and 6. Diatom assemblages beneath the 45-cm level (1922) in the Station 2 core and beneath the 40-cm level in the Station 6 core (1923) are dominated by *Aulacoseira distans* and *A. granulata*. Between 45 and 50-cm depth in both cores, numerous species of *Frustulia*, *Anomoeoneis*, *Eunotia*, *Pinnularia*, *Surirella*,

Stenopterobia, and *Tabellaria* were present, indicating acidic waters with low ionic content (Whitmore 1989). Between the 45 and 25-cm levels in the Station 2 core (c. 1922–1974) and in the Station 6 core (c. 1905–1974), more productive waters are indicated by diatoms that include *Aulacoseira ambigua* and *Nitzschia palea*. Diatoms at 20 cm and above in both cores (post-1980) are primarily periphytic, alkaline taxa dominated by *Staurosira construens* var. *venter* and *Aulacoseira italica*, which in Florida lakes indicate mesotrophic-to-eutrophic and eutrophic conditions, respectively (Whitmore 1989).

Inferred limnetic chlorophyll *a* values for the Station 2 core were $<15 \mu\text{g l}^{-1}$ between the 105-cm and the 40-cm (1942) levels, they increased to $35.5 \mu\text{g l}^{-1}$ in the 15-cm level (1986), then they declined slightly to $31 \mu\text{g l}^{-1}$ at the top of the core (Fig. 5). This increase in inferred limnetic chlorophyll *a* is consistent with patterns of increased deposition of total chlorophyll and total carotenoid pigments (Fig. 5). Total chlorophyll, total carotenoid, myxoxanthophyll, and oscillaxanthin concentrations show pronounced increases above the 40-cm level, which suggests that recent decades were characterized by a period of increased primary productivity.

$\delta^{13}\text{C}$ signatures of sedimented organic matter show further evidence of increased primary productivity. $\delta^{13}\text{C}$ values increased from -26.2‰ in the 45–50-cm interval (c. 1894) to -24.1‰ in the 15–20-cm interval (1980), then decreased slightly to -29.9‰ at the top of the Station 2 core (Fig. 6). $\delta^{15}\text{N}$ values increased from -1.3‰ in the 45–50-cm interval to 2.7‰ at the top of the sediment core, which suggests that an external source of N enrichment entered the lake.

pH autecological preference categories of diatoms in the Station 2 and 6 cores show a distinct transition from acidic to more alkaline conditions (Fig. 7). At the 105-cm level in the Station 2 sediment core, acidophilous individuals (pH optimum = 5.5–7) represented 41.3% and alkaliphilous individuals (pH optimum = 7–8.5) represented 0.6% of the diatom assemblage. A decline in acidophilous individuals and an increase in alkaliphilous individuals occurred after c. 1900, but this change occurred more rapidly above the 40-cm level (c. 1942). The 15-cm level (c. 1986) in the Station 2 core showed the largest percentage of diatom individuals (48%) with alkaliphilous preference. By the 0-cm sample in the Station 2 core,

