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ORIGINAL PAPER

# Stable isotope ($\delta^{13}C$ and $\delta^{15}N$) values of sediment organic matter in subtropical lakes of different trophic status

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**Abstract** Lake sediments contain archives of past environmental conditions in and around water bodies and stable isotope analyses ($\delta^{13}C$ and $\delta^{15}N$) of sediment cores have been used to infer past environmental changes in aquatic ecosystems. In this study, we analyzed organic matter (OM), carbon (C), nitrogen (N), phosphorus (P), and $\delta^{13}C$ and $\delta^{15}N$ values in sediment cores from three subtropical lakes that span a broad range of trophic state. Our principal objectives were to: (1) evaluate whether nutrient concentrations and stable isotope values in surface deposits reflect modern trophic state conditions in the lakes, and (2) assess whether stratigraphic changes in the measured variables yield information about shifts in trophic status through time, or alternatively, diagenetic changes in sediment OM. Three Florida (USA) lakes of very different trophic status were selected for this study. Results showed that both $\delta^{13}C$ and $\delta^{15}N$ values in surface sediments of the oligo-mesotrophic lake were relatively low compared to values in surface sediments of the other lakes, and were progressively lower with depth in the sediment core. Sediments of the eutrophic lake had $\delta^{13}C$ values that declined upcore, whereas $\delta^{15}N$ values increased toward the sediment surface. The eutrophic lake displayed $\delta^{13}C$ values intermediate between those in the oligo-mesotrophic and hypereutrophic lakes. Sediments of the hypereutrophic lake had relatively higher $\delta^{13}C$ and $\delta^{15}N$ values. In general, we found greater $\delta^{13}C$ and $\delta^{15}N$ values with increasing lake trophic state.

**Keywords** Eutrophication · Nutrients · Nitrogen · Microbial processes · Stable isotopes

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## Introduction

Some of the organic matter (OM) that enters a lake from the watershed (allochthonous) or is produced within the lake itself (autochthonous) is ultimately deposited on the lake bottom and becomes incorporated permanently into the lake sediments. Lakes thus function as sinks for OM and associated macro-elements such as carbon (C), nitrogen (N), and phosphorus (P). As a result, lake sediments contain an archive of past environmental conditions and biogeochemical processes in and around the water body and lake sediment cores can be used to document ecosystem changes through time (Smeltzer and Swain 1985). Macro-element and OM accumulation rates in sediments have been studied in conjunction with stable isotope analyses ($\delta^{13}C$ and $\delta^{15}N$) to infer past environmental changes in marine (Savage et al. 2004), lacustrine (Gu et al. 1996; Bernasconi et al. 1997; Hodell and Schelske 1998), and riverine ecosystems (McCallister et al. 2004). Measurements of $\delta^{13}C$ and $\delta^{15}N$ in dissolved and particulate matter in the water column and sediments have been used to identify the origin of lacustrine OM (Filley et al. 2001), infer past primary productivity (Hodell and Schelske 1998; Bernasconi et al. 1997), document historical eutrophication (Gu et al. 1996; Brenner et al. 1999), elucidate biogeochemical cycles (Terranes and Bernasconi 2000; Lehman et al. 2004), and shed light on microbial activity (Hollander and Smith 2001; Gu et al. 2004; Kankaala et al. 2006).

Past studies of stable isotope signatures in lake sediment OM enable a few generalizations. Allochthonous OM usually has more negative $\delta^{13}C$ values than does autochthonous OM. Values of $\delta^{13}C$ can also be used to distinguish OM deposited during periods of high versus low primary productivity. Fractionation occurs during photosynthesis because algae discriminate against the heavier $^{13}C$ isotope. Phytoplankton typically has $\delta^{13}C$ values $\sim$20‰ lower than the dissolved inorganic carbon (DIC) substrate used in photosynthesis. Under conditions of low to moderate primary productivity, algae are able to utilize lighter $^{12}C$ preferentially. Consequently, the resultant autochthonous OM displays very low $\delta^{13}C$. During periods of very high primary productivity, the $^{12}C$ pool in the water column is utilized preferentially, and once diminished, algae are forced to use the heavier isotope, yielding OM with relatively higher $\delta^{13}C$ (Mizutani and Wada 1982). Hypereutrophic lakes with high rates of primary productivity have low dissolved concentrations of carbon dioxide ($CO_2$) in the water column. Moreover, in high-pH waters, bicarbonate ($HCO_3^-$) dominates the DIC and has a $\delta^{13}C$ that is $\sim$8‰ higher than dissolved $CO_2$ (Fogel and Cifuentes 1993). High demand for DIC and low free $CO_2$ leads to utilization of $HCO_3^-$ as a C source, also yielding higher $\delta^{13}C$ values in algal OM (Goericke et al. 1994).

Stable isotope signatures of bulk lake sediment OM can sometimes be used to identify impacts of anthropogenic activities including wastewater and agricultural runoff that yield autochthonous OM with low $\delta^{13}C$ and high $\delta^{15}N$ (Burnett and Schaffer 1980; Savage et al. 2004). A stable isotope approach using $\delta^{15}N$ was also used to assess sources of N in Lake Lugano (Terranes and Bernasconi 2000). In that study, $\delta^{15}N$ was used to explore N-limitation of algae and N uptake by the phytoplankton community. The above generalizations about $\delta^{13}C$ and $\delta^{15}N$ of lake sediment OM may not hold in all cases because a multitude of processes affect OM stable isotope values. For instance, changing relative abundance of terrestrial versus aquatic OM in sediments across lakes, or within a lake through time, may complicate interpretations of relations between primary productivity and bulk sediment $\delta^{13}C$. Furthermore, although wastewater inputs tend to drive $\delta^{15}N$ values in sediment OM higher, many lakes that receive P-rich nutrient supplements develop N-fixing cyanobacteria blooms. There is no fractionation in the N-fixation process, and resultant blue-green biomass, i.e. OM, has a $\delta^{15}N$ signature near zero (Fogel and Cifuentes 1993).

Lake sediment OM and macro-elemental content, along with $\delta^{13}C$ and $\delta^{15}N$ signatures, can sometimes provide insights into: (1) the origin of OM in water bodies, (2) past lacustrine productivity, and (3) mineralization processes in lakes. In this study, we determined OM, C, N, P and $\delta^{13}C$ and $\delta^{15}N$ values in sediment cores from three subtropical lakes. We had two major objectives. First, we sought to evaluate whether macro-element concentrations and stable isotope values in surface sediment deposits reflect modern trophic state conditions in the lakes. Second, we wanted to assess whether stratigraphic changes in the measured variables might yield information about shifts in trophic status through time, or alternatively, diagenetic changes in sediment OM.

## Study sites

Three lakes in Florida (USA) were selected for this study, using trophic status criteria (Tables 1, 2; Fig. 1). Lake Annie is a small (0.37 km$^2$), relatively deep ($z_{max} = 20$ m), oligo-mesotrophic lake in south-central Florida (Highlands County), at the north edge of the Archbold Biological Station. The lake sits atop the Lake Wales Ridge and is situated

**Table 1** Long-term water quality data for the three Florida lakes used in this study

| Select variables | Minimum | Average | Maximum |
|---|---|---|---|
| Lake Annie (2000–2005) | | | |
| Total phosphorus concentrations (μg/L) (n = 62) | 4 | 9 | 27 |
| Total nitrogen concentrations (mg/L) (n = 62) | 0.26 | 0.43 | 0.74 |
| Total chlorophyll concentrations (μg/L) (n = 62) | 2 | 6 | 22 |
| Secchi depth (m) (n = 62) | 0.7 | 2.4 | 5.0 |
| Lake Okeechobee (mud zone) (1972–2010) | | | |
| Total phosphorus concentrations (μg/L) (n = 555) | 3 | 112 | 642 |
| Total nitrogen concentrations (mg/L) (n = 548) | 0.22 | 1.6 | 4.4 |
| Total chlorophyll concentrations (μg/L) (n = 454) | 1.5 | 19 | 66 |
| Secchi depth (m) (n = 445) | 0.04 | 0.3 | 1.4 |
| Lake Apopka (1987–2009) | | | |
| Total phosphorus concentrations (μg/L) (n = 276) | 58 | 167 | 377 |
| Total nitrogen concentrations (mg/L) (n = 276) | 2.5 | 4.8 | 9.7 |
| Total chlorophyll concentrations (μg/L) (n = 251) | 27 | 77 | 196 |
| Secchi depth (m) (n = 271) | 0.12 | 0.27 | 0.61 |

