J Paleolimnol
DOI 10.1007/s10933-010-9472-y

ORIGINAL PAPER

Identifying sources of organic matter in sediments of shallow lakes using multiple geochemical variables

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Received: 29 September 2009 / Accepted: 30 September 2010

Abstract We analyzed ^{210}Pb-dated sediment cores from four relatively shallow lakes ($z_{max} < 10$ m) in the Upper Ocklawaha River Basin, Florida, USA to compare primary producer community structure before and after anthropogenic impacts. We measured physical and chemical sediment variables including density, organic matter (OM), water-soluble phosphorus, polyphosphate (Poly-P), total P (TP), total carbon to total nitrogen mass ratios of OM (TC:TN), biogenic silica (diatoms, sponge spicules), total amorphous silica, and stable carbon and nitrogen isotope ratios of bulk OM. Principal component analysis showed that diatom biogenic silica, TC:TN, Poly-P and TP displayed discernible stratigraphic changes associated with the shift in the primary producer community. We applied k-means cluster analysis to these variables to identify macrophyte-derived, transitional, and phytoplankton-derived sediments. Our approach provides an objective method for identifying sediment sources that may be applied to shallow lakes in other regions. The four study lakes shifted from a macrophyte-dominated state to a transitional state before major anthropogenic disturbances, and became phytoplankton-dominated after ~1950.

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Keywords Florida · Organic matter · Sediment chemistry · Shallow lakes · Stable states

Introduction

Restoration of impacted water bodies requires information on ecosystem structure and function prior to human disturbance (Welch and Cook 1987). Where long-term limnological data are unavailable, paleolimnology may provide information about historic lake structure and function (Brenner et al. 1993). Routine limnological data gathering began in some Florida lakes in the 1980s, but anthropogenic disturbances in most of the state's watersheds occurred long before then, *ca*. 1850–1900 (Battoe et al. 1999). Paleolimnological techniques provide an opportunity to improve our understanding of pre-disturbance conditions in Florida lakes.

Florida possesses numerous shallow lakes in which the "alternative stable states" model (Scheffer et al. 1993) applies with respect to anthropogenic disturbances and associated changes in primary producer community structure (PPCS) (Kenney et al. 2002). The shallow lakes model (Scheffer et al. 1993) states that PPCS is most influenced by phosphorus (P) loading rate and consequent water column P concentration. When increased P loading causes the in-lake P concentration to exceed a critical threshold, phytoplankton replace macrophytes as the dominant primary producers. Other factors may influence changes in PPCS in shallow lakes.

Published online: 14 October 2010

In Lake Apopka, Florida, increased dissolved color and lake stage were shown to darken the lake bottom and accelerate the phosphorus-driven shift to phytoplankton dominance (Schelske et al. 2010). In two shallow lakes in Denmark, increased density of planktivorous fish and changes in macrophyte coverage explained more variability in algal abundance than did diatom-inferred limnetic phosphorus concentrations (McGowan et al. 2005). The duration of the growing season for north-temperate shallow lakes has been shown to influence changes in PPCS (Sayer et al. 2010). Differences between shallow lakes of north-temperate areas and shallow lakes in sub-tropical Florida may be a consequence of differences in the length of the growing season between the two regions.

In this study we used geochemical variables in deposits from four relatively shallow Florida lakes ($z_{max} < 10$ m) to identify the source of sediment organic matter (OM) and thus characterize historical changes in the dominant primary producer community in the water bodies. Past attempts to use surface sediment variables from a large suite of Florida lakes to characterize trophic state of the overlying waters proved largely unsuccessful (Binford and Brenner 1986; Brenner and Binford 1988). It was thought that inter-lake differences in dilution of OM by allochthonous inorganic inputs, as well as inter-lake variations in diagenesis of recent sediments, probably compromised the relation. Such variability is largely eliminated in studies of deposits from single lakes. A multi-proxy, paleolimnological approach identified the shift from macrophyte dominance to phytoplankton dominance in shallow Gundsømagle Sø, Zealand, Denmark (Rasmussen and Anderson 2005). Waters et al. (2005) used a multivariate statistical approach for evaluating the source of OM to identify three sediment types in shallow Lake Apopka, Florida. In a previous study of P-enriched, phytoplankton-dominated, very shallow ($z_{max} < 4$ m) Florida lakes, Kenney et al. (2002) characterized deposits in cores as macrophyte-derived, transitional, or phytoplankton-derived sediment types using the total carbon to total nitrogen ratio (TC:TN), concentration of total P (TP), and amount of sponge biogenic silica ($BSi_{Sponges}$). In this study, we tested the utility of several additional variables for evaluating historic PPCS shifts in four slightly deeper Florida lakes that were also subject to human impacts. The additional sediment variables we evaluated included diatom biogenic silica ($BSi_{Diatoms}$), water-soluble P (H_2O–P), polyphosphate P (Poly-P) (Kenney et al. 2001) and stable isotope ratios of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) in bulk sediment OM.

We measured H_2O–P, Poly-P and total P (TP) in the sediment as proxy variables for historic P loading (Kenney et al. 2001). H_2O–P proved to be a good estimator of bio-available P in the sediments of Florida's hypereutrophic Lake Apopka. Because intracellular reserves of P are formed in phytoplankton only when nutrient supplies exceed biological demand, Poly-P is a sensitive proxy for historic P enrichment. Poly-P was shown to be a reliable indicator of the phytoplankton contribution to sediment organic matter in Lake Apopka. Greater Poly-P sedimentation was associated with the historic development of phytoplankton dominance. Stable isotope signatures ($\delta^{13}C$ and $\delta^{15}N$) of OM in lake sediment cores have been used as indicators of historic lacustrine productivity (Brenner et al. 1999; Schelske and Hodell 1995) and past nitrogen sources (Brenner et al. 1999; Gu et al. 1996), respectively. Total carbon (TC) to total nitrogen (TN) ratios of OM can be used to assess the relative contributions of higher plants versus phytoplankton to sediments (Meyers and Teranes 2001; Muller and Mathesius 1999; Schelske et al. 1999; Kenney et al. 2002). We used concentrations of sponge and diatom biogenic silica (BSi) (Conley and Schelske 1993) in Florida lake sediments as indicators of the relative contribution of macrophytes and phytoplankton to the sediments, respectively (Kenney et al. 2002). Macrophytes are the predominant substrate for freshwater sponges in Florida's lakes, which lack other solid substrates.