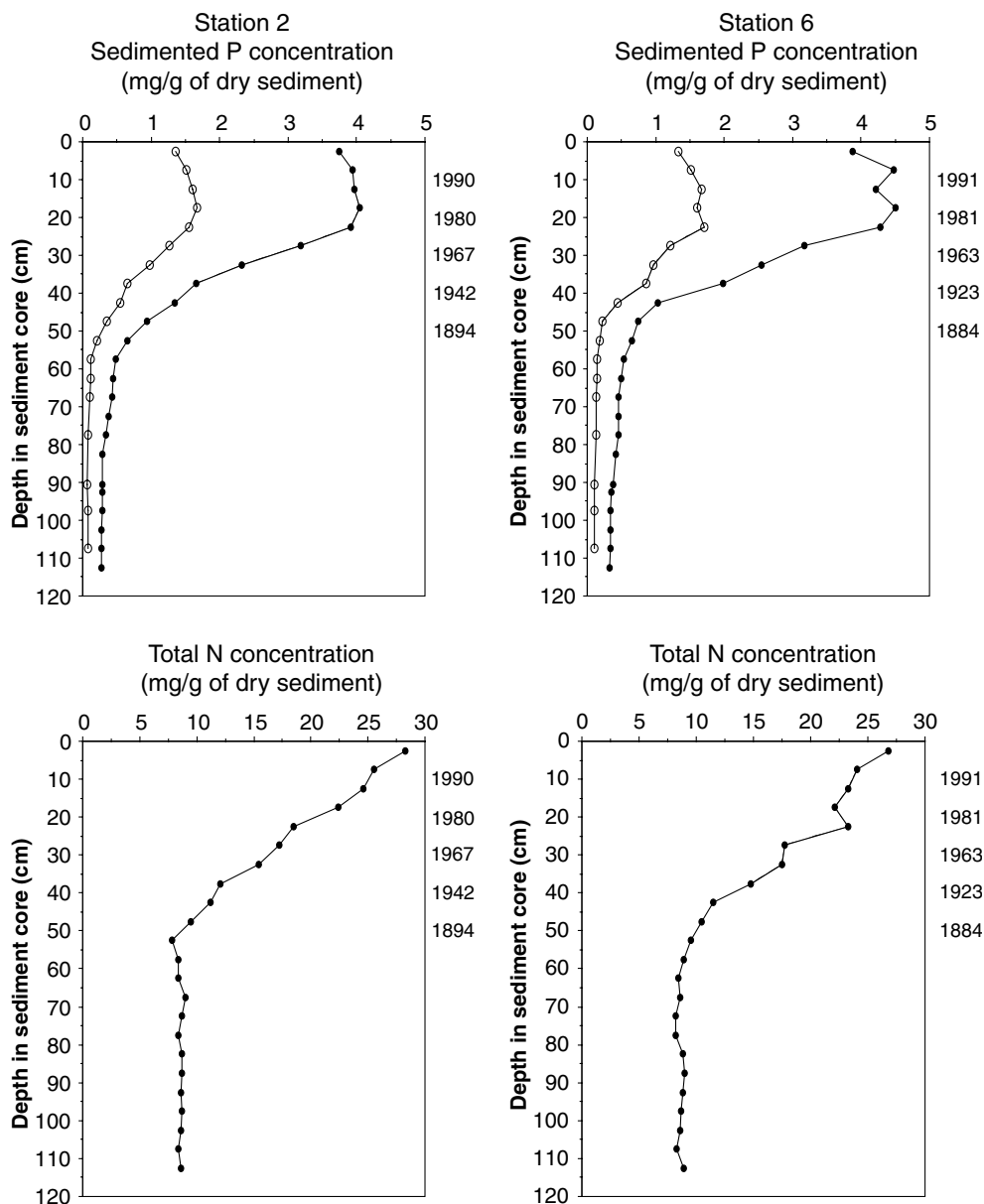


Fig. 4 Sedimented P and total N concentrations in sediment cores from Station 2 (left) and Station 6 (right). Closed circles denote total P, and open circles denote NTA-P

acidophilous individuals represented only 1.1% of the assemblage and alkaliphilous individuals represented 46.7% of the assemblage. A similar trend towards more alkaliphilous preference was shown by diatoms in the Station 6 sediment core (Fig. 7), with the period of most rapid change occurring above the 40-cm level (c. 1923) and the majority of individuals having alkaliphilous preference by the 15-cm level (c. 1987).

Diatom-inferred limnetic pH values document recent alkalization in the lake (Fig. 7). Between the 105-cm level and the 45-cm level (c. 1922) in the Station 2 core, the mean of inferred limnetic pH values was 6.06 (averaged from H^+ values), which is close to baseline pH conditions for other Intraridge Valley lakes in the vicinity (Canfield 1981). pH inferences increased very rapidly from 5.9 at the

