ORIGINAL PAPER

Recent trophic state changes of selected Florida lakes inferred from bulk sediment geochemical variables and biomarkers

T. E. Arnold · M. Brenner · W. F. Kenney · T. S. Bianchi

Abstract Short sediment cores (80–100 cm) from three Florida (USA) lakes (Sheelar, Wauberg, and Apopka) that range in trophic status, were analyzed for total organic carbon (TOC), total nitrogen, stable isotopes of organic carbon ($\delta^{13}C_{TOC}$) and biomarkers (n-alkanes and fatty acids), to identify the sources of organic matter in the lake deposits, and to link changes in primary productivity to anthropogenic activities during the last $\sim$ 150 years. Relatively small (0.07 km^2), ultra-oligotrophic Lake Sheelar is located in a state park, and sediment analyses indicate stable trophic status in the water body since at least the middle of the nineteenth century. Algal biomarkers are in low abundance throughout the core and terrestrial lipids and $\delta^{13}C_{TOC}$ values suggest that vascular plants were the primary source of TOC to the lake sediments during the period of record. In larger, eutrophic Lakes Wauberg (1.5 km^2) and Apopka (125 km^2), algal-derived biomarkers increase in recent sediments, whereas $\delta^{13}C_{TOC}$ values and concentrations of terrestrial biomarkers decrease toward the sediment surface. Increasing dominance through time of autochthonous carbon sources in the Lake Wauberg and Apopka sediment records coincides with specific anthropogenic activities in the respective watersheds. Submersed macrophytes in Lake Wauberg were replaced by algal communities in the mid-1980s, following expansion of residential development in the watershed. Biomarker data from the Lake Apopka core show there was an abrupt transition in the lake in the late 1940s, from domination by vascular plants to domination by algae, which has been documented by other paleolimnological studies that used alternative trophic state indicators. The trophic state shift in Lake Apopka corresponds to a period of increased nutrient input to the lake, associated with extensive farming along the north shore. Florida lakes have experienced different trophic state trajectories over the last $\sim$ 150 years, driven by specific human activities in their respective watersheds.

Keywords Eutrophication · Lipid biomarkers · Nutrients · Organic matter · Carbon isotopes · Sediments · Florida lakes

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Introduction

There are nearly 8000 lakes in the state of Florida (USA), with surface area > 10 ha. Most are relatively shallow dissolution features, with mean depth < 5 m, and maximum depth < 20 m (Brenner et al. 1990).

From a geologic perspective, these lakes are relatively recent features on the landscape. Most filled with water and began to accumulate lacustrine sediment in the early Holocene (by 8000 BP; Donar et al. 2009; Kenney et al. 2016), as the shallow water table rose, and climate became wetter (Watts 1980). Florida lakes span the entire trophic state continuum, from ultra-oligotrophic in the quartz sands of the Lake Wales Ridge and Trail Ridge, to hyper-eutrophic in some lower-lying urbanized and agricultural areas. Furthermore, many naturally eutrophic lakes are located in regions underlain by deposits of the phosphorus-rich Hawthorn Group. The trophic status of lakes in Florida is strongly correlated with the local geology, and water bodies in close proximity to the Hawthorn may have a long history of eutrophic conditions (Brenner et al. 1999).

Consequences of eutrophic conditions in fresh water bodies, whether caused by natural or anthropogenic factors, have been well documented since the early twentieth century (Hasler 1947). Many recent studies have established the strong correlation between excessive nutrient loading, primarily of nitrogen and phosphorus, and harmful algal blooms (Correll 1998; Anderson et al. 2002), fish kills (Landsberg et al. 2009), and reductions in biological diversity (Craft et al. 1995; Craft and Richardson 1997). A recent analysis of surface water quality in Florida classified 8% of rivers and streams, 26% of lakes, and 21% of estuaries in the state as impaired because of excessive nitrogen and/or phosphorus concentrations (Florida Department of Environmental Protection 2008).

Lake sediments are natural repositories for organic matter derived from aquatic (autochthonous) and terrestrial (allochthonous) primary and secondary productivity, and thus serve as archives of past changes in the lake water column and surrounding watershed. In Florida, paleolimnological studies have been undertaken to track past changes in lacustrine productivity (Riedinger-Whitmore et al. 2005; Kenney et al. 2014; Arnold et al. 2018). Element concentrations in dated sediment cores, including N, P, C and Si, have been used to infer temporal trends in eutrophication (Bianchi and Canuel 2011). Stable isotope ($\delta^{13}C$ and $\delta^{15}N$) measurements on bulk organic matter (Brenner et al. 1999; Torres et al. 2012) and photosynthetic pigments in sediments (Waters et al. 2015) have also been employed to reconstruct past

lacustrine trophic status and identify the primary producer communities.

Most previous work on eutrophication in Florida lakes relied on analysis of bulk sediment or bulk organic matter, which limited the ability to identify the source(s) of the analyzed material. Even if lipid biomarkers are assayed, such molecules represent only a small fraction of the total organic matter preserved within the lake. Thus, the identification of organic matter sources in sediments, as well as the determination of biogeochemical processes that occur in the water column and sediments, remain challenges for paleolimnologists. Combined use of bulk sediment and biomarker data, however, can help address questions about such processes, as well as specific questions about the sources of these elements to the overall organic matter pool. The three study lakes span different trophic states: oligotrophic (Sheelar), eutrophic (Wauberg), and hyper-eutrophic (Apopka). Wauberg and Apopka are surrounded by residential housing and agricultural fields, respectively, while Sheelar is relatively isolated in a state park. We hypothesize that lakes in areas of human activities, will record anthropogenic impacts in their sediment around the time when these activities commenced.

The primary goals of this paleolimnological study were to: (1) identify the relative importance of multiple source(s) of organic matter in the sediment of three subtropical Florida lakes with different trophic state (2) evaluate recent changes in trophic state of the water bodies, and (3) better understand recent human impacts on these aquatic ecosystems. We used a multi-biomarker approach that included *n*-alkanes and fatty acids, as well as bulk sediment isotope analyses, to examine recent changes in autochthonous and allochthonous organic carbon inputs to the three lakes. As a secondary goal, we compare the relative utility of bulk and biomarker data in reconstructing the sources of organic carbon to lacustrine sediments.

Sources of *n*-alkyl lipids in lake sediment

The major sources of alkanes in lake sediments are algae, bacteria, submersed and emergent macrophytes, and woody terrestrial plants. Because each of these sources typically synthesizes unique alkane homologues, alkanes can be used to identify the source of organic matter in lake sediments. Algae and bacteria

primarily synthesize short-chain *n*-alkanes, including *n*-C_{17-19} (Cranwell et al. 1987). Macrophytes synthesize a broad range of *n*-alkanes, but *n*-C_{21-25} predominate among the submersed taxa (Ficken et al. 2000). Odd-numbered, long-chain hydrocarbons (*n*-C_{27-33}) are characteristic of higher terrestrial plants and are stable over the longest time periods (Muri and Wakeham 2006).

Acyclic hydrocarbons are "defunctionalized" lipids and are therefore least susceptible to postdepositional degradation (Meyers 2003). Studies on hydrocarbon preservation in lakes demonstrated that these compounds are stable over at least decadal time scales (Wakeham et al. 2004). Other studies have reported stability of hydrocarbons over much longer, i.e. geologic timescales (Castañeda and Schouten 2011). This does not imply that *n*-alkanes are immune from decomposition/alteration, as biodegradation does occur in both aerobic and anaerobic environments, and preferentially targets low-molecular weight molecules (Wakeham et al. 2004; Bianchi and Canuel 2011).