Site description

The Harris chain of lakes possesses the major water bodies of the Upper Ocklawaha River Basin, Central Florida, USA. Hydrologic flow in the system begins at the Gourdneck Spring in the southwest part of Lake Apopka. Lake Apopka lies northwest of the city of Orlando and is hypereutrophic, largely as a result of past agricultural activity. Approximately 40% of the lakebed was reclaimed for agriculture in the middle of the twentieth century (Schelske et al. 2000; Battoe et al. 1999; Lowe et al. 1999). Lake Beauclair, one of our study lakes, is the first lake downstream

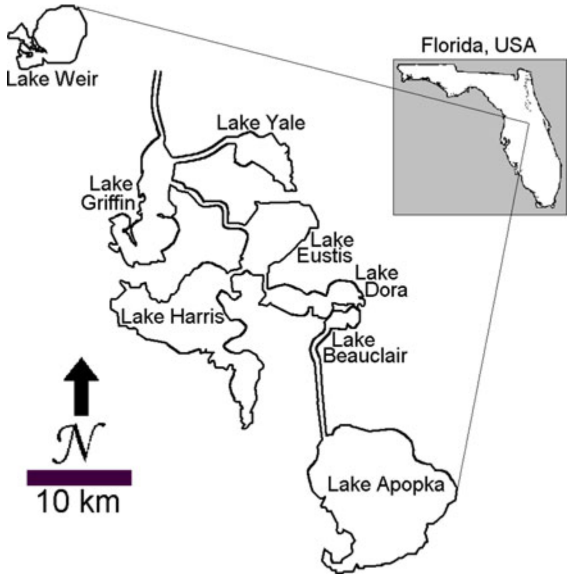


Fig. 1 Map of study area. Widths of canals and rivers are exaggerated. Construction of the canal connecting Lake Apopka to Lake Beauclair was completed by 1893

from Lake Apopka (Fig. 1) and is also hypereutrophic (Table 1). Other study lakes include Lakes Harris, Weir and Yale, which receive little or no flow from Lake Apopka and are considered mesotrophic (Fulton 1995). Residential development of the lakeshore is the primary anthropogenic impact to these mesotrophic lakes. Among our study sites, Lake Beauclair is shallower, smaller, and displays higher nutrient concentrations than the other three lakes.

Methods

Water depth was determined with an infrared nephelometer that is capable of detecting uppermost, unconsolidated sediments (Meyers and Schelske 2000) and sediment/water interface cores were collected with a piston corer (Fisher et al. 1992). We collected two cores in Lake Beauclair (LB), three cores in both Lakes Weir (LW) and Yale (LY), and nine cores in Lake Harris (LH). Cores were obtained at depositional sites throughout the lakes that were identified from maps of soft sediment thickness (Danek et al. 1991). Cores were extruded vertically and sectioned at 4-cm intervals in the field, aboard a motorboat. Samples were stored in low-density polyethylene cups in ice chests for transport to the laboratory, where they were refrigerated at ~5°C.

Analytical procedure for H_2O–P and Poly-P followed Kenney et al. (2001) and TP was measured according to Schelske et al. (1986). We define TP – [H_2O–P + Poly-P] as residual TP (R-TP). Dried samples were analyzed for $BSi_{Diatoms}$ and $BSi_{Sponges}$ using time-course leaching (Conley and Schelske 1993). Total amorphous silica (TSi) was determined as the amount dissolved after 20 h with 1% $NaCO_3$ at 85°C. TSi includes $BSi_{Diatoms}$ and $BSi_{Sponges}$, but does not include mineral forms of Si such as quartz.

Total C and TN of OM in dried samples were measured with a Carlo Erba NA1500 CNS elemental analyzer equipped with an auto-sampler (Verardo et al. 1990). Stable isotopes (δ^{13}C and δ^{15}N) of bulk OM in sediments were determined using a Carlo Erba NA1500 CNS analyzer interfaced with a PRISM Series II mass spectrometer. Isotope ratios are reported in standard delta notation, i.e. per mil (‰), relative to the VPDB for δ^{13}C and air for δ^{15}N. Organic matter content was determined by weight loss on ignition (LOI) after combustion at 550°C for 2 h. Sediment bulk density (rho) was determined by measurement of dry mass per wet volume.

Data were analyzed with a multivariate statistical computer software package (JMP Statistical Software, SAS 1998). Of all paleolimnological variables

Table 1 Limnological characteristics of the four study lakes

Lake	Surface area (km)	Mean depth (m)	Maximum depth (m)	TP (mg L^{-1})	TN (mg L^{-1})	Latitude (N)	Longitude (W)
Beauclair	4.4	2.1	4.7	0.235	4.206	28°46′30″	81°40′
Harris	76	3.7	9.7	0.042	1.794	28°47′	81°48′
Weir	23	5.8	9.8	0.015	0.714	29°01′	81°56′
Yale	16	3.7	7.9	0.025	0.95	28°55′	81°44′

Total phosphorus (TP) and chlorophyll *a* (Chl-*a*) are averages (Fulton 1995) for the water column

Table 2 Results from principal component analysis using organic matter content (LOI), normalized water soluble phosphorus (N–H_2O–P), normalized polyphosphate (N-Poly-P), normalized residual phosphorus (N-RTP), total carbon to total nitrogen mass ratio (TC:TN), carbon stable isotope ratio ($\delta^{13}C$), nitrogen stable isotope ratio ($\delta^{15}N$), normalized diatom silica (N-DSi), normalized sponge silica (N-SSi) and normalized mineral silica (N-MinSi)