Data were obtained from various sources. Lake Annie = Florida Lakewatch program; Lake Okeechobee = South Florida Water Management District (SFWMD). 2010. DBHYDRO. Lake Apopka = (Coveney 2010)

**Table 2** Characteristics of the sampling sites in the three Florida lakes, with sampling date, location, sediment type and water variables

| Variable | Lake Annie | Lake Okeechobee | Lake Apopka |
|---|---|---|---|
| Site | Central | M9 | West |
| Latitude | 27°12′27″ | 26°58′17.6″ | 28°38′01″ |
| Longitude | 81°21′44″ | 80°45′38.4″ | 81°39′36″ |
| Sampling date | June 2005 | July 2005 | May 2005 |
| Sediment type | Mud/clay | Mud | Organic |
| Water column depth (m) | 20 | 4.0 | 2.0 |
| Secchi depth (m) | 2.0 | 0.08 | 0.3 |
| Temperature (°C)[a] | 30.2 | 29.5 | 26.6 |
| Electrical conductivity (μS $cm^{-1}$)[a] | 41.9 | 385 | 443 |
| pH[a] | 5.1 | 7.8 | 7.6 |
| Dissolved oxygen (mg $O_2$ $L^{-1}$)[a] | 6.4 | 6.5 | 8.7 |
| Dissolved organic C (mg C $L^{-1}$)[b] | 13.8 | 14.5 | 31.1 |
| Total P (μg P $L^{-1}$)[b] | 33 | 256 | 70 |
| Dissolved reactive P (μg P $L^{-1}$)[b] | 7 | 90 | 11 |
| Total N (mg N $L^{-1}$)[b] | 1.81 | 3.44 | 11.15 |
| Ammonium (mg N $L^{-1}$)[a] | 0.18 | 0.10 | 0.12 |

The Annie TP value is very high relative to that reported by Lakewatch (long-term mean = 9 μg P $L^{-1}$)

[a] Measured at 1 m depth in the water column

[b] Mean concentration in the water column. For Lake Annie, values are the average of samples taken at the following depths: 0.5, 1.0, 2.0, 5.0, 10, 20 m; for Lake Okeechobee and Lake Apopka, values are an average of samples taken at 0.5, 1.0, and 2.0 m

in nutrient-poor quartz sands. Water enters the lake principally in direct precipitation and as shallow groundwater, but two man-made ditches contribute surface waters and associated nutrients during periods of high rainfall (Battoe 1985). Water leaves the lake via evaporation and a small outflow stream on the north shore. Sediments in the littoral zone are sandy to organic (Layne 1979), whereas deposits in

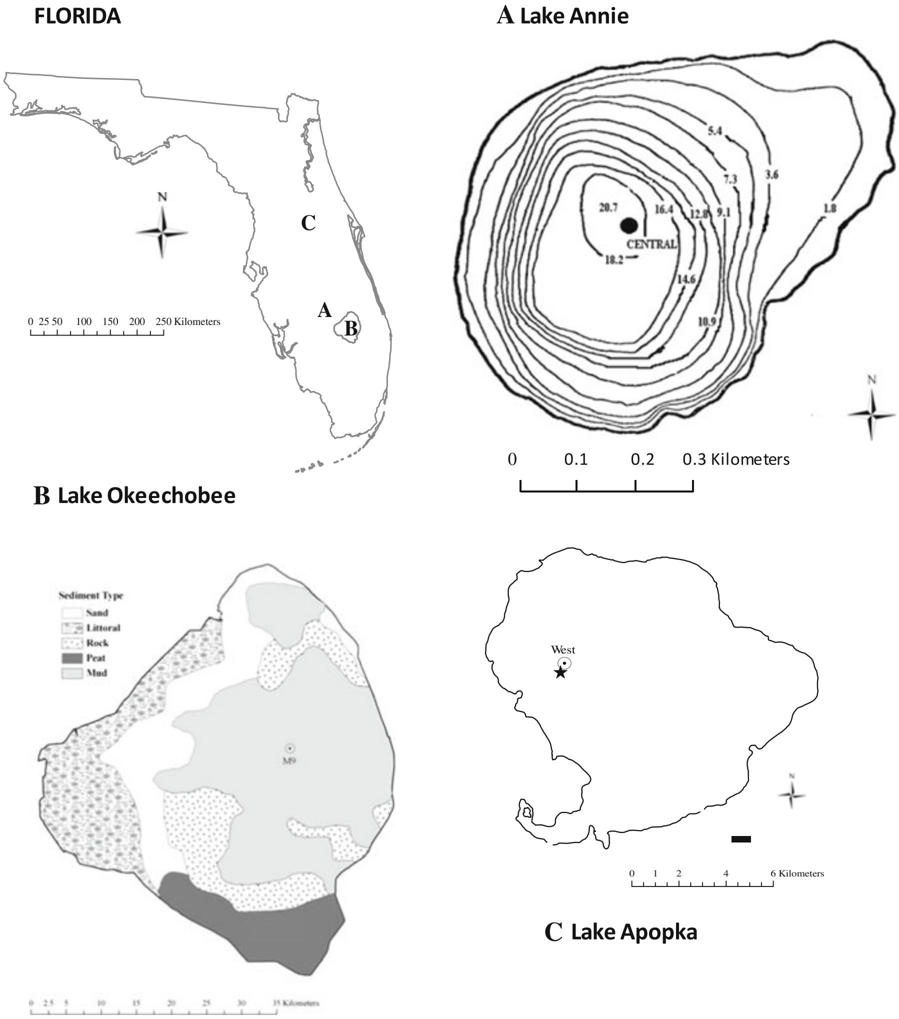


**Fig. 1** Maps of the three subtropical study lakes with sampling sites and lake location in Florida: **a** Lake Annie (with water column depth in meters, modified from Layne 1979), **b** Lake Okeechobee with different sediment types, and **c** Lake Apopka

deeper water have higher OM content. Because the lake is located in a private reserve, it is subject to relatively little anthropogenic impact (Layne 1979).

Lake Okeechobee is a large (1,730 $km^2$), shallow, eutrophic lake located in south Florida that has experienced cultural eutrophication over the last 50 years (Engstrom et al. 2006). Benthic sediments are characterized as mud (44% of the total lake surface area), sand and rock (28%), littoral areas dominated by macrophytes (19%), and peat or partially decomposed plant tissue (9%) (Fisher et al. 2001).

Lake Apopka is a shallow lake (125 $km^2$) located in central Florida. Once a clear-water, macrophyte-dominated lake, it changed in 1947 to a turbid, algal-dominated water body (Clugston 1963), following nutrient input from several sources, including agricultural drainage from adjacent vegetable farms (Schelske et al. 2005, 2010). Although these inputs were controlled and regulated to some degree, the eutrophication process continued and Lake Apopka is now considered hypereutrophic. Benthic sediments are unconsolidated and consist mainly of material of algal origin (Reddy and Graetz 1991).

## Materials and methods

### Field sampling

Sediment–water interface cores of variable lengths were collected using a piston corer (Fisher et al. 1992) or by SCUBA divers. Lake maps with sampling locations are shown in Fig. 1. One central site (60-cm core) was sampled in Lake Annie on June 25, 2005. A 73-cm core was collected on July 16, 2005 from the mud zone of Lake Okeechobee (site M9), an area that has the highest concentration of P among the different sediment types of this lake. A 72-cm core was taken from a western site in Lake Apopka on May 28, 2005. Sediment cores were sectioned at 4-cm intervals and samples were sealed in labeled plastic bags and returned to the laboratory on ice.

### Sediment properties

Sediment samples were dried in a Virtis Unitrap II freeze drier. Sediment bulk density was determined as dry weight per unit wet volume (g dry $cm^{-3}$ wet) following freeze-drying. Dried samples were ground in a mortar and pestle and passed through a 2-mm-mesh sieve. Organic matter content (LOI%) was estimated on fine sediment fractions (samples sieved through 2-mm screen) by weight loss on ignition at 550°C (LOI). Total P in samples was measured by ashing, followed by acid digestion (6 M HCl) and colorimetric measurement with a Bran + Luebbe Technicon™ Autoanalyzer II (Anderson 1976; EPA Method −365.1). Total carbon (TC) and total nitrogen (TN) were determined using a Flash EA-1121 NC soil analyzer (Thermo Electron Corporation).