Unlike hydrocarbons, fatty acids are more susceptible to diagenesis and alteration. A study from one lake demonstrated that fatty acids degraded twice as fast as alkanes in oxic sediments (Muri and Wakeham 2006). Another study of a 0.5-m-long lake sediment core showed that fatty acids were sensitive to postdepositional alteration, but hydrocarbons were not (Ho and Meyers 1994). Nevertheless, these lipids (fatty acids) have been used successfully to track sources of organic matter in many aquatic systems, as certain chain lengths are source specific regardless of post depositional alteration (Meyers 2003; Zhang et al. 2015). Freshwater algae and plankton synthesize C_{16} and C_{18} saturated fatty acids (chain lengths that are ubiquitous among higher lifeforms), as well as polyunsaturated ($C_{18:2}$ and $C_{18:3}$) and monounsaturated ($C_{16:1\omega7}$) varieties (Canuel 2001; Palomo and Canuel 2010). Odd-numbered (C_{15}, C_{17}), monosaturated ($C_{18:1\omega7}$ and $C_{18:1\omega9}$) and branched short-chain fatty acids (iso- and anteiso-C_{15}) are typically synthesized by bacteria, and even-numbered, long-chain fatty acids ($\geq C_{24}$) are from higher plants, including submersed and emergent macrophytes (Palomo and Canuel 2010).

Ratios of long-chain-length to short-chain-length lipids can be used to assess the relative contributions of terrestrial and aquatic organic matter to the sediments (Meyers 2003). For fatty acids the terrestrial to aquatic ratio (TAR_{FA}), this is calculated as:

$$TAR_{FA} = (C_{24} + C_{26} + C_{28})/(C_{12} + C_{14} + C_{16}) \tag{1}$$

and for hydrocarbons (TAR_{HC}) as:

$$TAR_{HC} = (C_{27} + C_{29} + C_{31})/(C_{15} + C_{17} + C_{19}) \tag{2}$$

Furthermore, the proportional contribution of submersed aquatic vegetation, relative to emergent and terrestrial vegetation, P_{aq} (Ficken et al. 2000), is calculated as:

$$P_{aq} = (C_{23} + C_{25})/(C_{23} + C_{25} + C_{29} + C_{31}) \tag{3}$$

These equations are broadly applicable but must be used with caution because shorter-chain-length *n*-alkyl lipids are preferentially degraded and multiple plant types can produce lipids of identical structure.

Study sites

Lake Sheelar (29.8392° N, 81.9579° W) is a small (0.07 km^2), relatively deep (z_{max} = ∼ 21 m) lake in Mike Roess Goldhead Branch State Park, north of Keystone Heights, Florida (Fig. 1). It is underlain by quartz sands and is a poorly buffered system, with low pH (5.4), low conductivity (18 µS cm^{-1}), and low total alkalinity (0.8 mg L^{-1} as CaCO$_3$). It is also oligotrophic (mean total phosphorus [TP] = 4 µg L^{-1}, mean total nitrogen [TN] = 86 µg L^{-1}, mean chlorophyll a = 1.7 µg L^{-1}), and has high water transparency (mean Secchi depth = 7.5 m) (Florida Lakewatch 2003). The lake receives some hydrologic input from shallow groundwater seeps along its northwest shore.

Lake Wauberg (29.5298° N, 82.3031° W) is located south of Gainesville, Florida and is primarily surrounded by hardwood pine and oak forests. The lake has a surface area of 1.5 km^2, and is shallow, with a maximum depth of ∼ 3.7 m (Florida Lakewatch 2003). Wauberg receives hydrologic input mainly from groundwater and direct rainfall, and a small outflow discharges into Sawgrass Pond. Unlike Sheelar, Wauberg is eutrophic, with mean concentrations of total phosphorus = 112 µg L^{-1}, total nitrogen = 1670 µg L^{-1}, and chlorophyll a = 82.1 µg L^{-1}, and
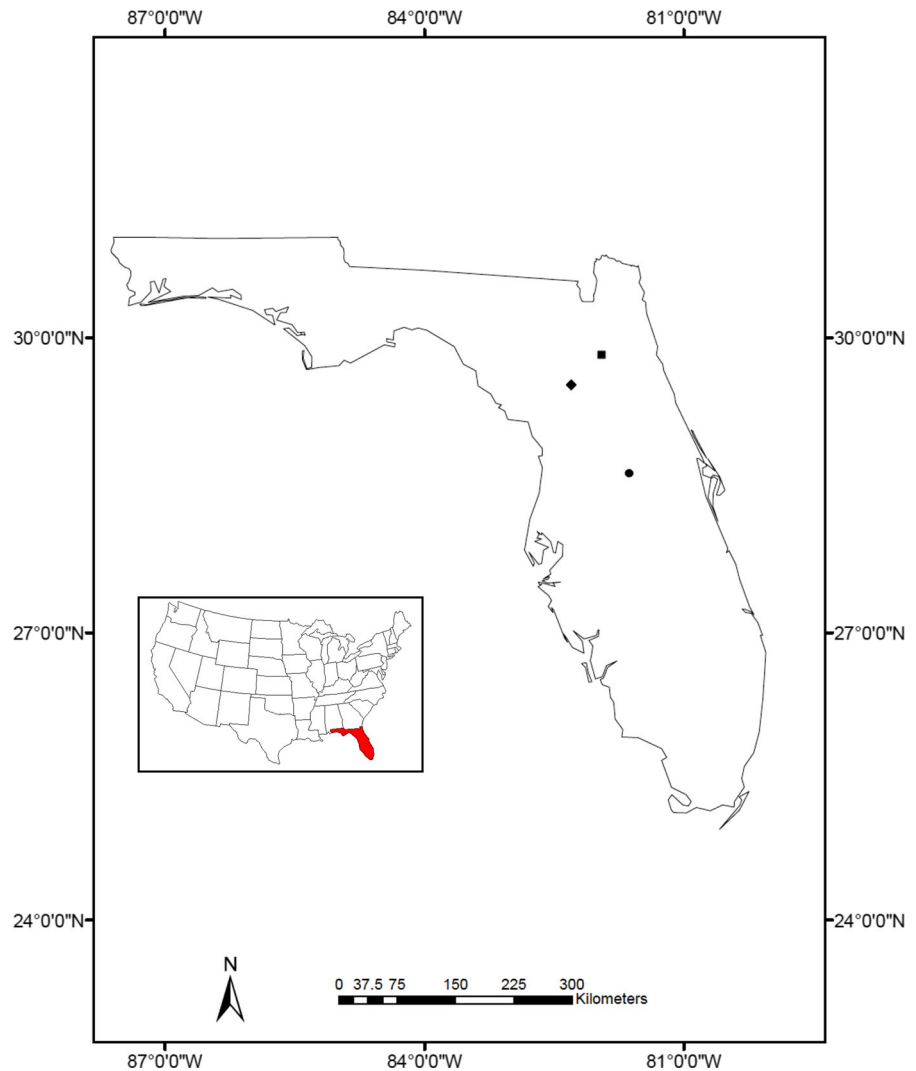
mean Secchi depth of 0.6 m (Florida Lakewatch 2003). Near-surface geology around the lake is phosphate-rich Hawthorn Formation, and high phosphorus concentrations have been measured in groundwater that enters the lake. Gu et al. (2006) reported that phytoplankton are the dominant primary producers in the lake, with limited macrophyte abundance, possibly a consequence of light limitation. The phytoplankton community has been a dominant feature of Lake Wauberg's flora since at least the 1930s (Carr 1934).