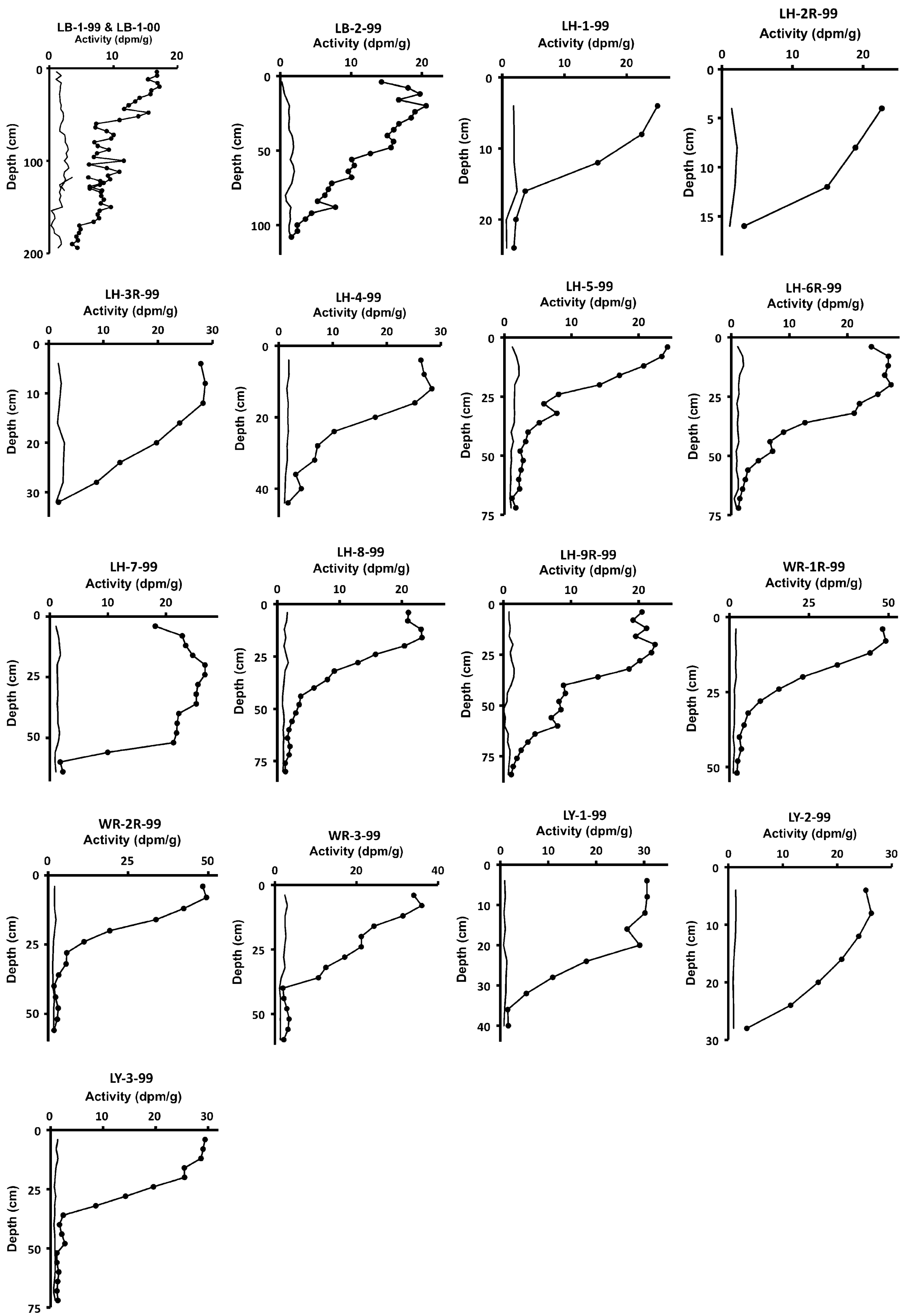
Eigen value	3.36	1.80	1.08	0.92	0.71	0.67	0.51	0.44	0.22	0.21
Percent	33.61	18.04	10.78	10.24	7.14	6.67	5.06	4.35	2.17	2.07
Cumulative percent	33.61	51.65	62.43	78.89	79.68	86.35	0.91	95.77	97.93	100.00
Eigen vectors										
LOI	0.34	−0.10	0.28	0.07	0.68	0.41	−0.29	−0.20	0.17	0.03
N–H_2O–P	−0.30	−0.26	−0.42	−0.15	0.36	0.41	0.54	0.12	−0.13	−0.13
N-Poly-P	0.42	0.27	0.05	0.25	0.14	−0.24	0.37	0.17	0.10	−0.66
N-RTP	0.36	0.44	−0.07	−0.06	0.20	−0.04	0.20	0.35	−0.04	0.58
TC:TN	−0.40	0.27	0.02	−0.05	0.18	0.08	−0.51	0.59	−0.16	−0.30
$\delta^{13}C$	−0.29	0.45	0.12	−0.42	0.17	−0.11	0.20	−0.07	0.64	0.11
$\delta^{15}N$	−0.20	0.15	−0.44	0.75	0.12	−0.04	−0.08	−0.01	0.33	0.23
N-DSi	0.39	−0.21	−0.22	−0.14	−0.34	0.32	−0.10	0.50	0.50	0.05
N-SSi	−0.07	−0.56	0.20	0.02	0.33	−0.58	0.07	0.37	0.14	0.18
N-MinSi	−0.23	0.01	0.66	0.37	−0.22	0.37	0.35	0.23	0.02	0.12

analyzed (Tables 1, 2), principal component analysis identified $BSi_{Diatoms}$, TC:TN, and Poly-P or TP as the variables in the data set that displayed clear stratigraphic patterns (i.e. had the largest eigenvectors in the first principal component), so these variables were used in cluster analyses. Preliminary cluster analysis grouped 22 samples from Lake Harris with high TC:TN (16.7 $\pm$ 1.9, $n = 22$) compared to the rest of the data set (TC:TN < 14, $n = 572$). Likewise, a subsequent preliminary cluster analysis grouped 13 samples from Lake Yale with high TN (3.96 $\pm$ 0.91%, $n = 13$) compared to the rest of the data set (2.77 $\pm$ 0.56%, $n = 581$). Both groups were from the oldest samples collected at the sites, i.e. from deepest samples in the short cores. We considered these sample groups to be outliers and excluded them from further analysis. Using input variables $BSi_{Diatoms}$, TC:TN, and TP or Poly-P, k-means cluster analysis grouped samples objectively into three sediment types. Poly-P and TP are correlated, so we compared cluster analyses using each of these variables to represent historic P loading. Because Poly-P, TP and $BSi_{Diatoms}$ concentrations (mg g^{-1}) varied by more than an order of magnitude within our data set, we normalized the data from each core to the maximum value in that core. We report these normalized values without units.