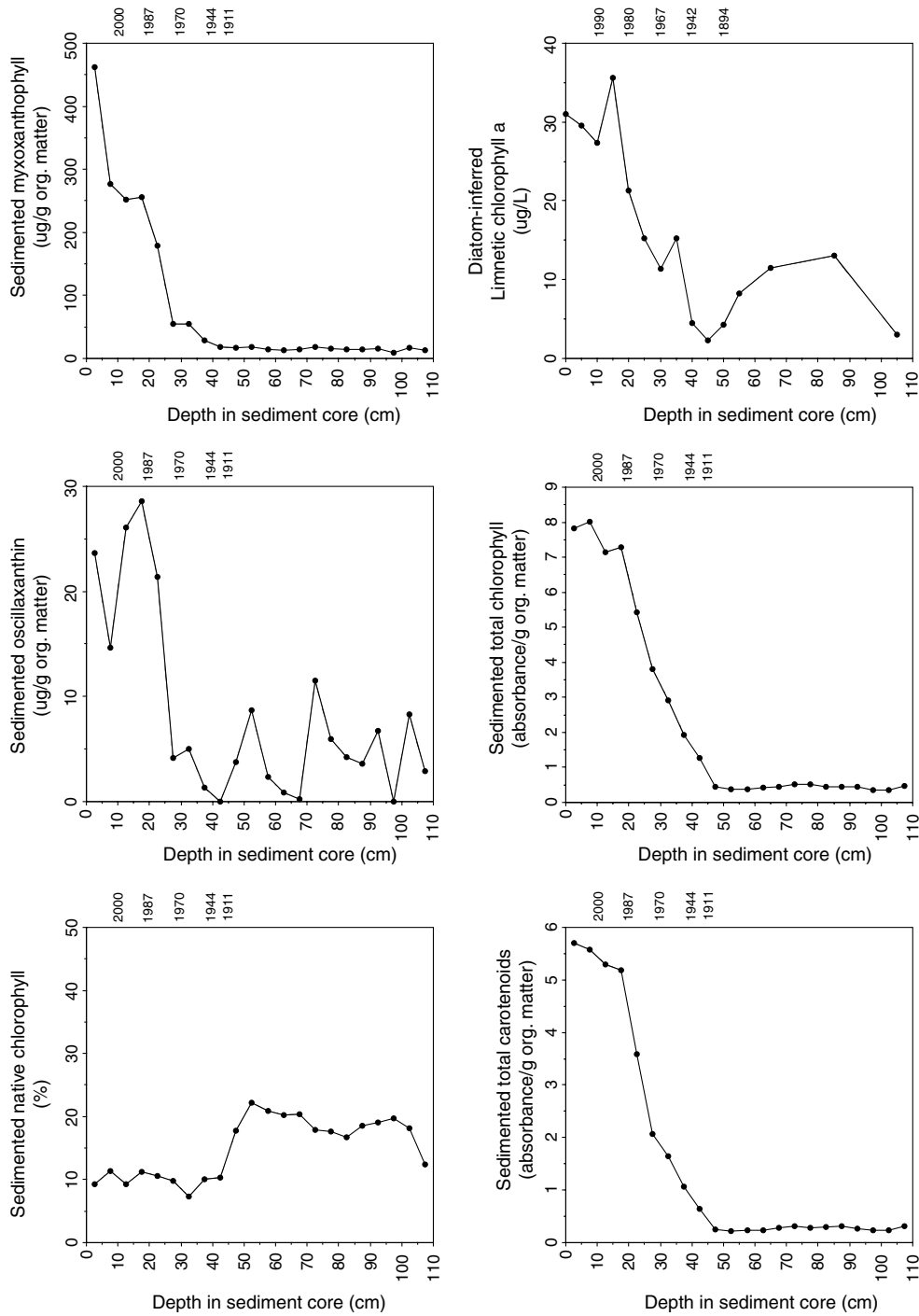


Fig. 5 Percent native chlorophyll, sedimented algal pigment concentrations, and diatom-inferred limnetic chlorophyll a concentrations from the 2005 Station 2 sediment core. Inferred limnetic chlorophyll a values are from the 1996 Station 2 sediment core