Lake Apopka, central Florida (28.6239° N, 81.6254° W), is the largest (124 km^2) and shallowest (z_{max} = 2.5 m) of the three study lakes. It is hypereutrophic, with a mean total phosphorus concentration of 192 µg L^{-1}, mean total nitrogen concentration of 3906 µg L^{-1}, mean chlorophyll a concentration of

96 µg L^{-1}, and mean Secchi depth of 0.3 m. Outflow from the lake flows into Beauclair Canal, which is hydrologically linked to other lakes in the Harris Chain of Lakes. Apopka shifted from a clear-water, macrophyte-dominated system to a phytoplankton-dominated water body in the middle of the twentieth century. This shift has been attributed to high phosphorus loading from muck farms that operated previously along the north shore (Schelske et al. 2005).

Materials and methods

We collected a sediment–water interface core from each of the three study lakes, using a piston corer designed to retrieve undisturbed sediments (Fisher

et al. 1992). In Lake Sheelar, 80 cm of sediment was retrieved, in Lake Wauberg, 90 cm, and in Lake Apopka, 100 cm. Cores were kept vertical and the poorly consolidated deposits were extruded upward and sampled into labeled containers at 2–4-cm intervals. Samples were frozen, freeze-dried, and ground with a mortar and pestle in preparation for geochemical analyses.

Cores were dated by ^{210}Pb, using gamma counting methods described by Schelske et al. (1994). Sediment ages were calculated using the constant rate of supply (CRS) model (Appleby and Oldfield 1983). Age errors were propagated using first-order approximations and calculated according to Binford (1990). [210]Pb dates could not be calculated for Lake Apopka, because the lake surface area was altered in the middle of the twentieth century, thus violating an assumption of the CRS model. A ^{210}Pb-based age model developed by Schelske (1997) for a core from the same site, however, showed that unsupported ^{210}Pb activity (dpm g^{-1}) was negligible below 70 cm core depth, suggesting an age at that depth of $\sim$ 110 years, i.e. five ^{210}Pb half-lives.

Total carbon and total nitrogen (TN) were measured on a Carlo Erba NA1500 CNS elemental analyzer. Inorganic carbon was measured on a UIC Coulometrics 5012 CO_2 coulometer coupled with an AutoMate automated carbonate preparation device (AutoMateFX.com). Total organic carbon (TOC) was calculated as the difference between total carbon and inorganic carbon. TOC:TN values are expressed on a molar basis. Dried sediment for $\delta^{13}C_{TOC}$ analyses was pretreated with 1 N HCl to remove inorganic carbon, and then measured on a Carlo Erba NA1500 CNS elemental analyzer interfaced with a Thermo Scientific Delta V Advantage isotope-ratio mass spectrometer. Isotope compositions were normalized to the VPDB scale, and reported in standard delta notation as follows:

$$\delta^{13}C = \left[\left(\left(^{13}C/^{12}C\right) \text{ sample}/\left(^{13}C/^{12}C\right) \text{ standard}\right) - 1 \right] \times 1000$$

(4)

Lipid extraction, purification, and quantification

Lipids were extracted from 1 g of freeze-dried sediment with an Accelerated Solvent Extractor ASE200 (Dionex), using 2:1 (v/v) dichloromethane (DCM):methanol through three extraction cycles at 10.3 MPa (1500 psi)

and 100 °C. Total lipid extracts (TLE) were concentrated under a gentle stream of nitrogen, and the neutral and acidic lipid fractions were separated with an aminopropyl solid phase extraction column. Neutral lipids were eluted from the column using 2:1 (v/v) DCM:IPA, and free fatty acids were eluted with 4% acetic acid in ethyl acetate. The acidic fraction was blown to dryness and derivatized with BF_3 in methanol and extracted again with DCM as fatty acid methyl-esters (FAMES). Neutral lipids were further separated, based on polarity, into compound classes, by column chromatography, using 5% deactivated silica gel, according to methods modified from Nichols (2011). Hydrocarbons were eluted from the silica gel column with 4.5 mL of 9:1 Hexane:DCM, and saturated hydrocarbons were separated from alkenes on 5% Ag-impregnated silica gel (w/w) with 4 mL of hexane and ethyl acetate, respectively. Branched and cyclic saturated hydrocarbons were isolated from n-alkanes with triple urea adduction.

Alkane and fatty acid concentrations were measured and identified on a Thermo Scientific Trace 1310 gas chromatograph with a Supelco Equity 5 column, interfaced to a Thermo Scientific TSQ 8000 triple quadrupole mass spectrometer with electron ionization. For the hydrocarbons, the inlet was operated in splitless mode at 280 °C. The column flow rate was set to 2.0 mL min^{-1} and the oven was programmed to an initial temperature of 60 °C and held for 1 min, then ramped to 320 °C at 6 °C min^{-1} and held for 20 min. Quantification was based on the calibration curves generated from the peak areas of external standards (C_7–C_{40}) with concentrations ranging from 5–250 μg mL^{-1}. Androstane was used as an internal standard, and recovery rates for n-alkanes were > 80%. For fatty acids, the split/splitless inlet was operated in split mode at 280 °C with a split ratio of 10:1. The column flow rate was 1.5 mL min^{-1} and the oven started at an initial temperature of 60 °C and was held for 1 min, followed by a ramp to 140 °C at 15 °C min^{-1}, and finally to 320 °C and held at that temperature for 20 min.

Results

Core chronologies

Sediment cores from Wauberg and Sheelar display low and relatively invariable [226]Ra concentrations,

with down-core activities in ^{226}Ra fluctuating by less than 3 dpm g^{-1} (Fig. 2). In both cores, total ^{210}Pb activities are higher than ^{226}Ra activities until an overlap occurs at ~ 100 cm in Wauberg and ~ 28 cm in Sheelar. The decrease ^{210}Pb activity represents the loss of unsupported, or excess, ^{210}Pb, and the overlap in the activities of ^{226}Ra and ^{210}Pb near the bottom of each core is the reestablishment of secular equilibrium between the two elements. A small ^{137}Cs peak occurs in Wauberg at ~ 1963, coinciding with the peak fallout of the radionuclide, however, no such peak is apparent in Sheelar. Over a century of deposition are represented in both cores: the ^{210}Pb date at 85–90 cm depth for Wauberg was ~ 1867 AD, and in Lake Sheelar, the ^{210}Pb date at 24 cm depth was 1886.

Bulk geochemistry

TOC, TOC/TN, and $\delta^{13}C_{TOC}$ are shown in Fig. 3. Highest average TOC values were found in Lake Wauberg sediments, followed by the sediments of Lake Apopka. Lowest average TOC values were measured in the Lake Sheelar core. Average TOC:TN was similar for the Lake Wauberg and Apopka cores, with values of 12.44 and 13.51, respectively, but was substantially higher in Sheelar (18.28). In Sheelar, the TOC:TN values decreased in the recently deposited sediments, from a maximum of 21.81 at 80 cm depth, to a minimum of 15.44 at 5 cm depth. Ranges of TOC:TN values are smaller in the Wauberg and Apopka cores, with values of 2.17 and 1.58, respectively. Mean $\delta^{13}C_{TOC}$ values in sediments of the three

lakes display an increase with greater trophic status, from − 29.11‰ (Sheelar), to − 22.82‰ (Wauberg), to − 20.32‰ (Apopka). The $\delta^{13}C_{TOC}$ values increase towards the top of the core in the Wauberg and Apopka sediments, whereas in the Sheelar core, $\delta^{13}C_{TOC}$ values remain relatively constant throughout.