Sediment cores were dated by ^{210}Pb. Radiometric measurements (^{210}Pb and ^{226}Ra) were made using low-background gamma counting with well-type intrinsic germanium detectors (Appleby et al. 1986; Schelske et al. 1994). Sediment ages were calculated using the constant rate of supply (CRS) model (Appleby and Oldield 1983; Oldfield and Appleby 1984). Age errors were propagated using first-order approximations and calculated according to Binford (1990). All radiometric data from this study are presented in Schelske et al. (2001) and available on the website listed in the references.

Results

In nearly all the cores, ^{210}Pb and ^{226}Ra activity profiles (Fig. 2) show systematic decreases in unsupported ^{210}Pb activity with depth. These data suggest that the CRS calculated dates for all but three cores are reliable. For LB-1-99, all sections (0–132 cm) had unsupported ^{210}Pb, so a deeper core, LB-1-00, was collected in 2000 at the same location. This core was sampled to 192 cm depth, but again, all samples (118–192 cm) had unsupported ^{210}Pb, so this combined profile was not datable. The unsupported ^{210}Pb shows a systematic decrease with depth, suggesting the profile could have been dated if deeper sediments had been retrieved. This core location is nearest the inlet for the Apopka-Beauclair canal, so a thick accumulation of recent sediments was expected. Data


LB-1-99 & LB-1-00
Activity (dpm/g)
Depth (cm)
LB-2-99
Activity (dpm/g)
Depth (cm)
LH-1-99
Activity (dpm/g)
Depth (cm)
LH-2R-99
Activity (dpm/g)
Depth (cm)
LH-3R-99
Activity (dpm/g)
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LH-4-99
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LH-5-99
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LY-3-99
Activity (dpm/g)
Depth (cm)

◀ **Fig. 2** ^{210}Pb (*dark circles*) and ^{226}Ra (*line only*) activities (dpm/g) are plotted against depth (cm) for the 17 study cores. LB-1-99 and LB-1-00 were collected at the same location on different dates. LB-1-99 (0–132 cm) did not penetrate deep enough to include samples without unsupported ^{210}Pb. LB-2-99 (118–194 cm) possessed deeper sediment sections, but basal deposits still contained unsupported ^{210}Pb

from LY-1-99 (0–20 cm) and LH-7-99 (0–52 cm) indicate the possibility of a mixed sediment layer in each core. Alternatively, these nearly constant activity profiles may result from an increasing sedimentation rate that compensates for the radioactive decay of ^{210}Pb. For these two cores, we opted for a conservative approach and only assigned dates below the mixed layer in each core.

We conducted principal component analysis (PCA) to determine which variables would be best suited for identifying sediment types with cluster analysis. Table 2 displays PCA results for fractions of phosphorus (H_2O–P, Poly-P and R-TP) and all other sediment variables. Table 3 displays PCA results for TP and all other sediment variables. Poly-P or TP, $BSi_{Diatoms}$ and TC:TN had the largest eigenvectors in the first principal component of the corresponding PCA.

In general, cluster analysis using Poly-P, $BSi_{Diatoms}$ and TC:TN yielded sediment groups that largely corresponded to depth (i.e. age) (Table 4). The group of most recent sediments ($n = 76$) had the greatest normalized concentrations of Poly-P (0.79 ± 0.19), TP (0.88 ± 0.12) and $BSi_{Diatoms}$ (0.75 ± 0.21), and the lowest TC:TN (9.2 ± 0.4). The group of oldest sediments ($n = 227$) had the lowest normalized concentrations of Poly-P (0.09 ± 0.09), TP (0.19 ± 0.14) and $BSi_{Diatoms}$ (0.17 ± 0.17), but had the greatest TC:TN (12.1 ± 0.7). Using information from previous studies on shallow Florida basins (Kenney et al. 2002), we concluded that recent sediments with high values of $BSi_{Diatoms}$ and low values of TC:TN are derived largely from phytoplankton, and that oldest sediments with lower values of $BSi_{Diatoms}$ and higher values of TC:TN are derived largely from macrophytes. Although the samples with intermediate age ($n = 256$) had intermediate TC:TN (10.7 ± 0.7), the Poly-P (0.13 ± 0.12) and TP (0.30 ± 0.17) means were similar to those from the macrophyte-derived sediments and the $BSi_{Diatoms}$ mean (0.73 ± 0.18) was similar to that from the phytoplankton-derived sediments. We classified samples with both intermediate age and TC:TN as "transitional."

Substituting TP for Poly-P in the cluster analysis changed the sediment groupings slightly in 13 of 17 cores, but only 24 of 594 samples were reclassified. Phytoplankton-derived sediments were never reclassified as macrophyte-derived sediments, and similarly, macrophyte-derived sediments were never reclassified as phytoplankton-derived deposits. Using TP instead of Poly-P as an input variable increased the number of phytoplankton-derived sediment samples by 17 and the number of macrophyte-derived

Table 3 Results from principal component analysis using dry bulk density (rho), organic matter content (LOI), normalized total phosphorus (N-TP) total carbon to total nitrogen mass ratio (TC:TN), carbon stable isotope ratio ($\delta^{13}C$), nitrogen stable isotope ratio ($\delta^{15}N$), normalized diatom silica (N-DSi), normalized sponge silica (N-SSi) and normalized mineral silica (N-MinSi)