### Stable isotope analyses

Sediment samples for organic C isotope analysis were pretreated with acid to remove inorganic (carbonate) C (Harris et al. 2001). Samples were weighed in silver capsules, placed in the wells of a microtiter plate, and 50 μL of deionized (DI) water was added to moisten the sediment. Plates were placed in a vacuum desiccator with 100 mL of concentrated HCl and exposed to HCl vapor for 24 h. Samples were dried at 60°C for 4 h to remove remaining HCl. Carbon (organic) and nitrogen (total) isotope values were determined using the method described by Inglett et al. (2007). Isotope analyses were conducted using a Costech Model 4010 Elemental Analyzer (Costech Analytical Industries, Inc., Valencia, CA) coupled to a Finnigan MAT Delta$^{Plus}$XL Mass Spectrometer (CF-IRMS, Thermo Finnigan) via a Finnigan Conflo II interface. Stable isotope results are expressed in standard delta notation, with samples measured relative to the Pee Dee Belemnite for C and atmospheric $N_2$ for N. Analytical accuracy and precision were established using known isotopic standards (wheat flour, $\delta^{13}C = -26.4$ ‰, $\delta^{15}N = 2.6$ ‰, Iso-Analytical; IAEA-N1, $\delta^{15}N = 0.4$ ‰; ANU-Sucrose, $\delta^{13}C = -10.5$ ‰). Analytical precision for standards was within ±0.1‰ for $\delta^{13}C$ and ±0.3‰ for $\delta^{15}N$.

## Results

### Water column characteristics

All three lakes had water transparency ≤2 m (Tables 1, 2). Most water-column variables represent the value for a sample collected at 1 m depth in the water column, whereas dissolved organic carbon (DOC), total phosphorus (TP), dissolved reactive phosphorus (DRP), and total nitrogen (TN) were measured at several depths in each lake and mean values were calculated (Table 2). For Lake Annie, values are the average of measurements taken at 0.5, 1, 2, 5, 10 and 20 m, whereas for Lake Okeechobee and Lake Apopka values are averages of samples taken at 0.5, 1 and 2 m. Electrical conductivity values reflect the trophic status of each lake, with the lowest mean value for Lake Annie (42 μS $cm^{-1}$), and higher mean values for Lake Okeechobee (385 μS $cm^{-1}$) and Lake Apopka (3,443 μS $cm^{-1}$). Lake Annie water column pH was low (5.1), whereas both Lake Okeechobee (7.8) and Lake Apopka (7.6) were above neutral. Daytime dissolved oxygen concentrations ranged from 6.4 to 8.7 mg $L^{-1}$, with highest values measured in Lake Apopka. Highest DOC values were found in Lake Apopka (31 mg C $L^{-1}$), whereas DOC values in the other lakes were similar, around 14 mg C $L^{-1}$. Total P in the water column was much higher in Lake Okeechobee (256 μg P $L^{-1}$) than in either Lake Apopka (70 μg P $L^{-1}$) or Lake Annie (33 P μg $L^{-1}$). These values represent only the day water samples were collected and are different from long-term average values presented in Table 1. Dissolved reactive phosphorus showed similar relations, with the greatest values in Lake Okeechobee (90 μg $L^{-1}$), and smaller values in Lake Apopka (11 μg P $L^{-1}$) and Lake Annie (7 μg $L^{-1}$). Total nitrogen, however, was greatest in Lake Apopka (11 mg N $L^{-1}$), with lower values measured in Lakes Okeechobee (3.4 mg N $L^{-1}$) and Annie

(1.8 mg N $L^{-1}$). Ammonium-N values were rather similar across the lakes, with Annie displaying the highest amount (0.18 mg N $L^{-1}$), and Apopka and Okeechobee both containing approximately 0.1 mg N $L^{-1}$.

## Sediment properties

### *Lake Annie*

Organic matter content (LOI %) in the Lake Annie core generally increased toward the sediment surface, from a low of about 50% to a high of about 56% (Fig. 2d). Lake Annie sediment TC:TN ratios displayed a slight increase with depth, from 13 to 15 (Fig. 2b). Total P in sediments was ~1,000 mg $kg^{-1}$ in the lower part of the core (28–60 cm), but increased to values between 1,500 and 1,900 mg $kg^{-1}$ in the upper 16 cm (Fig. 2a). The TN/TP ratio was 12.5 in surface sediments (0–4 cm) and decreased to 10 at 16 cm depth (Fig. 2a). This was followed by a steady increase in ratios to 15 (Fig. 2c). The $\delta^{13}C$ values ranged from about −28 to −29‰ in the lower portion of the core (60–16 cm), but then declined to the lowest value of −30‰ in the surface sediments (Fig. 2e). The $\delta^{15}N$ values were positive, varying between about 2.0 and 2.3‰, but declined to 0.9‰ in the topmost sediments (Fig. 2f). Surface sediments are low relative to subsurface sediments, by 1.2‰ ($\delta^{13}C$) and 1.1‰ ($\delta^{15}N$).

### *Lake Okeechobee*

Mud zone sediments from site M9 in Lake Okeechobee showed OM (LOI) values ranging from about 18

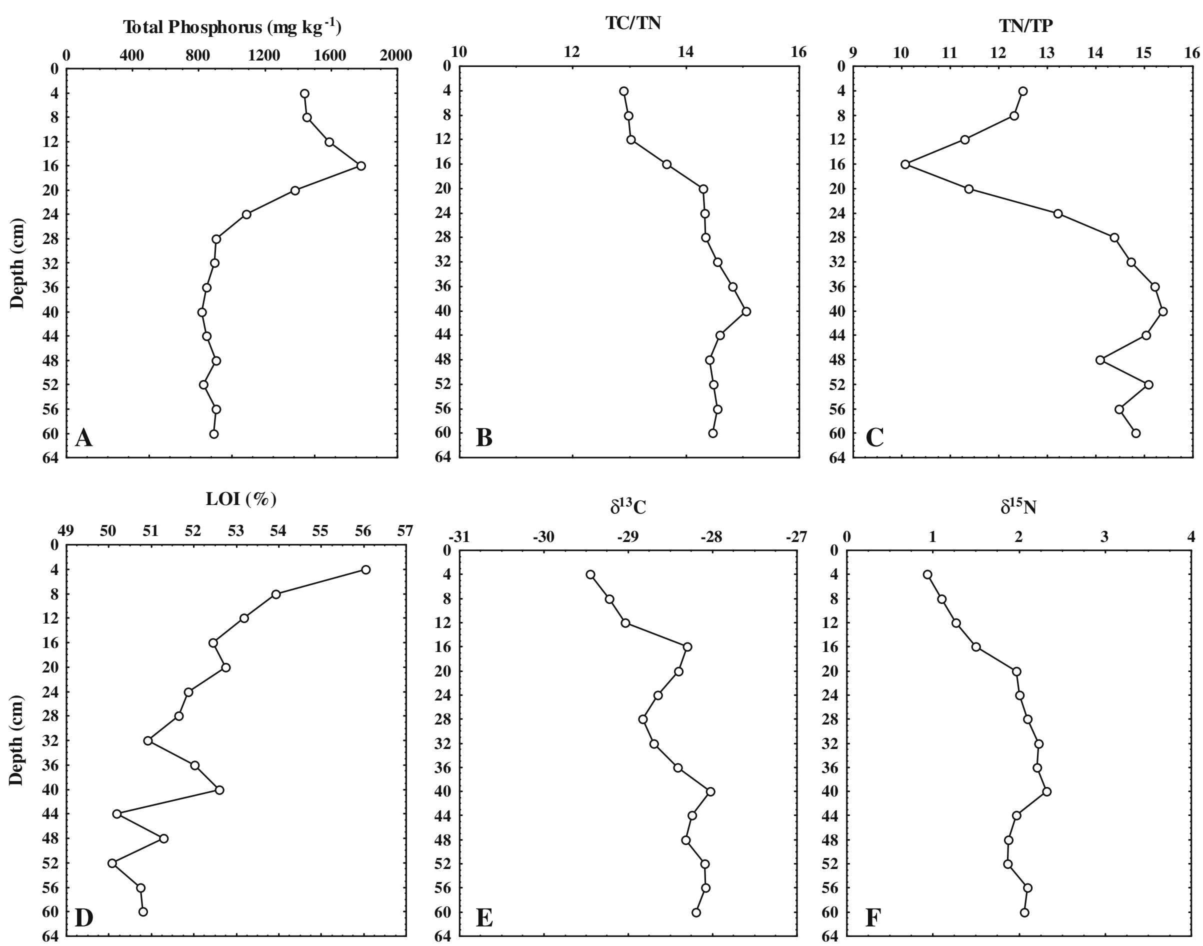


**Fig. 2** Lake Annie sediment depth profile of: **a** total phosphorus, **b** TC:TN ratio, **c** TN:TP ratio, **d** organic matter content (LOI), **e** $\delta^{13}C$ of sediment organic carbon and **f** sediment $\delta^{15}N$

to 40%, with highest values recorded in the uppermost deposits (Fig. 3d). The TC:TN ratios were relatively low ($\sim$18) near the base of the section, but increased to a maximum of $\sim$32 at 24 cm depth (Fig. 3b). Thereafter, the ratios decreased to 15 in the topmost 12 cm. Total P in surface sediments was approximately 1,000 mg P $kg^{-1}$ and steadily decreased to 500 mg P at depths >36 cm (Fig. 3a). Overall, $\delta^{13}C$ values ranged from −26 to −25‰, with surface sediments only slightly lower relative to subsurface sediments (Fig. 3e). Nitrogen isotope values vary from 2.6 to 3.9‰ and show $\sim$1.3‰ higher values in surface sediments relative to sub-surface sediments (Fig. 3f).