Alkane concentrations

Average chain length (ACL), P_{aq}, and TAR_{HC} values for the Lake Sheelar, Wauberg and Apopka cores are displayed in Tables 1, 2 and 3, respectively. ACL calculations help identify any systematic or post-depositional changes in long chain n-alkanes, and were determined using the following equation:

$$
\begin{aligned}
ACL = & \left(25C_{25} + 27C_{27} + 29C_{29} + 31C_{31} \right. \\
& \left. + 33C_{33} + 35C_{35}\right)/\left(C_{25} + C_{27} + C_{29}\right) \\
& + C_{31} + C_{33} + C_{35}
\end{aligned}
$$
(5)

Average ACL values for all three lakes were similar (~ 28) and varied only slightly within each core, and all values were within the range calculated from modern tree species (Diefendorf et al. 2014). Average P_{aq} values for the three lakes were also relatively similar, ranging from 0.44 to 0.49. Average TAR_{HC} values in Lake Sheelar (39.41), however, were approximately fourfold and tenfold higher than TAR_{HC} values in Wauberg (10.98) and Apopka (3.49).

Alkanes were grouped by their most probable biological source: algae (n-C_{17-19}), macrophyte (n-C_{23-25}), and terrestrial (n-C_{27-31}). Representative

Fig. 2 Total ^{210}Pb, ^{226}Ra, and ^{137}Cs activities in the Wauberg and Sheelar sediment cores. Select dates are plotted to the left. Both cores show low variability in ^{226}Ra concentrations, and ^{210}Pb concentrations reach supported levels near the core-bottom
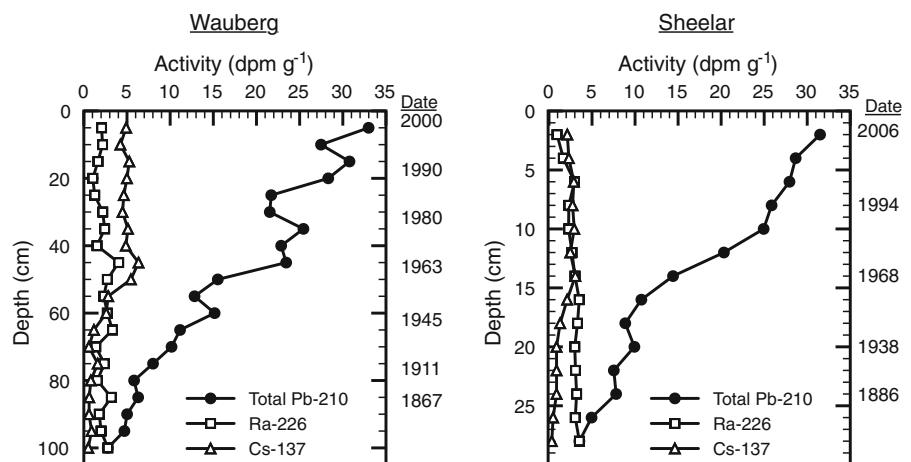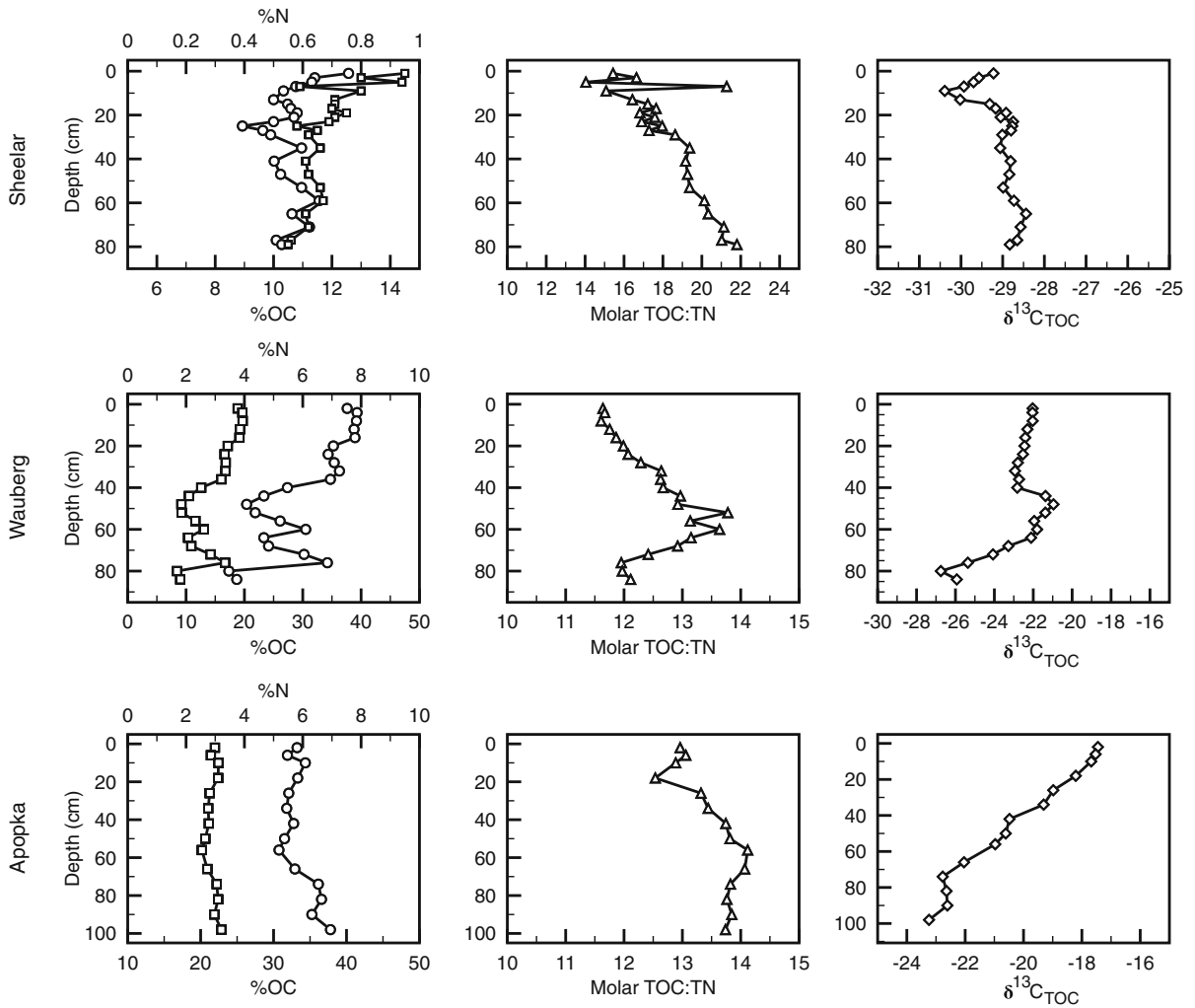
Fig. 3 Concentration of total carbon (TOC%, open circles), total nitrogen (TN%, open squares), molar TOC:TN ratio, and $\delta^{13}C_{TOC}$ versus depth in the sediment cores from Lakes Sheelar, Wauberg, and Apopka

homologues are shown in Fig. 4. In Sheelar, there was no discernible stratigraphic trend in the concentrations of *n*-alkanes among the three groups. Of note, however, are the low concentrations of algal-derived hydrocarbons, which never exceed 15 µg g^{-1} TOC throughout the core, and the high concentrations of terrestrial alkane *n*-C$_{29}$ throughout the entire core. In contrast to Sheelar, *n*-C$_{17}$ concentration in the Wauberg and Apopka cores increases by an order of magnitude at ~ 40 cm depth, reaching maximum concentrations in the upper 10 cm. This is the most abundant chain length in the top 20 cm of sediment of both lakes. The increasing trend in algal derived *n*-C$_{17}$ concentration in Wauberg and Apopka is

accompanied by a decrease in terrestrial-derived alkanes, by 119.3 µg g^{-1} TOC and 37.8 µg g^{-1} TOC, respectively.