Eigen value	3.63	1.37	1.17	0.92	0.73	0.50	0.29	0.22	0.16
Percent	40.37	15.25	13.03	10.24	8.14	5.57	3.21	2.40	1.79
Cumulative percent	40.37	55.62	68.65	78.89	87.03	92.60	95.81	98.21	100.00
Eigen vectors									
Rho	0.45	0.12	−0.27	−0.22	−0.10	0.03	−0.06	−0.08	0.80
LOI	−0.35	−0.16	0.30	0.53	0.22	−0.35	0.18	0.00	0.53
N-TP	−0.36	0.44	0.05	0.10	0.10	0.55	−0.34	0.43	0.19
TC:TN	0.45	−0.06	−0.09	0.23	0.10	−0.37	−0.21	0.72	−0.13
$\delta^{13}C$	0.23	0.27	0.61	0.39	0.26	0.03	0.49	0.21	0.02
$\delta^{15}N$	0.26	0.38	−0.37	0.53	0.21	0.22	0.49	−0.14	−0.14
N-DSi	−0.38	−0.06	−0.39	−0.22	−0.37	−0.09	0.55	0.44	0.07
N-SSi	0.09	−0.71	−0.10	−0.03	0.39	0.52	0.14	0.14	0.06
N-MinSi	0.26	−0.16	0.39	0.35	−0.71	0.32	0.10	0.06	0.02

Table 4 Data for sediment variables listed by sediment types, which were determined by cluster analysis using N-Poly-P, TC:TN and N-$BSi_{Diatoms}$

Sediment type		Sample ID cm	Rho (g/cm^3)	LOI (%)	H_2O–P mg/g	N–H_2O–P	Poly-P mg/g	N-Poly-P	TP mg/g	N-TP	TC:TN mass	$\delta^{13}C$	$\delta^{15}N$	DSi SiO_2 mg/g	N-DSi	SSi SiO_2 mg/g	N-SSi	TSi SiO_2 mg/g	N-TSi
Phytoplankton	Mean	14	0.02	68	0.02	0.16	0.35	0.79	1.28	0.88	9.2	−22.9	1.3	76.2	0.75	14.9	0.26	93.4	0.69
$n = 76$	SD	11	0.01	5	0.03	0.12	0.17	0.19	0.38	0.12	0.4	2.4	0.8	23.2	0.21	9.5	0.18	22.9	0.18
Transitional	Mean	61	0.05	58	0.08	0.53	0.06	0.13	0.47	0.30	10.7	−21.5	1.4	81.0	0.73	30.4	0.46	116.5	0.81
$n = 256$	SD	30	0.01	7	0.09	0.25	0.07	0.12	0.36	0.17	0.7	1.8	1.8	27.6	0.18	18.2	0.24	31.1	0.14
Macrophyte	Mean	99	0.07	56	0.07	0.53	0.02	0.09	0.24	0.19	12.1	−20.1	2.4	15.6	0.17	33.2	0.48	56.5	0.47
$n = 227$	SD	32	0.03	11	0.05	0.24	0.02	0.09	0.18	0.14	0.7	3.4	1.5	15.5	0.17	30.9	0.28	38.2	0.25
TC:TN > 14	Mean	123	0.08	44	0.06	0.45	0.01	0.04	0.61	0.50	16.7	−9.2	1.6	0.5	0.01	4.7	0.08	10.1	0.07
$n = 22$	SD	15	0.02	9	0.02	0.18	0.02	0.08	0.11	0.09	1.9	2.2	0.3	0.6	0.01	3.1	0.03	2.1	0.01
TN Outliers	Mean	108	0.10	40	0.03	0.49	0.01	0.01	0.05	0.04	7.4	−22.2	2.2	18.3	0.23	44.7	0.57	73.3	0.83
$n = 13$	SD	16	0.01	6	0.01	0.13	0.00	0.00	0.02	0.01	1.4	0.5	0.3	7.6	0.10	17.6	0.22	9.1	0.10

Variables include: maximum depth of the sediment interval (Sample ID), bulk density (Rho), loss on ignition (LOI), water soluble P (H_2O–P and N–H_2O–P), Poly-P and N-Poly-P, total P (TP and N-TP), TC:TN, $\delta^{13}C$ organic matter, $\delta^{15}N$ organic matter, $DSi_{Diatoms}$ and N- $BSi_{Diatoms}$, $BSi_{Sponges}$ and N- $BSi_{Sponges}$) and total amorphous silica (TSi and N-TSi). "N-" indicates data were normalized to the maximum value in each core. SD = standard deviation

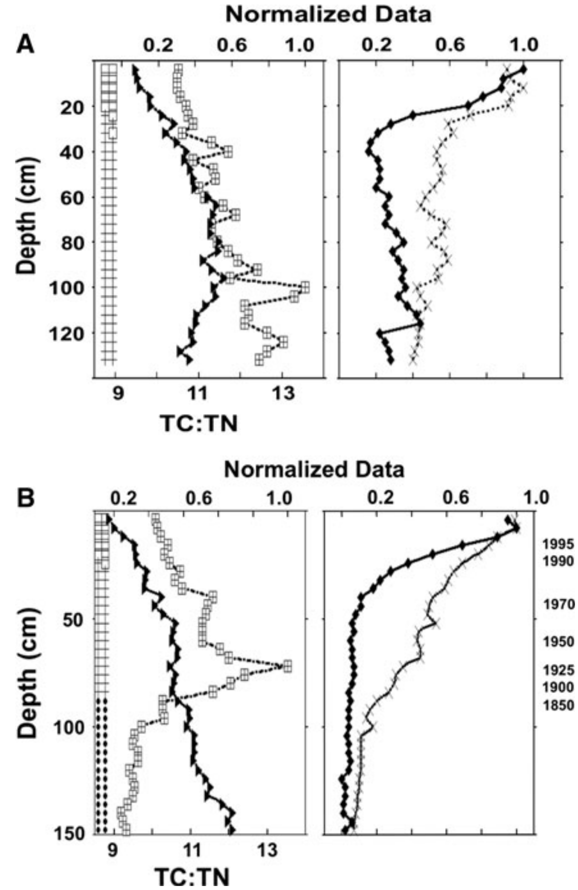

Fig. 3 Sediment total carbon to total nitrogen mass ratios (*dark triangles*), and normalized diatom biogenic silica (*open squares with crosses*), normalized polyphosphate (*dark diamonds*) and normalized total phosphorus (x) concentrations versus depth (cm) for Lake Beauclair cores LB-1-99 (**a**) and LB-2-99 (**b**). Macrophyte (*dark circle*), transitional (*black cross*), and phytoplankton (*open square*) sediment classifications are presented on the depth axis. The left classification is based on normalized polyphosphate, normalized diatom biogenic silica and the total carbon to total nitrogen ratio. The right classification is based on normalized total phosphorus, normalized diatom biogenic silica and the total carbon to total nitrogen ratio. ^{210}Pb dates are plotted on the right axis