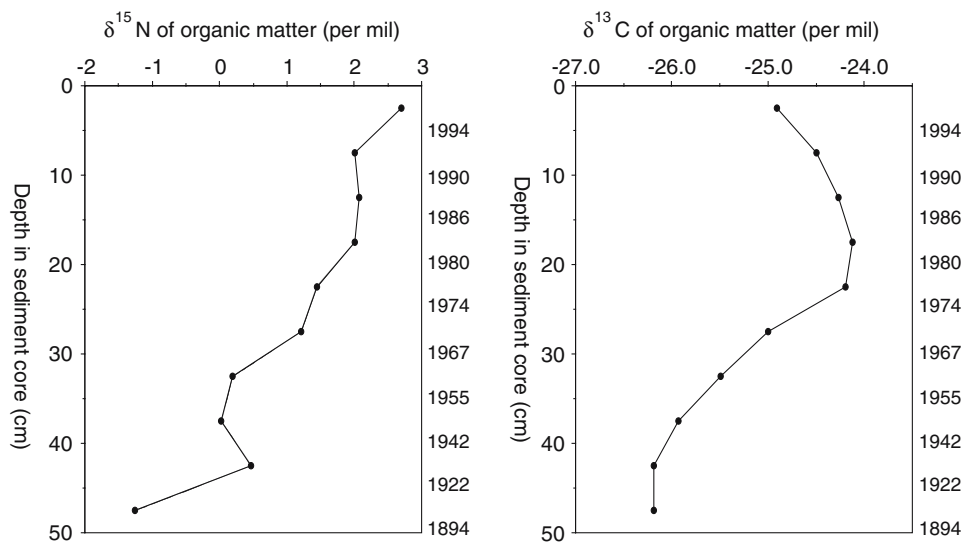


Fig. 6 $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signatures of sedimented organic matter from the Station 6 sediment core

45-cm level to 7.2 at the 35-cm level (c. 1955), then continued to increase at a slower but steady rate to 7.6 at the top of the Station 2 core. In the Station 6 sediment core (Fig. 7), mean limnetic pH was 6.15 (averaged from H^+ values) between the 105-cm and 45-cm (c. 1905) levels. pH increased rapidly to 7.1 at the 35-cm level (c. 1947), then continued to increase more slowly to a value of 7.7 in the 0-cm sample.

Cation concentrations in the 2005 Station 8 sediment core remained fairly constant between the 125-cm and 55-cm levels, then showed a period of rapid increase above the 55-cm level (c. 1940) to the top of the core (Fig. 8). Magnesium and potassium concentrations increased 2–3-fold from the base of the core to values of 1.29 mg g^{-1} and 0.81 mg g^{-1} , respectively, at the top of the core. Calcium concentrations increased >5-fold from 1.8 mg g^{-1} at the base of the core to 9.9 mg g^{-1} in the 0–5-cm interval. Sodium showed an 11-fold increase from 0.3 mg g^{-1} at the base of the core to 3.6 mg g^{-1} in the top sample. Aluminum averaged 5.5 mg g^{-1} below the 55-cm level, it increased rapidly to a peak of 37.0 mg g^{-1} in the 35–40-cm interval, then declined to a value of 20.1 mg g^{-1} at the top of the sediment core. Cation concentrations are highly correlated with organic matter content (e.g., r for loss on ignition and $\text{Ca}^{2+} = 0.941$, $\text{Mg}^{2+} = 0.688$, $\text{K}^+ = 0.896$, $\text{Na}^+ = 0.911$), which suggests that cations largely were scavenged to sediments with sedimented organic matter.

Discussion

The most noteworthy environmental change that Little Lake Jackson has undergone during the last century is alkalization that apparently resulted from human influence on the lake's watershed. Little Lake Jackson is located in a region of poorly drained, acidic soils, and the lake was acidic and low in nutrient content 100 years ago. Subsurface waters 0.8 km hydrologically upstream from the lake still are acidic (pH = 3.7–4.1 at ~4.0-m depth and pH = 4.7–5.3 at 9.7-m depth: SWFWMD unpublished data). Since the 1920s, the lake has been subject to stormwater inputs, nutrient inputs from residential septic systems, and to turfgrass liming and fertilization on recreational lands that currently have about twice the lake's surface area. In a lotic study that addressed similar watershed influences, Morgan and Good (1988) showed that reductions in H^+ and increases in Ca^{2+} , Mg^{2+} , K^+ , SO_4^{2-} and NO_3^- occurred in streams of the New Jersey Pinelands because of fertilizer and septic sources associated with agriculture and residential development. Sediment cores 2 and 6 show that the period of most rapid alkalization occurred between the mid-1960s and the early 1980s. During that period, deep-well irrigation began at Sebring Municipal Golf Course, the Harder Hall Golf Course was constructed, and temporary suspension of outflow to Lake Jackson occurred.