Fatty acid concentrations

Fatty acids were grouped based on their primary source, in a manner similar to the *n*-alkanes. These data for the Sheelar, Wauberg and Apopka cores, along with TAR$_{FA}$ values for each lake, are displayed in Tables 1, 2 and 3, respectively. Terrestrial, long-chain fatty acids represent the sum of even-carbon fatty acids from C$_{24}$ to C$_{30}$. Algae-derived polyunsaturated fatty acids are the sum of C$_{18:2}$ and C$_{18:3}$.

Table 1 Lake Sheelar sediment core alkane and fatty acid data

Depth (cm)	ACL	P_{aq}	TAR_{HC}	LCFA	PUFA	BDFA	TAR_{FA}
2	28.81	0.36	88.06	5261.7	7.1	2262.0	0.53
8	28.31	0.51	21.61	7685.7	5.5	1299.6	1.08
16	28.13	0.53	17.37	8339.1	2.2	492.4	2.58
24	28.40	0.44	18.82	8570.7	1.7	410.9	3.31
34	28.14	0.50	21.10	8230.0	3.5	393.6	3.07
40	28.64	0.41	136.16	7785.5	1.9	316.7	3.32
46	28.31	0.47	18.22	5021.9	2.3	245.7	3.04
52	28.35	0.46	21.91	5207.1	2.0	268.5	3.26
58	28.42	0.44	24.97	4690.0	2.1	271.4	2.53
64	28.56	0.39	29.43	4871.1	1.5	236.2	2.96
70	28.63	0.38	42.66	5964.7	2.1	221.7	3.56
78	28.57	0.41	32.66	4571.0	0.9	153.5	4.90
Average	28.44	0.44	39.41	6349.9	2.7	547.7	2.84

Average chain length (ACL), submersed to emergent/terrestrial vegetation ratio (P_{aq}), ratio of long- to short-chain hydrocarbons (TAR_{HC}), sum of long-chain fatty acid (LCFA) concentrations ($\mu g \ g^{-1}$ OC), the sum of algal-derived polyunsaturated fatty acid (PUFA) concentrations ($\mu g \ g^{-1}$ OC), bacterial derived fatty acid (BDFA) concentrations ($\mu g \ g^{-1}$ OC) (BDFA), and the ratio of long- to short-chain fatty acids (TAR_{FA})

Table 2 Lake Wauberg alkane and fatty acid data

Depth (cm)	ACL	P_{aq}	TAR_{HC}	LCFA	PUFA	BDFA	TAR_{FA}
3	28.08	0.40	1.33	3149.7	10.5	1925.8	0.39
8	28.16	0.41	1.57	3588.6	20.9	1490.6	0.61
16	28.19	0.40	2.60	3581.5	5.6	1163.4	0.70
24	28.06	0.43	5.25	3885.9	2.5	851.4	0.91
32	28.21	0.40	7.38	3969.2	6.1	579.7	1.68
40	28.19	0.41	10.17	3929.5	0.7	257.8	2.76
48	28.17	0.44	8.24	2366.7	1.3	165.1	2.69
56	28.15	0.46	8.89	4154.4	0.9	169.1	4.31
64	28.05	0.48	13.65	5296.4	3.8	251.2	4.16
72	28.13	0.51	19.63	2395.4	0.6	100.4	5.11
80	28.21	0.41	27.10	4944.0	1.0	137.6	7.06
88	28.11	0.44	26.00	3321.3	0.8	192.8	3.64
Average	28.14	0.43	10.98	3715.2	4.5	607.1	2.84

See Table 1 for full description

Bacterial fatty acids are represented in this study by the following chain lengths: branched iso and anteiso-$C_{15:0}$, monounsaturated $C_{16:1\omega7}$, $C_{18:1\omega7}$, $C_{18:1\omega9}$, and the odd-carbon-number saturated fatty acids, $C_{15:0}$ and $C_{17:0}$.

Long-chain, saturated fatty acids dominated the record in all three lakes, with $C_{12:0}$, $C_{16:0}$, $C_{24:0}$, $C_{26:0}$, and $C_{28:0}$ being the most abundant homologues. Each of the lakes display more recent concentration increases in algae- and bacteria-derived fatty acids,

and to a lesser magnitude, decreases in long-chain fatty acid concentrations (Fig. 5). Of note are distinct patterns of bacteria-derived fatty acid abundances in the sediment records. In the three lakes, these fatty acids display similar concentration patterns to non-bacterial, short chain C_{16} and C_{18} fatty acids.

Table 3 Lake Apopka alkane and fatty acid data

Depth (cm)	ACL	P_{aq}	TAR_{HC}	LCFA	PUFA	BDFA	TAR_{FA}
2	28.14	0.48	0.75	2484.9	248.8	3639.9	0.29
8	28.08	0.47	0.82	1807.3	164.7	3147.2	0.23
16	28.08	0.49	1.46	3241.1	97.9	2190.9	0.42
26	28.06	0.49	2.62	4401.3	18.3	1636.5	0.66
34	28.06	0.51	3.14	4605.2	10.5	1379.1	0.78
42	27.99	0.50	5.10	4619.9	4.2	535.4	1.78
50	28.01	0.53	5.26	7142.1	3.3	413.3	3.03
58	27.97	0.50	4.32	6735.2	2.5	275.6	5.10
66	27.89	0.48	4.72	7073.5	4.0	206.4	7.07
74	27.91	0.48	4.60	6895.5	1.9	142.1	8.69
82	27.89	0.46	4.69	6870.4	1.5	132.7	9.40
90	27.89	0.46	4.41	5493.1	2.2	152.5	6.95
Average	28.00	0.49	3.49	5114.1	46.6	1154.3	3.70

See Table 1 for full description

Fig. 4 Concentrations of select *n*-alkane chain lengths versus depth in the Sheelar, Wauberg, and Apopka sediment cores. The chain lengths are assigned to the following biological sources: *n*-C_{17} (algae, squares), *n*-C_{23} (macrophytes, circles), *n*-C_{29} (woody terrestrial vegetation, triangles)
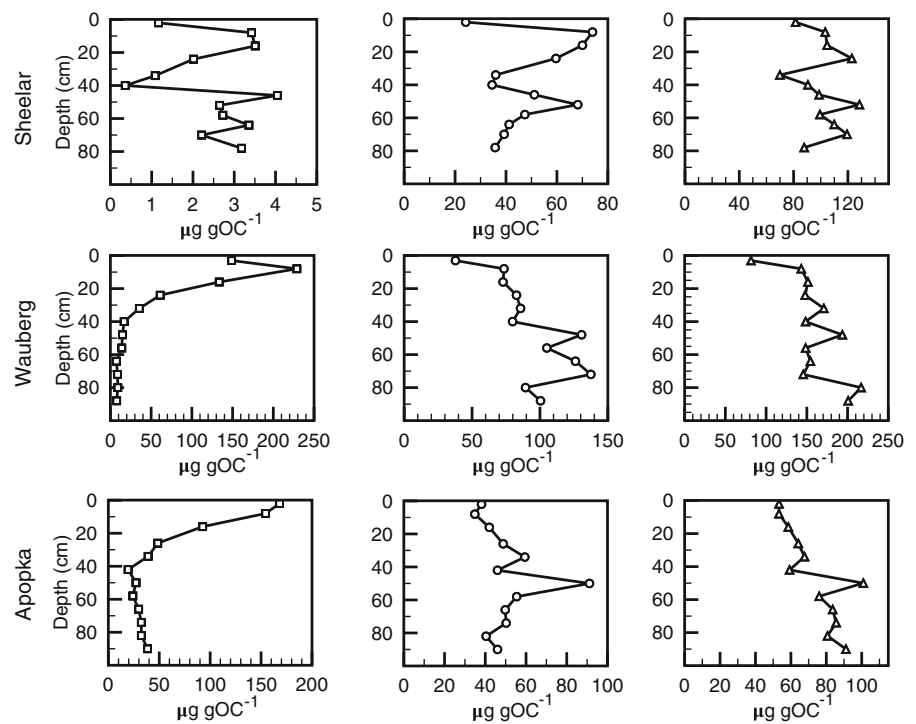
Discussion