sediment samples by three, all of which came from the transitional group, as originally determined using Poly-P. Stratigraphic distributions for the sediment groups identified using these variables are shown in Figs. 3, 4, 5, 6, 7, and 8.

In general, rho (g dry cm^{-3} wet) increased with sample age and LOI decreased with sample age. LOI and rho displayed stratigraphic trends, but these variables may autocorrelate with depth because of diagenesis and compaction, so they were not included

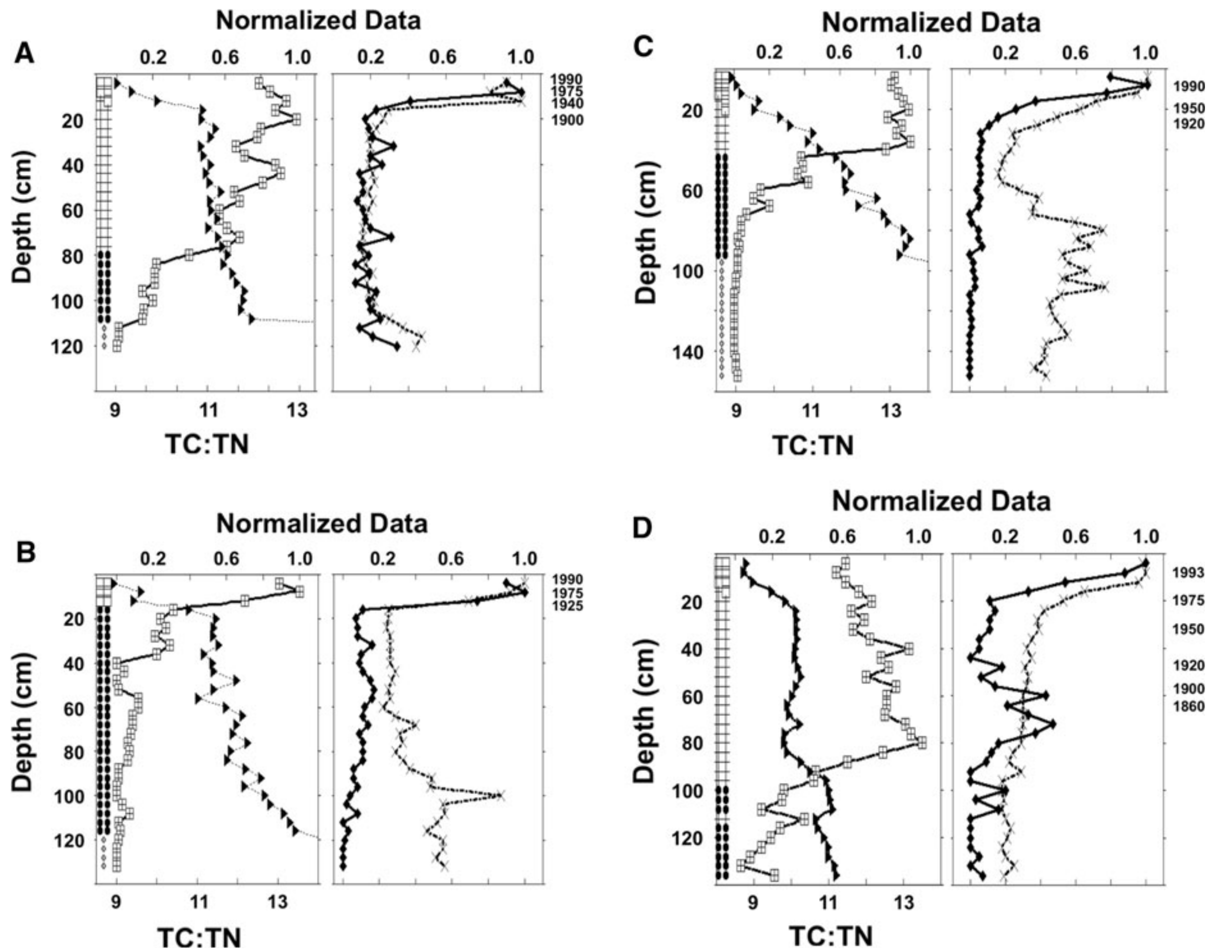

Fig. 4 Sediment total carbon to total nitrogen mass ratios (*dark triangles*), and normalized diatom biogenic silica (*open squares with crosses*), normalized polyphosphate (*dark diamonds*) and normalized total phosphorus (x) concentrations versus depth (cm) for Lake Harris cores LH-1-99 (**a**), LH-2R-99 (**b**), LH-3R-99 (**c**) and LH-5-99 (**d**). Macrophyte (*dark circle*), transitional (*black cross*), and phytoplankton (*open square*) sediment classifications are presented on the depth axis. Samples with a total carbon to total nitrogen ratio greater than 14 (*open cross*) were considered outliers as described in the text. The left classification is based on normalized polyphosphate, normalized diatom biogenic silica and the total carbon to total nitrogen ratio. The right classification is based on normalized total phosphorus, normalized diatom biogenic silica and the total carbon to total nitrogen ratio. ^{210}Pb dates are plotted on the right axis

in the cluster analysis. Sediment variables H_2O–P, $\delta^{13}C$, $\delta^{15}N$, $BSi_{Sponges}$ and TSi displayed poorly defined stratigraphic trends compared to the strong trends for input variables used in the cluster analysis. Normalized H_2O–P was lower in phytoplankton-derived sediments (0.16 ± 0.12) compared to H_2O–P in transitional (0.53 ± 0.25) and macrophyte-derived (0.53 ± 0.24) sediments. The trend of $BSi_{Sponges}$ was similar to that for H_2O–P. Normalized $BSi_{Sponges}$ was lower in phytoplankton-derived sediments (0.26 ± 0.18) than in transitional (0.46 ± 0.24) and macrophyte-derived (0.48 ± 0.28) sediments. Because of the large variability in the $BSi_{Sponges}$ and H_2O–P data, they were not powerful indicators of sediment type.