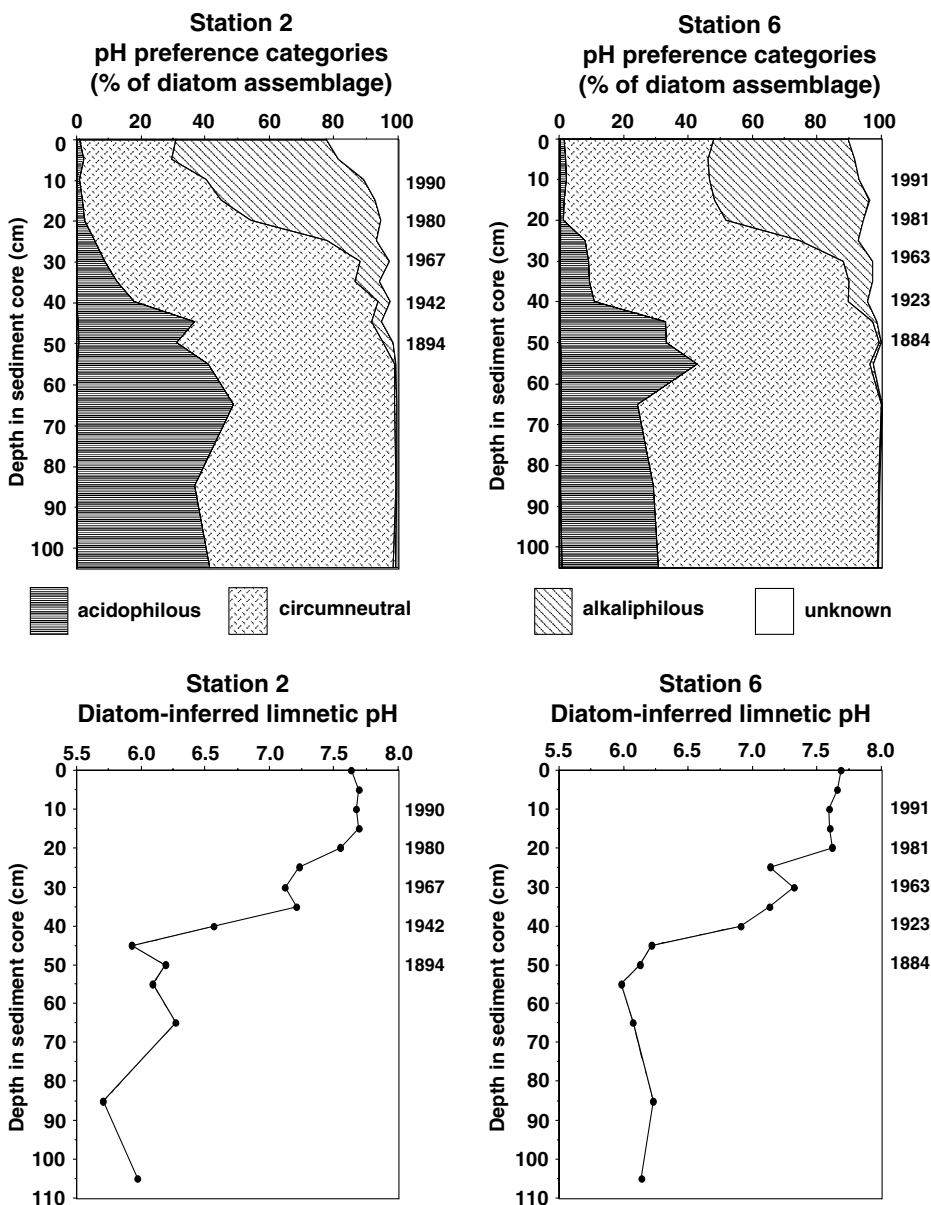


Fig. 7 Top row: percentages of diatom assemblages in pH autecological preference categories for the Stations 2 and 6 sediment cores. The percentage of acidobiontic individuals (pH

optimum <5.5) is shown as a narrow line against the left margin of the figures. Bottom row: diatom-inferred limnetic pH values for Stations 2 and 6 sediment cores

Subsurface outseepage is known to be a significant component of the water budget in many Florida lakes (Fellows and Brezonik 1980). Subsurface out seepage occurs along the entire eastern shore of Little Lake Jackson, and it carries water at $0.014\text{--}0.056\text{ m}^3\text{ s}^{-1}$ towards a wetland on the east (SWFWMD unpub. data). If hydrologic balance is to be maintained in Little Lake Jackson, considerable subsurface inflow

must enter the lake from topographically higher areas to the west and south where residential and recreational areas are located.