Bulk geochemistry

The three lakes in this study can be assigned to trophic state categories using geochemical measures on the bulk sediment. The Sheelar core has the lowest TOC concentrations, highest TOC:TN values, and lowest $\delta^{13}C_{TOC}$ values throughout, whereas the Lake Apopka and Wauberg cores have higher OC levels, lower TOC:TN, and less negative $\delta^{13}C_{TOC}$ values. Values of these three variables in the Sheelar core are indicative of lower trophic status, and in Apopka and Wauberg of higher trophic state (Meyers 1997; Brenner et al. 1999). There are, however, limitations to using data from bulk sediment to infer trophic status. These become apparent when comparing temporal changes in sediment TOC:TN and $\delta^{13}C_{TOC}$ values. The Lake
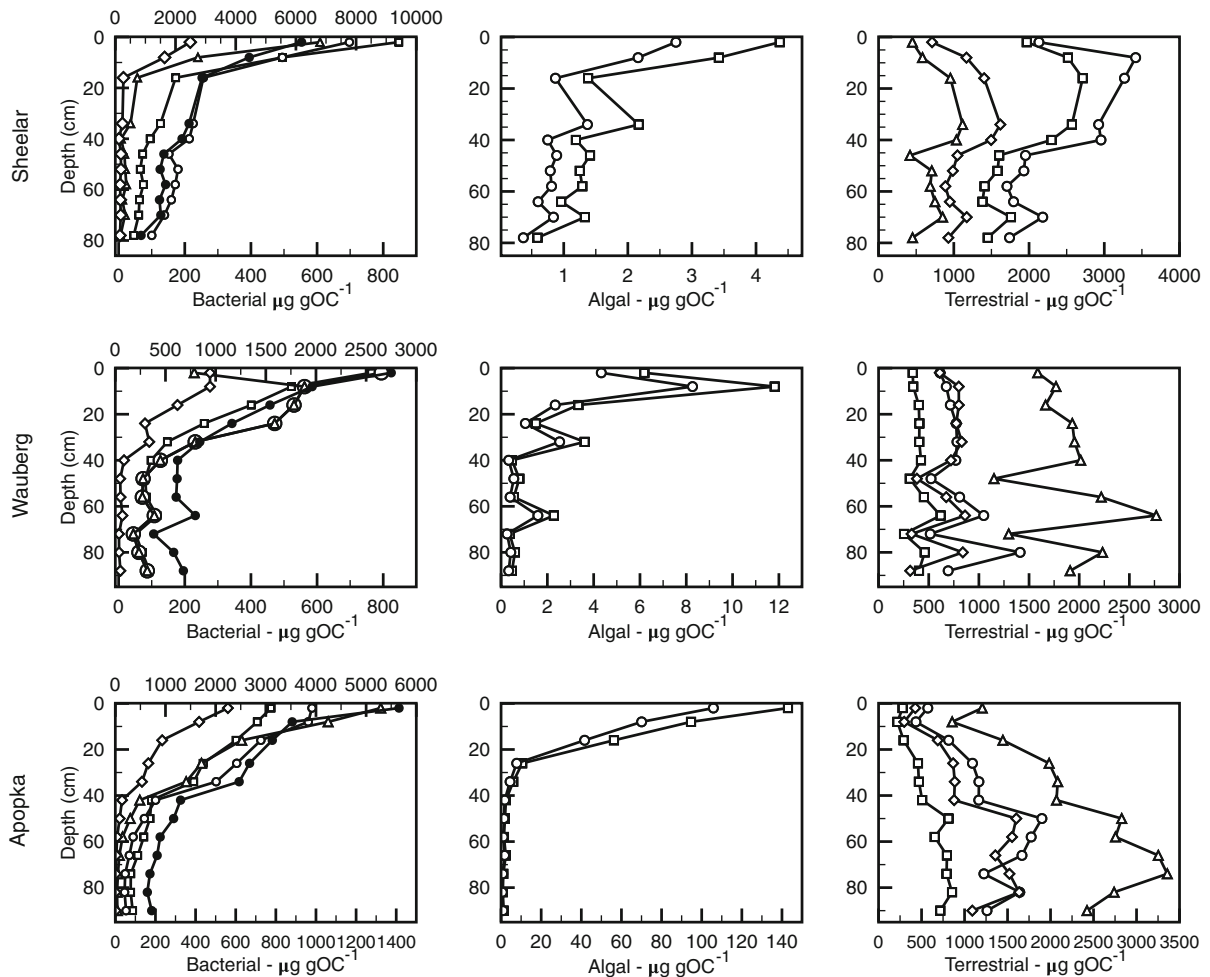
Fig. 5 Concentrations of select fatty acid chain lengths versus depth in the Lake Sheelar, Wauberg, and Apopka sediment cores. We grouped the bacteria-derived fatty acids together with other chain lengths based upon similar down-core concentration patterns. Bacterial fatty acids include saturated, branched *iso* and *anteiso*-$C_{15:0}$ (squares), $C_{15:0+17:0}$ (circles), $C_{18:1\omega9+18:1\omega7}$ (triangles), $C_{16:1\omega7}$ (diamonds), and $C_{16:0+18:0}$ (filled squares, plotted on the secondary x-axis). The algal fatty acids include $C_{18:2}$ (squares) and $C_{18:3}$ (circles). The terrestrial fatty acids include $C_{24:0}$ (square), $C_{26:0}$ (circle), $C_{28:0}$ (triangle), and $C_{30:0}$ (diamonds)

Sheelar, core exhibits the largest decrease in TOC:TN towards the top of the core, suggesting an increase in the relative contribution of algal organic matter to the sediment through time. Across the same depth interval, however, $\delta^{13}C_{TOC}$ values remain essentially unchanged, which implies no change in the dominant primary producers or primary productivity. Furthermore, the carbon isotope values in the sediments, which range from $-30.39‰$ to $-28.44‰$, are consistent with a primarily C_3, terrestrial carbon source (Peterson and Fry 1987; Magill et al. 2013). The decrease in TOC:TN near the top of the Sheelar core (Fig. 3) may reflect bacterially mediated

diagenesis in the sediments (Haglund et al. 2003). The stratigraphic distribution of TOC and TN would therefore be a reflection of bacterial activity, with lower values resulting from greater bacterial activity in near surface sediments. This hypothesis is further supported by the bacterially derived fatty acid data (Fig. 5) which shows reduced bacterial activity below 20 cm core depth.