### *Lake Apopka*

Among the three lakes, OM content in the Apopka sediment core was greatest, varying between about 62 and 70%, with low values observed at depths 32–48 cm (Fig. 4d). Lake Apopka sediments displayed a narrow range of TC:TN ratios, $\sim$11–12 (Fig. 4b). There was a general decrease from about 72–12 cm depth, and then an increase to the sediment surface (Fig. 4b). Total P concentration more than doubles between the base of the core ($\sim$600 mg P $kg^{-1}$) and 20 cm depth (>1,400 mg P $kg^{-1}$) (Fig. 4a). The TN:TP ratios declined twofold moving upcore, reflecting recent increases in P concentration (Fig. 4c). Organic matter $\delta^{13}C$ increased from

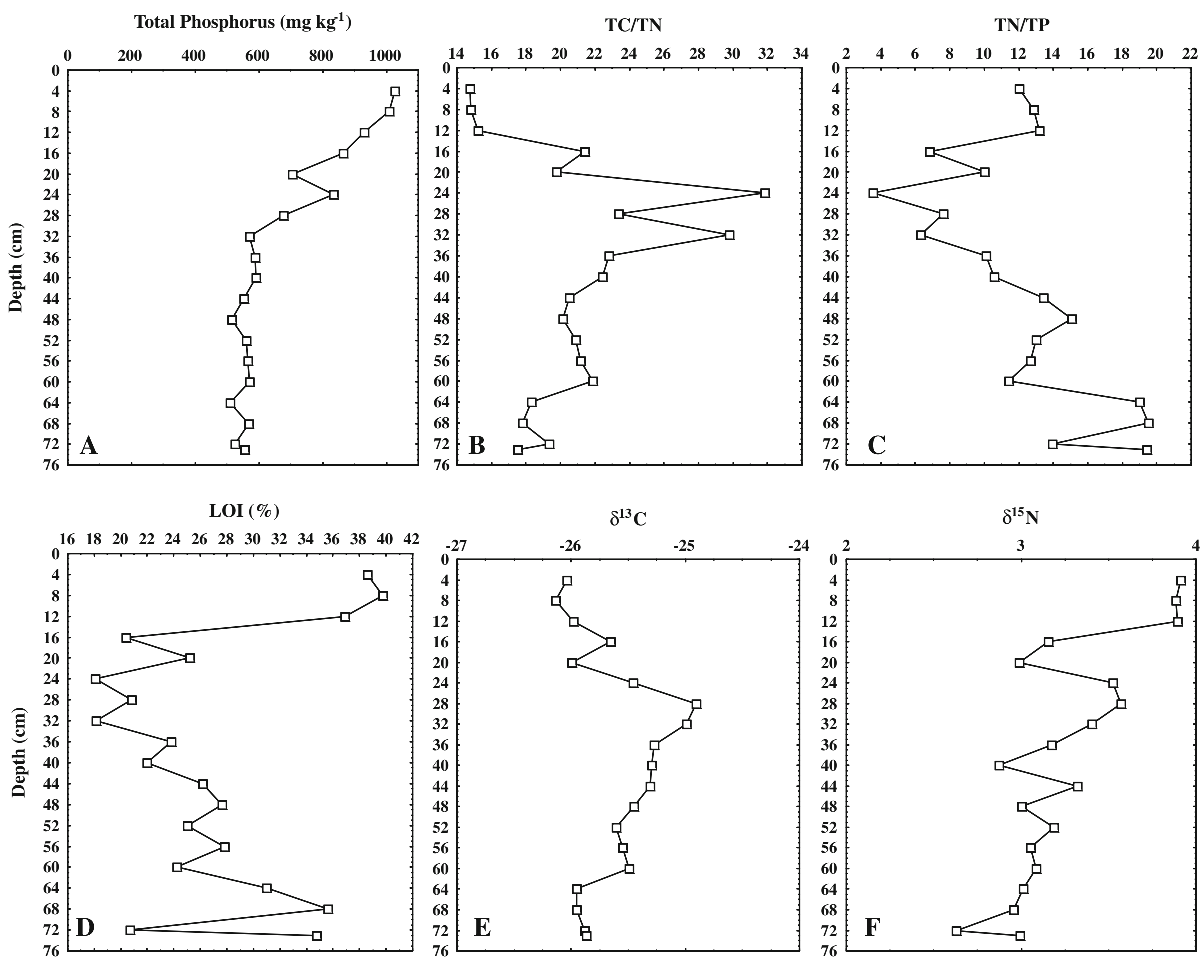


**Fig. 3** Lake Okeechobee sediment depth profile of: **a** total phosphorus, **b** TC:TN ratio, **c** TN:TP ratio, **d** organic matter content (LOI), **e** $\delta^{13}C$ of sediment organic carbon and **f** sediment $\delta^{15}N$