In a 4.2-m test well on the west side of Little Lake Jackson between Sebring Municipal Golf Course and the lake, mean hardness (41 mg l^{-1}) and mean bicarbonate alkalinity (25 mg l^{-1}) values were low between 1996 and 1997 (SWFWMD unpub. data).

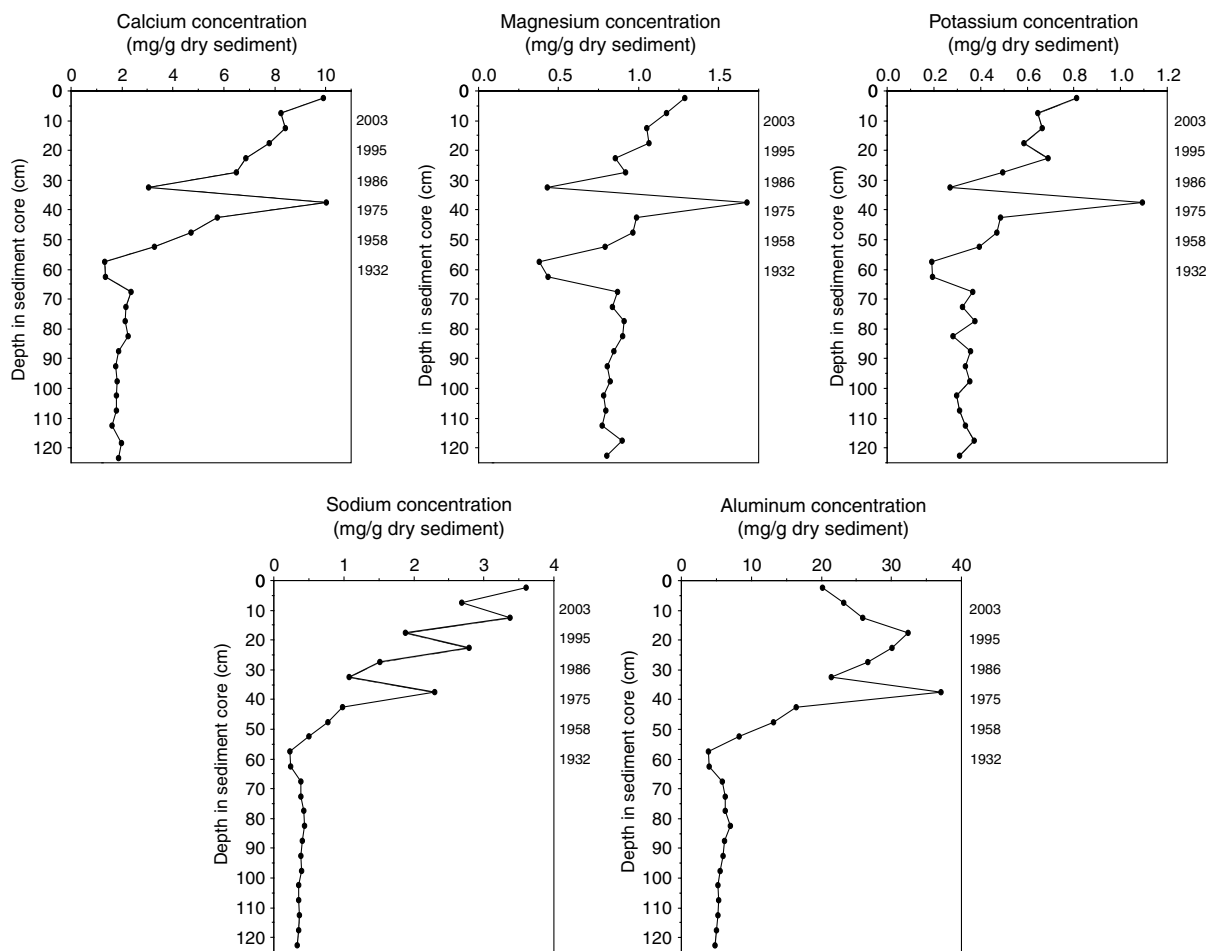


Fig. 8 Cation concentrations in the Station 8 sediment core

Calcium content in this well averaged 11 mg l^{-1} and magnesium content averaged 2.8 mg l^{-1} . In contrast, nutrient concentrations in well waters were high during this period, and the mean total P value was $1264 \mu\text{g l}^{-1}$ (SWFWMD, unpublished data).