In the Lake Apopka core, TOC:TN values decrease slightly near the top of the core, while $\delta^{13}C_{TOC}$ values increase substantially, from $-23.24‰$ to $-17.45‰$. A similar pattern occurs in Lake Wauberg, where $\delta^{13}C_{TOC}$ increases by nearly 4‰, from $-25.93‰$ to

− 22.03‰ and TOC:TN varies by < 2. Although the TOC:TN values and $\delta^{13}C$ values in Apopka and Wauberg both indicate primarily algal sources of organic carbon in the sediment (Filley et al. 2001), the small changes in TOC:TN fail to capture the increasing algal contributions and productivity indicated by increases in $\delta^{13}C$ values towards the top of the core. A possible explanation for this discrepancy may lie in the historic concentrations of algal and aquatic macrophyte communities. If substantial populations of both phytoplankton and submerged macrophytes with similar TOC:TN values (Bianchi and Canuel 2011) were already well established in both lakes, a further increase in trophic state and algal populations would cause an increase in $\delta^{13}C_{TOC}$ values, but not significantly affect TOC:TN ratios.

Using $\delta^{13}C_{TOC}$ values alone, we infer relatively stable, oligotrophic conditions in Lake Sheelar throughout the time period represented by the core, about 150 years. The ^{210}Pb date at 24 cm is AD 1886, indicating relatively low mean sedimentation rate and organic matter production, further confirming the historic oligotrophic status of the lake. Carbon isotope measures on a sediment core from Lake Annie, a similar oligotrophic lake in south-central Florida, also yielded low $\delta^{13}C_{TOC}$ values that indicated predominantly allochthonous organic matter contributions to the sediments (Torres et al. 2012). More recent increases in $\delta^{13}C_{TOC}$ values in the Wauberg and Apopka cores suggest the trophic status of both lakes increased over the time spans represented by the profiles. Towards the top of the core, $\delta^{13}C_{TOC}$ increases are probably associated with greater phytoplankton abundance and consequent higher rates of productivity, which results in rapid uptake of ^{12}C and reduced discrimination against ^{13}C, and/or active uptake of HCO_3^- (Brenner et al. 1999). Gu et al. (2006) found greater $\delta^{13}C$ values in water column particulate organic matter in Lake Wauberg during periods of high productivity and carbon limitation. In the Apopka core, both the mean $\delta^{13}C_{TOC}$ value and the magnitude of ^{13}C enrichment were greater than in the Wauberg core. Some of this enrichment was certainly a consequence of high $\delta^{13}C$ of dissolved inorganic carbon (DIC) in the lake. Carbon-13 enrichment of the DIC pool in Lake Apopka (average δ^{13} DIC = 9.0‰) was documented by Gu et al. (2004) and attributed to methanogenesis in the sediments. Methanogenesis produces isotopically depleted CH_4, and isotopically enriched CO_2 (Whiticar 1999). Subsequent utilization of this ^{13}C-enriched carbon source for photosynthesis by primary producers elevates their $\delta^{13}C$ values. Over time, as the lake becomes more productive and photosynthetic incorporation of carbon in ^{13}C-enriched CO_2 increases, the $\delta^{13}C$ value of the sedimented organic matter becomes greater.

Geochemical data on bulk sediment in the lake cores enabled us to conclude: (1) Lake Sheelar is and has been oligotrophic over the last ∼ 150 years, and its sediment carbon pool comes primarily from allochthonous sources, with a relatively small contribution from autochthonous inputs. TOC:TN values decrease near the top of the core, suggesting an increase in algal relative to terrestrial input, but $\delta^{13}C_{TOC}$ values remain within the terrestrial range throughout the entire core; (2) The Wauberg and Apopka cores both show evidence for recent increases in lake primary productivity and greater contributions of algal biomass to the sediments, as indicated by recent increases in $\delta^{13}C_{TOC}$ and decreases in TOC:TN values. The increase in $\delta^{13}C_{TOC}$ in both cores is likely a result of carbon limitation and/or uptake of HCO_3^-. In the Apopka core, sediment $\delta^{13}C_{TOC}$ values are very high because of methanogenesis, which results in ^{13}C-enriched DIC.

Alkyl lipids

Concentrations of *n*-alkanes in the Sheelar core suggest negligible change in organic matter sources through time. From the bottom to the top of the core, *n*-C_{17} concentrations remain low, while *n*-C_{23-25} and *n*-C_{27-31} concentrations, although variable, are the most abundant homologues. There is no evidence for a shift in trophic state in the hydrocarbon record, i.e. there is no increase in *n*-C_{17} concentration or rise in $\delta^{13}C_{TOC}$ values. In addition, hydrocarbon proxy ratios TAR_{HC} and P_{aq} both indicate that the primary contributions to the sediment organic carbon pool come from terrestrial and submersed/emergent macrophytes. These data, however, are at odds with bulk TOC:TN values, which decrease towards the top of the core, implying relatively greater algal contributions to the sediment, and hence increased lacustrine productivity. TOC:TN values, however, can be misleading and are susceptible to in situ alteration (Meyers 2003). Furthermore, the large range in ratios results in overlapping TOC:TN values for terrestrial and aquatic organic

matter sources (Bianchi and Canuel 2011). What is more, the sediment TOC:TN data are at odds with modern lake water phosphorus (4 µg L^{-1}), nitrogen (86 µg L^{-1}) and chlorophyll a (1.7 µg L^{-1}) concentrations, all of which indicate very low limnetic production.

From the bottom of the Lake Wauberg core (88 cm) to ∼ 40 cm depth, vascular plant n-alkanes (n-C$_{23-31}$) dominate the hydrocarbon record. A shift occurs above 40 cm (AD 1986) at which point $\delta^{13}C_{TOC}$ values, TOC concentrations, and algal-derived n-alkane abundances all increase. Along with these trends that suggest increasing primary productivity, TOC:TN ratios decrease, vascular plant biomarkers reach their lowest levels, and TAR$_{HC}$ values approach 1. Furthermore, all P$_{aq}$ values fall within the range reported for submersed macrophytes, meaning that for the entirety of the Wauberg record, chain lengths > n-C$_{21}$ were derived primarily from aquatic sources (Ficken et al. 2000). Together these data suggest that phytoplankton populations replaced submersed macrophytes as the primary source of organic carbon to Lake Wauberg's sediments after 1986. This shift was likely the result of substantial development of the Lake Wauberg watershed, which began after 1980. That development caused an increase in anthropogenically derived nutrient fluxes from the surrounding watershed, which resulted in decreased water transparency.

Interpretation of the Wauberg n-alkane record contrasts with inferences based on cyanobacterial pigment data and diatom analysis of another core from the lake, which showed persistent eutrophic conditions and stable primary producer populations since at least AD 1894 (Riedinger-Whitmore et al. 2005). Some of the variability in the pigment record (Riedinger-Whitmore et al. 2005) may reflect post-depositional alteration of pigments. The authors reported that native chlorophyll abundance declined by 50% from the base of the core (10%) to the surface (5%). Percent native chlorophyll is a metric used to quantify preservation of photosynthetic pigments in sediments (Swain 1985). The more recent reduction in pigment preservation may have caused an underestimation of cyanobacterial abundance in the most recent sediments.