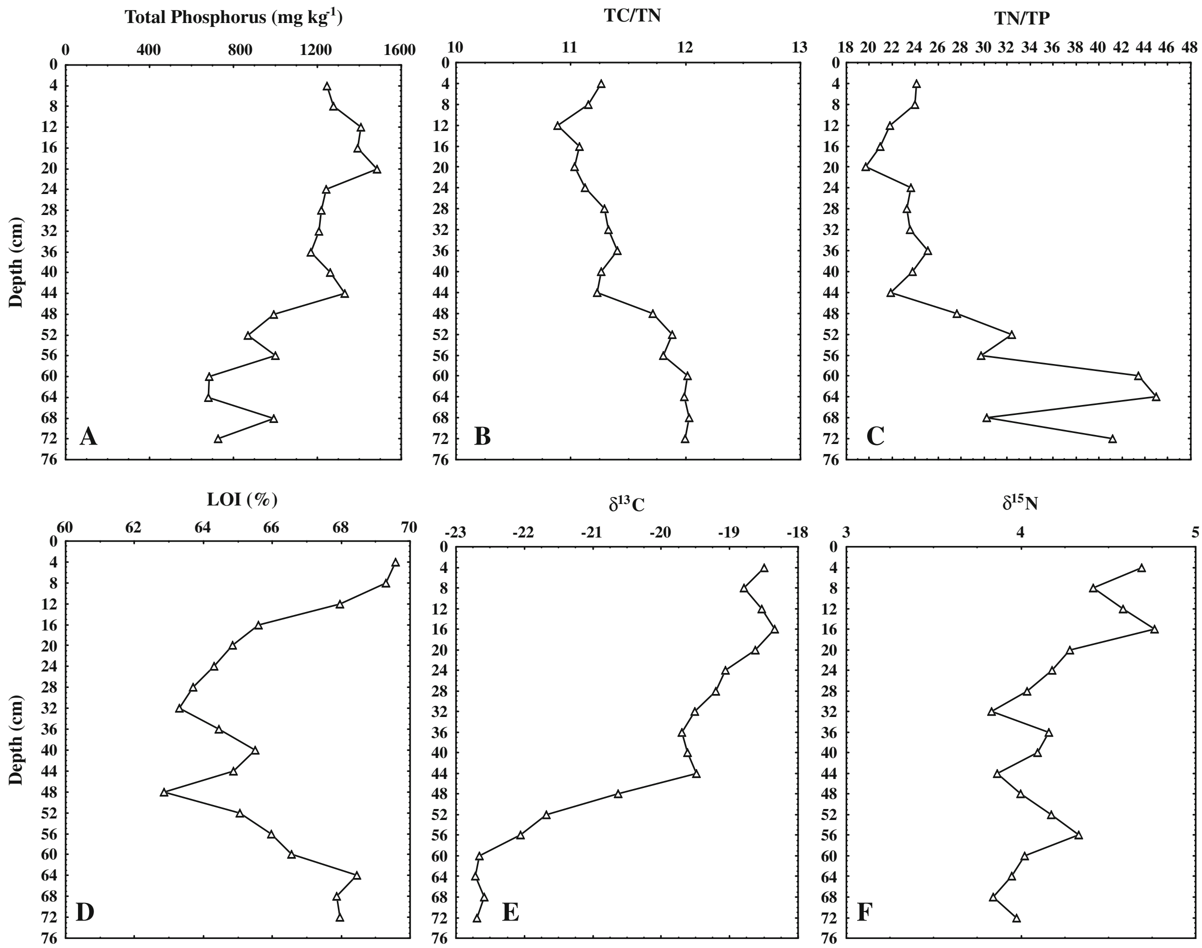


**Fig. 4** Lake Apopka sediment depth profile of: **a** total phosphorus, **b** TC:TN ratio, **c** TN:TP ratio, **d** organic matter content (LOI), **e** $\delta^{13}$C of sediment organic carbon and **f** sediment $\delta^{15}$N

−23‰ in subsurface sediments to −18‰ in surface sediments (Fig. 4e). Nitrogen isotope values also display an increase upcore, from 3.9‰ (lower depths) to 4.7‰ (surface sediments) (Fig. 4f).

## Discussion

### Lake Annie

Stratigraphic fluctuations in the $\delta^{13}$C and $\delta^{15}$N values of Lake Annie sediment OM probably reflect a combination of factors, including a shift in relative contribution of autochthonous/allochthonous OM, changing autochthonous primary productivity, and relative microbial biomass and activity (Torres et al. 2011). Small, oligotrophic lakes might be expected to have relatively high proportions of allochthonous C contribution to sediment OM (Gu et al. 1996). Terrestrial $C_3$ plants discriminate against $^{13}$C, and organic matter derived from these plants typically has $\delta^{13}$C values between −27 and −29‰ (Meyers 1997). Hammarlund et al. (1997) related progressive depletion of $^{13}$C in Lake Tibetanus (Sweden) to increases in the input of OM from surrounding vegetation. Jonsson et al. (2001) reported negative $\delta^{13}$C values of dissolved C in humic Lake Örträsket, Sweden, resulting from the mineralization of allochthonous OM. Also, phytoplankton discriminate against $^{13}$C in the water column when $CO_2$ concentration is high, which should be the case in this low-pH lake. Consequently, autochthonous OM in Lake Annie might also be expected to show low $\delta^{13}$C values.

The heterotrophic microbial community can also contribute to low $\delta^{13}$C. Heterotrophic uptake of DOC preserves the C isotope signature of the source, and biomass associated with chemoautotrophic and methanotrophic microorganisms is thus generally depleted in $^{13}C$ (Kankaala et al. 2006). An isotope study on sediments from eutrophic Lake Mendota, Wisconsin illustrated that mineralization of C by the heterotrophic microbial community, associated with expansion of anoxic conditions in the water column, led to sediment OM with low $\delta^{13}C$ values (Hollander and Smith 2001). Both seasonal and long-term increases in the contribution of depleted microbial biomass to sediments caused lower $\delta^{13}C$ values (Hollander and Smith 2001). Lehman et al. (2002) reported that anaerobic decomposition in Lake Lugano, on the Swiss-Italian border, led to $^{13}C$-depleted OM of sinking particles and sediments. Terranes and Bernasconi (2005) linked the $\delta^{13}C$ of sediment OM in Lake Baldeggersee, Switzerland to the relative inputs of eukaryotic biomass enriched in $^{13}C$, and to inputs of $^{13}C$-depleted microbial biomass produced in anoxic bottom waters. In Lake Annie, the thermocline has been moving to shallower depths, i.e. higher in the water column during thermal stratification, with anoxia and sulfate reduction occurring below 5 m depth (Gaiser et al. 2009). The increasing volume of anoxic bottom water probably led to anaerobic decomposition of already $^{13}C$-depleted suspended OM, resulting in deposition and preservation of undecomposed OM.

Similar processes affect N isotope signatures in Lake Annie. Plants discriminate against $^{15}N$ during inorganic N uptake (Inglett and Reddy 2006). Allochthonous OM derived from $C_3$ terrestrial plants generally has a $\delta^{15}N$ value of about +0.4‰ (Peterson and Howarth 1987). Autochthonous OM in aquatic ecosystems also typically has higher $\delta^{15}N$ signatures, whereas N-fixing algae possess values near that of atmospheric $N_2$, i.e. 0‰ (Peterson and Howarth 1987). Several other microorganisms fix nitrogen, including aerobic and anaerobic heterotrophic bacteria, methane-oxidizing bacteria, and sulfate reducers. N-fixing algae have not been detected in Lake Annie (E. Gaiser pers. commun.), however, $N_2$-fixation may occur in the heterotrophic microbial community.

High N availability in the Lake Annie water column and sediments (Torres 2007) can lead to autochthonous OM with low $\delta^{15}N$, as high N concentrations allow greater discrimination by algae against $^{15}N$ (Fogel and Cifuentes 1993). For this reason, it is difficult to determine with certainty the main factors that influence the C and N isotope signatures of Lake Annie sediment OM. For instance, allochthonous particulate and dissolved OM with relatively low $\delta^{13}C$ may be a major source of C in the lake. The microbial community that mineralizes and utilizes this C will have $^{13}C$-depleted biomass. Isotopically-depleted end products, such as $CO_2$ and $NH_4^+$, which result from heterotrophic metabolism, will be utilized by primary producers that display isotopically-depleted autochthonous OM. Surface enrichment of TP in sediments suggests that external P input occurred in the lake. Lake water quality data, however, show oligotrophic to mestrophic conditions. It is also likely that some dissolved P may have mobilized from subsurface sediments and precipitated with oxidized iron oxides. A more detailed study of $\delta^{13}C$ and $\delta^{15}N$ in several compartments (e.g. DIC, DOC, nitrate, ammonia, phytoplankton biomass, bacteria biomass) may elucidate the principal processes that shape the isotopic signature of Lake Annie sediments.

## Lake Okeechobee

High TC:TN values in the middle section of the sediment core probably indicate a large contribution from allochthonous OM, or perhaps loss of N through mineralization. Low TC:TN values in recent deposits probably reflect a greater relative contribution from phytoplankton. The concurrent increase in total P and decline in TC:TN suggest recent eutrophication and greater primary production in the lake, fueled by greater P input. TN:TP shows a general decrease from the bottom of the sediment core to the surface, reflecting more rapid increase of TP relative to TN concentration (Fig. 3c). A similar trend was reported by Engstrom et al. (2006) in sediment cores from the mud zone of Lake Okeechobee and was attributed to increasing TP content of uppermost sediments, as a consequence of eutrophication.

The $\delta^{13}C$ sediment profile shows a pattern similar to that for TC:TN (Fig. 3b, e). Similar patterns, i.e. lower $\delta^{13}C$ and higher $\delta^{15}N$, were reported by Rosenmeier et al. (2004) in a study of recent eutrophication of Lake Petén Itzá, Guatemala, where changes were related to sewage input with depleted $^{13}C$ and enriched $^{15}N$, and increased presence of cyanobacteria. Engstrom et al. (2006) also found higher $\delta^{15}N$ values (1‰) in recent deposits from

Okeechobee's mud zone, but did not discuss the mechanisms responsible. Stratigraphic changes in $\delta^{13}C$ and $\delta^{15}N$ in the mud zone were probably controlled by the nature of autochthonous OM, availability of C and N, and varying intensities of mineralization. Lake Okeechobee mud zone sediments are probably C- and N-limited, and N demand is high in these sediments (Torres 2007). In the mud zone of Lake Okeechobee, high dissolved OM and abundant suspended material in the water column make light the limiting factor for the phytoplankton community during most of the year (Aldridge et al. 1995). During summer months, light limitation is relaxed and N becomes the limiting factor for the phytoplankton community (Aldridge et al. 1995). The $\delta^{15}N$ of OM in sediments of eutrophic and hypereutrophic lakes can be influenced by cyanobacterial $N_2$-fixation (Gu et al. 1996; Rosenmeier et al. 2004), however non-$N_2$-fixing cyanobacteria typically dominate the phytoplankton community and the $N_2$ fixation rate is low in the central area of Lake Okeechobee (Cichra et al. 1995; Gu et al. 1997). Under non-$N_2$ fixing conditions, N limitation can lead to autochthonous OM with higher $\delta^{15}N$, as algae discrimination against $^{15}N$ diminishes (Meyers 1997; Peterson and Howarth 1987).