Although Little Lake Jackson has undergone significant alkalization during recent decades, lake waters remain poorly buffered. During 1995–1996, total alkalinity at the center of the lake averaged 17 mg l^{-1} and hardness averaged 38 mg l^{-1} (SWFWMD, unpublished data). Limnetic Ca^{2+} and Mg^{2+} concentrations remain low (10 mg l^{-1} and 3 mg l^{-1} , respectively). In the main stormwater canal that enters Little Lake Jackson on the west shore near the golf courses, mean total hardness (37 mg l^{-1}) and mean bicarbonate alkalinity (7 mg l^{-1}) also were low between May 1995 and August 1996 (SWFWMD unpublished data),

possibly in part because of adsorption by organic ligands (mean color = 152 Pt l^{-1}). Calcium content in the stormwater canal averaged 8.5 mg l^{-1} and magnesium content averaged 3 mg l^{-1} .

Sediment concentrations of Ca^{2+} and Mg^{2+} show significant increases over time because of ionic loading. One consequence of increased cation input to Little Lake Jackson might have been adsorption of Ca^{2+} and Mg^{2+} by the lake's sediments. Cation influx might have reduced the lake's resistance to alkalization by binding sediment exchange sites, but cation exchange sites would have become saturated and led to greater hardness of limnetic waters if alkalization had been caused by ionic loading alone. Despite considerable lime and groundwater application in the watershed, alkalization of the lake appears to have been influenced by additional factors.

Increased nutrient loading also might have contributed towards alkalization of Little Lake Jackson during recent decades. Accelerated nutrient loading to the lake might have increased primary productivity and led to higher diurnal pH values because of a shift in the bicarbonate equilibrium caused by the CO₂ uptake of photosynthesizing algae. More importantly with respect to sustained alkalization, however, phosphate loading might have contributed to alkalization because it led to increased base generation through higher nitrate assimilation.

Phosphorus influx to Little Lake Jackson, particularly as orthophosphates, is high and has increased substantially during the last 100 years. Water in the main input canal to Little Lake Jackson during 1995–1997 showed a mean total P value of 172 µg l⁻¹ (152 µg l⁻¹ as orthophosphate) and a mean total N value of 1500 µg l⁻¹ during normal base flow activity (Kolasa 1999). During stormwater events, inflow volume increased and canal waters showed a mean total P value of 250 µg l⁻¹ (210 µg l⁻¹ as orthophosphate) and a mean total N value of 1800 µg l⁻¹. One exceptional stormwater event occurred the day after fertilizer application to Sebring Municipal Golf Course and introduced waters with a total P concentration of 701 µg l⁻¹ (650 µg l⁻¹ as orthophosphate) and a total N concentration of 3220 µg l⁻¹ (Kolasa 1999).

The annual fertilizer application rate for Sebring Municipal Golf Course, which is one of the two golf courses in the watershed, is equivalent to 54 tons of 15–5–15 (N–P–K). Despite the apparently high nutrient loading from golf courses, they are not necessarily the largest source of nutrient loading in the watershed. Of the estimated annual watershed surface loading of 29–41 tons of total N, approximately 16% is from septic effluent, 55% is from residential fertilizers, 23% is from golf-course fertilizers, and the balance is from rainfall (Kolasa 1999). Similarly for total P, of the estimated 7.6–9.6 tons applied to the watershed land surface, approximately 19% is from sewage effluent, 49% is from residential fertilizer, and 31% is from golf-course fertilizers (Kolasa 1999). Although watershed loading of nutrients is considerable, we do not know what proportions of these loadings actually reach the lake.