With the exception of Lake Beauclair, cores displayed some intervals with low $\delta^{13}C$ values associated with the shift from macrophytes to phytoplankton. Considering all cores, the organic carbon from phytoplankton-derived sediments ($\delta^{13}C = -22.9 \pm 2.4‰$, $n = 76$) was slightly depleted in ^{13}C compared to transitional ($\delta^{13}C = -21.5 \pm 1.8‰$, $n = 256$) or macrophyte-derived sediments ($\delta^{13}C = -20.1 \pm 3.4‰$, $n = 227$). Failure of carbon isotopes to identify the OM source was not

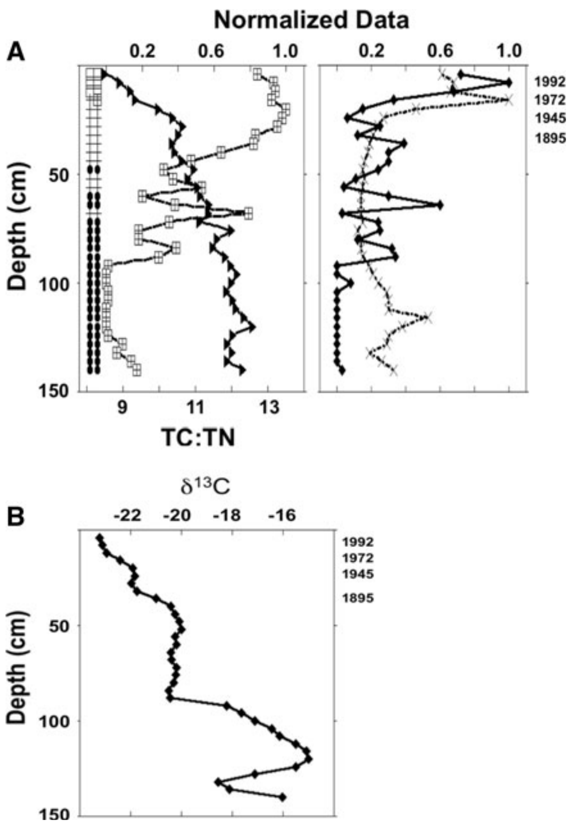

Fig. 5 Sediment total carbon to total nitrogen mass ratios (*dark triangles*), and normalized diatom biogenic silica (*open squares with crosses*), normalized polyphosphate (*dark diamonds*) and normalized total phosphorus (x) concentrations versus depth (cm) for Lake Harris core LH-4-99 (**a**). Macrophyte (*dark circle*), transitional (*black cross*), and phytoplankton (*open square*) sediment classifications are presented on the depth axis. The left classification is based on normalized polyphosphate, normalized diatom biogenic silica and the total carbon to total nitrogen ratio. The right classification is based on normalized total phosphorus, normalized diatom biogenic silica and the total carbon to total nitrogen ratio. Carbon stable isotope ratios of organic matter are plotted against depth for core LH-4-99 (**b**). ^{210}Pb dates are plotted on the right axis

unexpected. In a previous study of another shallow, macrophyte-dominated Florida lake, OM in surface sediments was relatively depleted compared to the isotopic signatures of abundant submersed aquatic plant taxa in the basin (Brenner et al. 2006). Although δ^{13}C was not a strong indicator of sediment type, outlier TC:TN samples from the Lake Harris cores (LH-1, LH-2, LH-3), with values > 14 that probably indicate a macrophyte origin, had greater δ^{13}C values ($\delta^{13}C = -9.2 \pm 2.2‰$, $n = 22$) compared to the other samples ($\delta^{13}C = -21.1 \pm 2.8‰$, $n = 572$).

Discussion

Chronology of lake biological responses

In our study lakes, development of lake-wide phytoplankton dominance occurred after the initial anthropogenic disturbance *ca.* 1870. Cluster analysis indicates only a few of the 93 phytoplankton-derived samples were deposited before ~1950. All were identified in core LH-7-99, and were deposited after ~1870. Other than these few samples, the sediment records suggest there was a protracted period of macrophyte dominance in the lakes before anthropogenic disturbance. In general, these lakes shifted from the macrophyte-dominated state to a transitional state before major anthropogenic disturbances, but only became phytoplankton-dominated after ~1950.

The boundary between transitional sediments and phytoplankton-derived sediments occurred earlier (i.e. deeper in cores) when sediments were classified using TP instead of Poly-P in the cluster analysis. This was expected. As total P loading increased, incorporation of Poly-P into algal cells and sedimentation of Poly-P were delayed until TP loading exceeded biological demand (Kenney et al. 2001). Increased TP loading began before the biological response (Poly-P storage and sedimentation) occurred. Sediment TP concentrations increased at depths greater than or equal to depths of increased sediment Poly-P concentrations. Consequently, cluster analysis using TP, TC:TN and $BSi_{Diatoms}$ ($n = 93$) classified more samples as phytoplankton sediments than did cluster analysis using Poly-P, TC:TN and $BSi_{Diatoms}$ ($n = 76$).