As in the Wauberg core, the most striking trend in the Lake Apopka lipid concentration data is the rapid increase in algal-derived biomarkers beginning at ∼

40 cm depth (Fig. 4). It is well known that Lake Apopka transitioned from a macrophyte-dominated system to an algal-dominated system in the late 1940s and multiple paleolimnological studies corroborate that shift (Schelske et al. 2000; Kenney et al. 2001; Shumate et al. 2002; Waters et al. 2005, 2015). The increase in algal biomarker concentrations at 40 cm likely represents this shift. In an earlier study on a core taken from the same site in Lake Apopka, TAR$_{HC}$ values indicated a shift from macrophyte-dominated organic matter at 65 cm core depth, to mixed macrophyte/phytoplankton sediments at 50 cm, and finally to phytoplankton-dominated sediments at 30 cm (Silliman and Schelske 2003). In our Apopka core, concentrations of macrophyte-derived n-C$_{23}$ dominated the n-alkane record beginning at ∼ 60 cm depth, before declining at 50 cm, and eventually being replaced by n-C$_{17}$ as the dominant chain length at 40 cm. The TAR$_{HC}$ values are consistent with this finding, and their decrease at 40 cm indicates a switch to organic matter dominated by phytoplankton remains. Our P$_{aq}$ results confirm that terrestrial leaf waxes were never a significant source of n-alkanes in Lake Apopka sediment. Rather, long-chain n-alkanes in sediments from this lake were derived primarily from aquatic macrophytes. Because the age of the sediments in Lake Apopka is well constrained by the disappearance of unsupported ^{210}Pb below 70 cm, we are confident that the rise in phytoplankton hydrocarbon concentrations at 40 cm represents the primary producer shift that occurred in the late 1940s.

The fatty acid data suggest a mixture of organic matter sources and bacterial reworking of various chain lengths (Fig. 5). In the Sheelar core, odd-numbered saturated and iso/anteiso branched fatty acids, represented here as C$_{15}$, C$_{17}$, a-C$_{15}$ and i-C$_{15}$, are likely the product of sulfate-reducing bacteria (Canuel 2001), and monosaturated isomers, represented here as C$_{16:1\omega7}$, C$_{18:1\omega7}$, and C$_{16:1\omega9}$, are the product of non-sulfate-reducing anaerobic fatty acid synthesis (Parkes and Taylor 1983; Pearson et al. 2001). These chain lengths show concentration patterns similar to those of other chain lengths not specifically derived from bacteria (e.g. short-chain fatty acids: C$_{14}$, C$_{16}$ and C$_{18}$), indicating that these acids originate from a common source. Higher concentrations of short-chain acids near the core surface are related to the presence of bacterial communities that utilize these fatty acids as their carbon source.

This utilization has also been reported in studies from estuaries (Zhang et al. 2015) and marine sediments (Parkes and Taylor 1983). Presence of diverse bacteria communities in lakes is not surprising, given the range of redox conditions in the water column and sediments, and studies have demonstrated that under anaerobic and aerobic settings, bacteria produce different fatty acids (Parkes and Taylor 1983).

Algal-derived, polyunsaturated fatty acids ($C_{18:2}$ and $C_{18:3}$) display slightly different patterns throughout the Sheelar core, but broadly follow concentration patterns of bacteria-derived fatty acids, i.e. low concentrations at the bottom of the core, and a sharp increase above 16 cm depth (Fig. 5). We infer from the low abundances (< 10 μg g^{-1} OC) throughout the core, that algal communities were never well established in Lake Sheelar. In contrast, long-chain fatty acids (C_{24-28}) are the most abundant homologues throughout the sediments, as these chain lengths are unsuitable for bacterial consumption (Haddad et al. 1992; Pearson et al. 2001). Their concentration profiles do not follow any of the bacteria-derived fatty-acid profiles, therefore their abundances in the Sheelar core reflect changes in terrestrially derived organic carbon. The ratio of these fatty acid concentrations to bacterial- and algal-derived fatty acids (Table 1), indicates that allochthonous TOC is the primary source of carbon in Sheelar sediments.

In the Wauberg and Apopka cores, bacteria-derived fatty acids display low concentrations in older sediments before increasing above ~ 40 cm depth (Fig. 5). The profiles of these fatty acids are roughly similar to non-source-specific C_{16} and C_{18} fatty acids. From this, we infer that concentration trends of the bacteria-derived fatty acids are not solely the result of changing primary productivity, but instead reflect increased bacterial activity in the uppermost sediment. Thus, we cannot identify the ultimate sources of these fatty acids. Abundance profiles of $> C_{20}$ fatty acids (Fig. 5) indicate a decline in terrestrially derived organic carbon since the 1980s in Lake Wauberg and since the 1940s in Lake Apopka. As in the Sheelar sediments, the long-chain fatty acids are not susceptible to bacterial reworking. A cautious approach is required when trying to use the more labile short-chain fatty acids to identify organic matter sources because concentration patterns of these chain lengths in the sediment are influenced by post-depositional alteration.

Biomarker data from the three lakes serve as reliable proxies for lacustrine productivity. In Lake Sheelar, low n-C_{17} concentrations throughout the core imply negligible algal input to the sediments. Dominance of n-C_{23-31} and long-chain fatty acids in the sediments confirms that organic matter in the sediments of Lake Sheelar is primarily of vascular plant origin, and that the water body has been a low-productivity, oligotrophic system throughout the last ~ 150 years. Sheelar sits in a flat, upland region of north-central Florida, surrounded by dense pine and oak scrub forests. It's geographic isolation separates it from the deleterious effects of agricultural and urban nutrient run-off, and has sustained it's low productivity status over the past century. The Lake Wauberg and Apopka sediment cores display increases in n-C_{17} and decreases in terrestrial fatty acids over time in response to human activities in their watersheds. Over the last several decades, algae contributed the majority of hydrocarbons to the sediment record, and terrestrial fatty acid biomarkers have declined markedly. In Wauberg, this increase occurred only after watershed development in the 1980s. In Lake Apopka, the transition from a macrophyte-dominated to a phytoplankton-dominated state in the late 1940s is documented by the n-alkane and fatty acid concentration data and correlates with the draining of adjacent wetlands and the implementation of nutrient intensive muck farming along its north shore (Schelske 1997). The timing of the shift in these proxies for primary producer communities correlates well with the timing of shifts documented using other sediment variables, such as total phosphorus concentrations and diatom microfossils (Schelske et al. 2000). In all three study lakes, short-chain ($< C_{20}$) fatty-acid biomarkers show evidence of bacterially mediated diagenesis, which may be post-depositional. We advise against using short-chain fatty acid data to establish definitively the source of these compounds in sediments, and future work on fatty-acid biomarkers, especially compound-specific isotope analyses, should provide insights into the extent of post-depositional changes.

Conclusions

Bulk and biomarker data from sediment cores indicate that Lake Sheelar has remained a low productivity system dominated by macrophyte and terrestrial

inputs since at least the nineteenth century. Increases in algal contributions, measured as $n\text{-}C_{17}$ concentrations, in Lake Wauberg in the 1980s and Lake Apopka in the 1940s, demonstrate the detrimental impacts of anthropogenic influences on lacustrine systems. Both systems increased in trophic status and transitioned from macrophyte to algal dominated systems after human alteration of the landscape. In all three lakes fatty acid concentration profiles display increased bacterial activity in more recent sediments and post depositional alteration of several fatty acid chain lengths. Bulk elemental and isotopic data, while somewhat diagnostic, are plagued by myriad issues [see overview in Bianchi and Canuel (2011)]. Overall, the hydrocarbon data represents the most source specific and stable biomarker, and therefore concentrations of n-alkane chain lengths can be used for reconstructions of organic matter sources and trophic status over decadal to centennial timescales.

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