δ¹⁵N values of sedimented organic matter in Little Lake Jackson provide information about the sources of nutrients that reach the lake. Agricultural fertil-

ization affects the nitrate content of seepage flows (Fellows and Brezonik 1981), and changes in δ¹⁵N values are influenced by the sources of nitrate enrichment (Aravena et al. 1993). δ¹⁵N values of commercial fertilizers, for example, range between -2‰ and +4‰, and they can become further enriched by up to +6‰ by ammonia volatilization, particularly in the presence of calcareous soil or lime applications. Nitrate from nitrification of organic soils ranges from +3‰ to +8‰, and nitrate from fecal wastes, including septic systems, ranges from +10‰ to +20‰. Commercial fertilizer applications apparently were responsible for δ¹⁵N enrichment of sediments in Lake Persimmon (Riedinger-Whitmore et al. 2005), which lies 14 km south of Little Lake Jackson. Nitrate influx from residential and golf-course fertilizer applications and from septic systems in Little Lake Jackson's watershed likely account for the δ¹⁵N enrichment that was observed in Little Lake Jackson's sediments as well.

Some of the phosphorus that enters Little Lake Jackson probably becomes bound to aluminum and is unavailable for biological assimilation. High pH in Little Lake Jackson likely results in rapid precipitation of aluminum as it enters the lake from acidic surface and subsurface waters (Porcella et al. 1990). When pH is raised by assimilatory and dissimilatory removal of nitrates and sulfates, colloidal aluminum hydroxides form, and they adsorb some water-column orthophosphate and cause it to co-precipitate (Kopacek et al. 2000). Aluminum hydroxides increase the adsorption of orthophosphate to sediments and bind some portion of that P irreversibly, even under anoxic conditions. NaOH-P extraction methods would overestimate aluminum-bound P in Little Lake Jackson's organic-rich sediments because this method can extract P from organic material. NTA digestion for cation-bound P, in contrast, has little effect on organic material. NTA-P values in the Station 2 and 6 cores show that approximately 29% of the total P concentration at the base of the cores and approximately 35% of total P at the tops of the cores was cation-bound.

Increased sediment accumulation rates of P indicate that P loading to Little Lake Jackson increased during the last century. P loading led to a distinct increase in primary productivity, as shown by increases in sedimented δ¹³C values and in organic matter accumulation rates. A shift from macrophyte

to algal dominance also occurred, as indicated by inferred chlorophyll *a* values, increased deposition of algal pigments (Riedinger-Whitmore et al. 2005), decreased C/N ratios (Brenner et al. 2006), and a decline in sponge silica concentrations (Kenney et al. 2002). Davison et al. (1995) have demonstrated that even small additions of phosphate that result in modest amounts of phytoplankton growth can have appreciable effects on pH through increased nitrate assimilation. Increased organic matter deposition also can result in greater remobilization of nutrients from sediments, which can lead to a self-sustaining increase in productivity and pH (Davison et al. 1995). Alkalization of Little Lake Jackson might have been facilitated, therefore, by the increase in P loading.

An accurate ANC equivalency of the increased P loading can not be determined because of unquantifiable variables, such as how much P was remobilized and reassimilated over time. To illustrate potential ANC effects of P addition in basic terms, however, if biologically available P in sediments is defined as the difference between cation-bound and total P in sediments (i.e. TP-NTA-P), the net annual increase in P deposition over the last 100 years would have an ANC equivalency of several metric tons of CaCO₃ addition to the lake each year. Given the persistent low ionic content of lake waters, stormwater inputs, and subsurface seepage but the increased nutrient loading and organic matter deposition that occurred in Little Lake Jackson, it seems probable that base generation from nitrate assimilation contributed significantly towards the increase in limnetic pH.

Perhaps >70 lakes in southwest Florida have been alkalized to varying degrees by direct augmentation with ion-rich groundwater to maintain lake stage (D. Leeper, Southwest Florida Water Management District, pers. commun.). However, many other poorly buffered lakes, similar to Little Lake Jackson, are likely to have undergone inadvertent alkalization because of ionic and nutrient loading on their watersheds from liming, irrigation, stormwater runoff, septic systems, and from fertilization of turfgrass and agriculture. In other areas where basement geology is igneous, lakes are less likely to be influenced by groundwater pumping for irrigation, although agricultural liming and other activities in watersheds still might contribute to alkalization. Considerable effort was invested during the 1980s to document acidification of selected lakes in Florida,

but alkalization might prove to be a more widespread phenomenon in this region.

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