Some studies indicate that the isotopic signature of OM is resistant to alteration during water-column or post-burial diagenesis (Meyers and Eadie 1993; Hodell and Schelske 1998; Terranes and Bernasconi 2000). Other studies, however, have shown that selective degradation of OM fractions alters the isotopic signature (Bernasconi et al. 1997; Meyers 1997; Lehman et al. 2002, 2004). Labile organic compounds including carbohydrates, proteins and amino acids are generally more enriched in $^{13}C$, while lipids and cellulose are isotopically lighter (Meyers 1997). Selective loss of "heavy" amino acids, proteins and carbohydrates, which are particularly susceptible to microbial degradation, leaves residual (substrate) OM isotopically lighter, with respect to $\delta^{13}C$, than the original material (Hedges et al. 1988).

Loss of compounds that are relatively rich in $^{15}N$ (e.g. amino acids) can also occur, lowering the $\delta^{15}N$ in residual OM. Nevertheless, decomposition of OM is generally thought to increase $\delta^{15}N$ through preferential loss of $^{14}N$. Bernasconi et al. (1997) reported shifts to lower $\delta^{13}C$ and higher $\delta^{15}N$ of sinking OM in Lake Lugano, which they attributed to selective removal of C and N compounds during mineralization. Additionally, isotopic analysis of sediment in Lake Lugano indicates a decline in $\delta^{13}C$ during early sediment diagenesis (Lehman et al. 2002). In the Lake Okeechobee mud zone, several factors probably influence the $\delta^{13}C$ and $\delta^{15}N$ values in the OM of sediments. They include the nature of the phytoplankton community, N limitation in the water column, high demand for C and N in sediments, and selective mineralization of OM.

Lake Apopka

Nitrogen availability is high in Lake Apopka sediments (Torres 2007). In Lake Apopka sediments, nitrification is high in surface sediments where aerobic conditions prevail, and dissimilatory $NO_3^-$ reduction to $NH_4^+$ is high in anaerobic sediments when the ratio of C/electron acceptors is high (D'Angelo and Reddy 1993). Among the lakes, Lake Apopka has the highest $\delta^{13}C$ values and showed the greatest increase in values through time. In a study of 83 Florida lakes that ranged in trophic state, Lake Apopka plankton also had the highest $\delta^{13}C$ (Gu et al. 1996). Gu et al. (2004) found evidence for extreme $^{13}C$ enrichment of DIC in the water column and sediment pore water of this shallow polymictic, hypereutrophic lake. Greater $\delta^{13}C$ towards the surface probably indicates increased primary productivity, reflecting recent eutrophication (Brenner et al. 1999).

The C isotope signature of autochthonous OM is influenced by the $\delta^{13}C$ of the dissolved inorganic C pool in lake water. Hodell and Schelske (1998) related the seasonal pattern of $\delta^{13}C_{org}$ in Lake Ontario to seasonality of primary productivity. Gu et al. (2006) reported that $^{13}C$ enrichment of particulate OM in Lake Wauberg (Florida) resulted from reduced isotopic fractionation due to C-limitation and use of inorganic $^{13}C$ for photosynthesis. Lehman et al. (2004) concluded that the most important process controlling the C-isotopic signature of suspended particulate OM in Lake Lugano is the concentration of $CO_2$ in surface water, which is a function of phytoplankton photosynthesis. Algae fractionate against $^{13}C$, so autochthonous OM is depleted in $^{13}C$ relative to the DIC pool. During periods of high primary productivity, however, this fractionation diminishes and more $^{13}C$ is incorporated into primary producer biomass (Mizutani and Wada 1982).

Hypereutrophic lakes with high rates of primary productivity have $^{13}C$-enriched $CO_2$ (aq) in the water column as a consequence of selective uptake of lighter $^{12}C$ during photosynthesis. Moreover, in alkaline waters bicarbonate ($HCO_3^-$) is the dominant form of inorganic C, and is ~8‰ heavier than C in dissolved $CO_2$ (Fogel et al. 1992). High demand for inorganic C and low free $CO_2$ leads to utilization of $HCO_3^-$ as a carbon source, resulting in higher $\delta^{13}C$ values of fixed OM (Goericke et al. 1994). Gu et al. (2004) showed that high $\delta^{13}C$ DIC in the water column was a result of isotopic fractionation during methanogenesis in the sediments. Methanogenesis produces $^{13}C$-rich $CO_2$ and $^{13}C$-poor methane ($CH_4$) (Games and Hayes 1976). The Lake Apopka water column has low $CO_2$ partial pressure, high pH, and high buffering capacity. Consequently, $^{13}C$-rich $CO_2$ is transferred from the sediments to the DIC of the water column (Gu et al. 2004). Lake Apopka sediments display high $CH_4$ production rates (Torres et al. 2011). Furthermore, most of the OM generated by primary productivity in this lake is deposited in its sediments (Gale and Reddy 1994). Primary productivity is dominated by cyanobacteria (*Synechococcus* sp., *Synechocystis* sp. and *Microcystis incerta*) (Carrick et al. 1993; Carrick and Schelske 1997). Cyanobacteria are capable of active $CO_2$ transport or utilizing $HCO_3^-$ (Espie et al. 1991), and both can result in higher $\delta^{13}C$ values in phytoplankton biomass. Jones et al. (2001) reported that high phytoplankton $\delta^{13}C$ in Loch Ness (Scotland) resulted from high $\delta^{13}C$ DIC. Similar results were found in urban Lake Jyväskylä (Finland), where high $\delta^{13}C$ DIC resulted in high $\delta^{13}C$ of phytoplankton and zooplankton biomass (Syväranta et al. 2006). High $\delta^{13}C$ DIC in the water column, with high demand for inorganic C due to high primary productivity, produces autochthonous OM with high $\delta^{13}C$, which is deposited in the sediments.

It is generally thought that eutrophic and hypereutrophic lakes have low $\delta^{15}N$ as a consequence of high rates of $N_2$ fixation (Fogel and Cifuentes 1993). We, however, observed $^{15}N$ enrichment in Lake Apopka sediments. High phytoplankton productivity reduces isotopic discrimination, causing high isotope values. Gu et al. (1996) also reported high $\delta^{15}N$ in Lake Apopka sediments. In Lake Apopka, N assimilated by phytoplankton is supplied primarily by transformation of organic N to $NH_4^+$ and then to $NO_3^-$ by nitrification (D'Angelo and Reddy 1993). Although the phytoplankton community is dominated (> 90%) by cyanobacteria (Carrick et al. 1993), $N_2$ fixation is relatively unimportant in N dynamics (Schelske et al. 1992). High $NO_3^-$ availability can also lead to autochthonous OM with low $\delta^{15}N$ values (Meyers 1997). If, however, N incorporation uses a significant amount of the lake's $NO_3^-$ pool, residual $NO_3^-$ is enriched, ultimately leading to an increase in the $\delta^{15}N$ of newly produced OM (Terranes and Bernasconi 2000; Syväranta et al. 2006). Jones et al. (2004) reported higher sediment $\delta^{15}N$ when inorganic N was low in the water column, reflecting reduced isotopic fractionation under N limitation. Nitrogen is the primary limiting nutrient in Lake Apopka, though co-limitation with P can occur (Aldridge et al. 1993). Periods of N limitation in the water column can lead to enrichment of autochthonous OM and stratigraphic variation in the $\delta^{15}N$ signature of sediment OM in Lake Apopka may indicate periods of N limitation.

Other mechanisms may also influence the $\delta^{15}N$ of Lake Apopka sediments. The N isotopic signature of sediment integrates multiple fractionation processes that occur in the sediment and water column (Lehman et al. 2004). Ammonium production via OM mineralization is high in these sediments (Torres 2007). Such mineralization processes can potentially lead to either higher isotope values in the remaining OM through preferential loss of isotopically lighter compounds (Bernasconi et al. 1997), or have little effect on the $\delta^{15}N$ of the original organic matter (Inglett et al. 2007). Moreover, denitrification discriminates against $^{15}N$, and increases in denitrification rates have been related to higher $\delta^{15}N$ signatures in sediments (Terranes and Bernasconi 2000; Savage et al. 2004). Thus, the N isotope signature in Lake Apopka sediments is generated by multiple factors, including the isotopic signature of autochthonous N sources, the primary producer community, and N-related processes in the water column and sediments.

When stable C and N isotope data ($\delta^{13}C$ and $\delta^{15}N$) were plotted against each other in "isotope space," there was fairly good separation among sediments from the three study lakes (Fig. 5). Oligo-mesotrophic Lake Annie has the lowest values for both $\delta^{13}C$ and $\delta^{15}N$, and displays no overlap with samples from Okeechobee or Apopka. Lake Okeechobee displays intermediate, distinct $\delta^{13}C$ values, but its $\delta^{15}N$ values overlap to some degree with samples from Lake Apopka. Lake Apopka displays the highest values with respect to both $\delta^{13}C$ and $\delta^{15}N$. All its $\delta^{13}C$ signatures are greater than values determined for

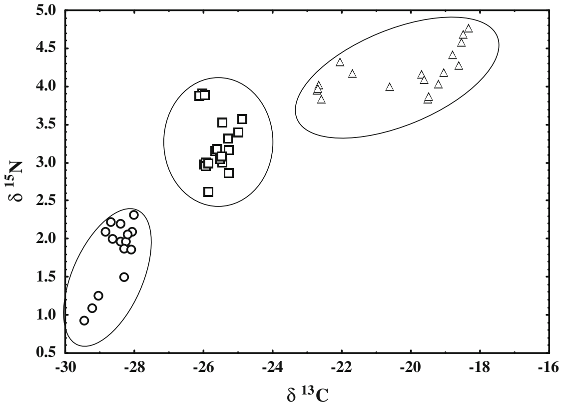


**Fig. 5** Carbon versus nitrogen isotope values of sediment core samples from Lake Annie (*circles*), Lake Okeechobee (*squares*), and Lake Apopka (*triangles*), Florida

sediment OM in the other two lakes, but its $\delta^{15}$N values show some overlap with Okeechobee $\delta^{15}$N values. High OM decomposition rates in shallow lakes (Apopka and Okeechobee) typically results in enriched $^{13}$C, compared to deep lakes (Annie), where OM is well preserved. In general, there is higher $\delta^{13}$C and $\delta^{15}$N with increasing trophic state. Enrichment in $^{13}$C with increasing lake productivity agrees with findings from other studies (Brenner et al. 1999). We found, however, that $\delta^{15}$N generally increases in the autochthonous OM as trophic state increases, in agreement with the findings of Gu (2009), but contrary to those of Brenner et al. (1999), who observed decreases in $\delta^{15}$N as lakes became more eutrophic.

## Conclusions

The $\delta^{13}$C and $\delta^{15}$N signatures of sediment OM in Lakes Annie, Okeechobee and Apopka result from multiple mechanisms, some of which are related to trophic state. Both carbon and nitrogen isotope signatures in Lake Annie sediments are relatively low compared to values in sediments from the other lakes, probably reflecting a combination of factors, such as shifting allochthonous/authochthonous OM input and high microbial biomass and activity in Lake Annie. In the Lake Okeechobee mud zone, $\delta^{13}$C values declined while $\delta^{15}$N values increased towards the sediment surface. Nevertheless, Lake Okeechobee displayed distinctive $\delta^{13}$C values, intermediate between those of Lake Annie and Lake Apopka. Only the topmost three samples in Okeechobee showed overlap with $\delta^{15}$N values from Lake Apopka. The Lake Okeechobee isotope signatures resulted from several factors, including the nature of the phytoplankton community, high demand for C and N in sediments, and selective mineralization of OM. In Lake Apopka, high $\delta^{13}$C DIC in the water column, with high demand for inorganic C as a consequence of high primary productivity, produced autochthonous OM with high $\delta^{13}$C. The high $\delta^{15}$N signature in Lake Apopka sediments was probably generated by a combination of factors, including the isotopic signature of autochthonous N sources, the primary producer community, and N-related processes in the water column and sediments. Water depth differences among the three study lakes may be a key factor influencing the isotope values in sediments, with better preservation of OM deposited in deep Lake Annie compared to shallow Lakes Apopka and Okeechobee. A more detailed study of $\delta^{13}$C and $\delta^{15}$N in various compartments, i.e. DIC, DOC, different N compounds, phytoplankton biomass, bacteria biomass, and other particulate OM in the water column and sediment, may lead to a better understanding of the major processes affecting the isotope signatures of OM in the sediments from these lakes.

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## References

Aldridge FJ, Schelske CL, Carrick HJ (1993) Nutrient limitation in a hypereutrophic Florida lake. Arch Hydrobiol 127:21–37

Aldridge FJ, Phlips EJ, Schelske CL (1995) The use of nutrient enrichment bioassays to test for spatial and temporal distribution of limiting factors affecting phytoplankton dynamics in Lake Okeechobee, Florida. Arch Hydrobiol 45:177–190

Anderson JM (1976) An ignition method for determination of total phosphorus in lake sediments. Water Res 10:329–331

Battoe LE (1985) Changes in vertical phytoplankton distribution in response to natural disturbance in a temperate and a subtropical lake. J Fresh Ecol 3:167–174

Bernasconi SM, Barbieri A, Simona M (1997) Carbon and nitrogen isotope variations in sedimenting organic matter in Lake Lugano. Limnol Oceanogr 42:1755–1765

Brenner M, Whitmore TJ, Curtis JH, Hodell DA, Schelske CL (1999) Stable isotope ($\delta^{13}$C and $\delta^{15}$N) signatures of sedimented organic matter as indicators of historic lake trophic state. J Paleolimnol 22:205–221

Burnett WC, Schaffer OA (1980) Effect of ocean dumping on $^{13}C/^{12}C$ ratios in marine sediments for the New York Bight. Est Coast Mar Sci 2:605–611

Carrick HJ, Schelske CL (1997) Have we overlooked the importance of small phytoplankton in productive waters? Limnol Oceanogr 42:1613–1621

Carrick HJ, Aldridge FJ, Schelske CL (1993) Wind influences phytoplankton biomass and composition in a shallow, productive lake. Limnol Oceanogr 38:1179–1192

Cichra MF, Badylak S, Henderson N, Rueter BH, Phlips EJ (1995) Phytoplankton structure in the open water zone of a shallow subtropical lake (Lake Okeechobee, Florida, USA). Arch Hydrobiol 45:157–175

Clugston JP (1963) Lake Apopka, Florida, a changing lake and its vegetation. Quart J Florida Acad Sci 26:168–174

Coveney MF (2010) Water quality changes in Lake Apopka, Florida—St. Johns River Water Management District's Restoration Program. Unpublished report. Environmental Sciences Division, St. Johns River Water Management District, Palatka, FL

D'Angelo EM, Reddy KR (1993) Ammonium oxidation and nitrate reduction in sediments of a hypereutrophic lake. Soil Sci Soc Am J 57:1156–1163

Engstrom DR, Schottler SP, Leavitt PR, Havens KE (2006) A reevaluation of the cultural eutrophication of Lake Okeechobee using mulitproxy sediment records. Ecol Appl 16:1194–1206

Espie GS, Miller AG, Kandasamy RA, Canvin DT (1991) Active $HCO_3^-$ transport in cyanobacteria. Can J Bot 69:936–944

Filley TR, Freeman KH, Bianchi TS, Baskaran M, Colarusso LA, Hatcher PG (2001) An isotopic biogeochemical assessment of shifts in organic matter input to Holocene sediments from Mud Lake, Florida. Org Geochem 32: 1153–1167

Fisher MM, Brenner M, Reddy KR (1992) A simple, inexpensive piston corer for collecting undisturbed sediment/water interface profiles. J Paleolimnol 7:157–161

Fisher MM, Reddy KR, James RT (2001) Long-term changes in the sediment chemistry of a large shallow subtropical lake. Lake Reserv Manage 17:217–232

Fogel ML, Cifuentes LA (1993) Isotope fractionation during primary production. In: Engel MH, Macko SA (eds) Organic geochemistry. Plenum Press, NY, pp 73–98

Fogel ML, Cifuentes LA, Velinsky DJ, Sharp JH (1992) Relationship of carbon availability in estuarine phytoplankton to isotopic composition. Mar Ecol Prog Ser 82:291–300

Gaiser EE, Deyrup ND, Bachmann RD, Battoe LE, Swain HM (2009) Multidecadal climate oscillations detected in a transparency record from a subtropical Florida lake. Limnol Oceanogr 54:2228–2232

Gale PM, Reddy KR (1994) Carbon flux between sediment and water column of a shallow subtropical, hypereutrophic lake. J Environ Qual 23:965–972

Games LM, Hayes JM (1976) On the mechanisms of $CO_2$ and $CH_4$ production in natural anaerobic environments. In: Nriagu JO (ed) Environmental biogeochemistry. Ann Arbor Sci, pp 51–73

Goericke R, Montoya JP, Fry B (1994) Physiology of isotopic fractionation in algae and cyanobacteria. In: Lajtha K, Michener RH (eds) Stable isotopes in ecology and environmental science. Blackwell, Oxford, pp 187–221

Gu B (2009) Variations and controls of nitrogen stable isotopes in particulate organic matter of lakes. Oecologia 160: 421–431

Gu B, Schelske CL, Brenner M (1996) Relationships between sediment and plankton isotope ($\delta^{13}C$ and $\delta^{15}N$) and primary productivity in Florida lakes. Can J Fish Aquat Sci 53:875–883

Gu B, Havens KE, Schelske CL, Rosen BH (1997) Uptake of dissolved nitrogen by phytoplankton in a eutrophic subtropical lake. J Plankton Res 19:759–770

Gu B, Schelske CL, Hodell DA (2004) Extreme $^{13}C$ enrichments in a shallow hypereutrophic lake: implications for carbon cycling. Limnol Oceanogr 49:1152–1159

Gu B, Chapman AD, Schelske CL (2006) Factors controlling seasonal variations in stable isotope composition of particulate matter in a soft water eutrophic lake. Limnol Oceanogr 51:2837–2848

Hammarlund D, Aravena R, Barnekow L, Buchardt B, Possnert G (1997) Multi-component carbon isotope evidence of early Holocene environmental change and carbon-flow pathways from a hard-water lake in northern Sweden. J Paleolimnol 18:219–233

Harris D, Horwath WR, van Kessel C (2001) Acid fumigation of soils to remove carbonates prior to total organic carbon or carbon-13 isotopic analysis. Soil Sci Soc Am J 65:1853–1856

Hedges JI, Clark WA, Cowie GL (1988) Fluxes and reactivities of organic matter in a coastal marine bay. Limnol Oceanogr 33:1137–1152

Hodell DA, Schelske CL (1998) Production, sedimentation, and isotopic composition of organic matter in Lake Ontario. Limnol Oceanogr 46:200–214

Hollander DJ, Smith MA (2001) Microbially mediated carbon cycling as a control on the $\delta^{13}C$ of sedimentary carbon in eutrophic Lake Mendota (USA): new models for interpreting isotopic excursions in the sedimentary record. Geochim Cosmochim Acta 65:4321–4377

Inglett PW, Reddy KR (2006) Investigating the use of macrophyte stable C and N isotopic ratios as indicators of wetland eutrophication: patterns in the P-affected everglades. Limnol Oceanogr 51:2380–2387

Inglett PW, Reddy KR, Newman S, Lorenzen B (2007) Increase soil stable nitrogen isotopic ratio following phosphorus enrichment: historical patterns and tests of two hypotheses in a phosphorus limited wetland. Oecologia 153:99–109

Jones RI, Grey LJ, Quarmby C, Sleep D (2001) Sources and fluxes of inorganic carbon in a deep, oligotrophic lake (Loch Ness, Scotland). Global Biogeochem Cycles 15: 382–391

Jones RI, King L, Dent M, Maberly SC, Gibson CE (2004) Nitrogen stable isotope ratios in surface sediments, epilithon, and macrophytes from upland lakes with differing nutrient status. Freshwater Biol 49:382–391

Jonsson A, Meili M, Bergström AB, Jansson M (2001) Whole-lake mineralization of allochthonous and autochthonous organic carbon in a large humic lake (Örträsket, N. Sweden). Limnol Oceanogr 46:1691–1700

Kankaala P, Taipale S, Grey J, Sonninen E, Arvola L, Jones RI (2006) Experimental $\delta^{13}C$ evidence for a contribution of methane to pelagic food webs in lakes. Limnol Oceanogr 51:2821–2827

Layne JN (1979) Natural features of the Lake Annie tract, Highlands County, Florida. Archbold Biological Station, FL

Lehman MF, Bernasconi SM, Barbieri A, Mckenzie JA (2002) Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis. Geochim Cosmochim Acta 66:3573–3584

Lehman MF, Bernasconi SM, Mckenzie JA, Barbieri A, Simona M, Veronesi M (2004) Seasonal variation of the $\delta^{13}$C and $\delta^{15}$N of particulate and dissolved carbon and nitrogen in Lake Lugano: constraints on biogeochemical cycling in a eutrophic lake. Limnol Oceanogr 49:415–429

Mccallister SL, Bauer E, Cherrier JE, Ducklow HW (2004) Assessing sources and ages of organic matter supporting river and estuarine bacterial production: a multiple-isotope ($\Delta^{14}$C, $\delta^{13}$C and $\delta^{15}$N) approach. Limnol Oceanogr 49: 1687–1702

Meyers PA (1997) Organic geochemical proxies of paleoceanographic, paleolimnologic and plaeoclimatic processes. Org Geochem 27:213–250

Meyers PA, Eadie B (1993) Sources, degradation and recycling of organic matter associated with sinking particles in Lake Michigan. Org Geochem 20:47–56

Mizutani M, Wada H (1982) Effect of high atmospheric $CO_2$ concentrations on $\delta^{13}$C of algae. Origins Life Evol B 12: 377–390

Peterson BJ, Howarth RW (1987) Sulfur, carbon, and nitrogen isotopes used to trace organic matter flow in the salt-marsh estuaries of Sapelo Island, Georgia. Limnol Oceanogr 32: 1195–1213

Reddy KR, Graetz DA (1991) Internal nutrient budget for Lake Apopka. Special Publ. SJ91-SP6. St Johns River Water Mgt District. Palatka, Florida

Rosenmeier MF, Brenner M, Kenney W, Whitmore TJ, Taylor CM (2004) Recent eutrophication in the southern basin of Lake Petén Itzá, Guatemala: human impact on a large tropical lake. J Paleolimnol 511:161–172

Savage C, Leavitt PR, Elmgren R (2004) Distribution and retention of effluent nitrogen in surface sediments of a coastal bay. Limnol Oceanogr 49:1503–1511

Schelske CL, Aldridge FJ, Carrick HJ (1992) Phytoplankton-nutrient interactions in Lake Apopka. Special Publ SJ92-SP9. St Johns River Water Mgt District. Palatka, Florida, 181 pp

Schelske CL, Lowe EF, Battoe LE, Brenner M, Coveney MF, Kenney W (2005) Abrupt biological response to hydrologic and land-use changes in Lake Apopka, Florida, USA. Ambio 34:192–198

Schelske CL, Lowe EF, Kenney WF, Battoe LE, Brenner M, Coveney MF (2010) How anthropogenic darkening of Lake Apopka induced benthic light limitation and forced the shift from macrophyte to phytoplankton dominance. Limnol and Oceanogr 55:1201–1212

Smeltzer E, Swain EB (1985) Answering lake management questions with paleolimnology. In: Lake and reservoir management—practical applications. Proceedings of the 4th annual conference and international symposium. North America Lake Management Society, pp 268–274

Syväranta J, Hämäläinen H, Jones RI (2006) Within-lake variability in carbon and nitrogen stable isotope signatures. Freshwater Biol 51:1090–1102

Terranes JL, Bernasconi SM (2000) The record of nitrate utilization and productivity limitation provided by $\delta^{15}$N values in lake organic matter—a study of sediment trap and core sediments from Baldeggersee, Switzerland. Limnol Oceanogr 45:801–813

Terranes JL, Bernasconi SM (2005) Factors controlling $\delta^{13}$C values of sedimentary carbon in hyertrophic Baldeggersee, Switzerland, and implications for interpretating isotope excursion in lake sedimentary records. Limnol Oceanogr 50:914–922

Torres IC (2007) Linkage between biogeochemical properties and microbial community in lakes sediment: biotic control of organic phosphorus dynamics. PhD dissertation, University of Florida, Gainesville, FL

Torres IC, Inglett KS, Reddy KR (2011) Heterotrophic microbial activity in lake sediments: effects of organic electron donors. Biogeochemistry 104:165–181