We compared transitional and macrophyte-derived sediments over the entire data set and found differences between the two types with respect to TC:TN and $BSi_{Diatoms}$, but only minor differences in sediment P (Poly-P or TP) between the two sediment groups. This result differs from the findings of a previous study in shallow Florida lakes (Table 5) (Kenney et al. 2002), in which transitional sediments had intermediate TP values compared to macrophyte-derived and phytoplankton-derived sediments. In the current study, the shift to a transitional state occurred before major anthropogenic disturbance in the drainage basin. It is possible that these pre-disturbance changes in PPCS coincided with the onset of wetter climate, which may have caused increased water

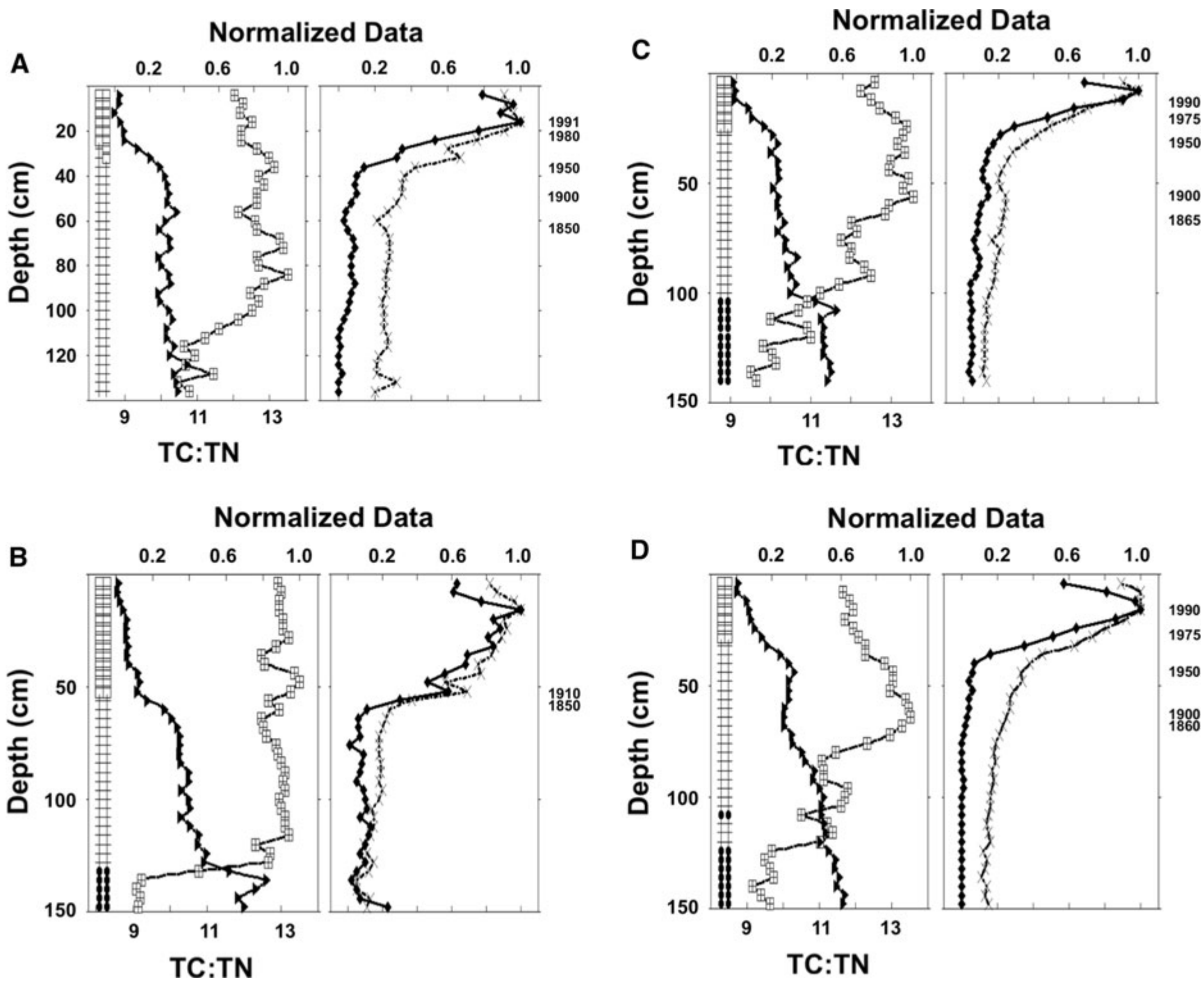

Fig. 6 Sediment total carbon to total nitrogen mass ratios (*dark triangles*), and normalized diatom biogenic silica (*open squares with crosses*), normalized polyphosphate (*dark diamonds*) and normalized total phosphorus (x) concentrations versus depth (cm) for Lake Harris cores LH-6R-99 (**a**), LH-7-99 (**b**), LH-8-99 (**c**) and LH-9R-99 (**d**). Macrophyte (*dark circle*), transitional (*black cross*), and phytoplankton (*open square*) sediment classifications are presented on the depth axis. The left classification is based on normalized polyphosphate, normalized diatom biogenic silica and the total carbon to total nitrogen ratio. The right classification is based on normalized total phosphorus, normalized diatom biogenic silica and the total carbon to total nitrogen ratio. ^{210}Pb dates are plotted on the right axis

depth, greater water color, or both. Lake stage and water color have been shown to influence PPCS in shallow lakes (Rasmussen and Anderson 2005; Schelske et al. 2010).

Spatial and temporal variability of lake sedimentation

Had Lake Harris core LH-4-99 (Fig. 5) been studied alone, it would have yielded a paleoenvironmental reconstruction different from that generated by the other Lake Harris cores and from the other lake cores. Some older (pre-1850) sediments in LH-4-99 display oscillations in phytoplankton indicators that do not coincide with changes in sediment TP concentration. In sediments between 88 and 52 cm, $BSi_{Diatoms}$ and Poly-P display similar, rapid fluctuations. Over the same section, TC:TN gradually decreases up-core and δ^{13}C shows an abrupt −2.4‰ shift from deeper sediments at 88 cm. Although nearby core LH-5-99 displays variability in Poly-P and $BSi_{Diatoms}$ in deeper sediments, LH-4-99 was the only core in our study with pre-1850 sediments showing such extreme fluctuations in these variables.

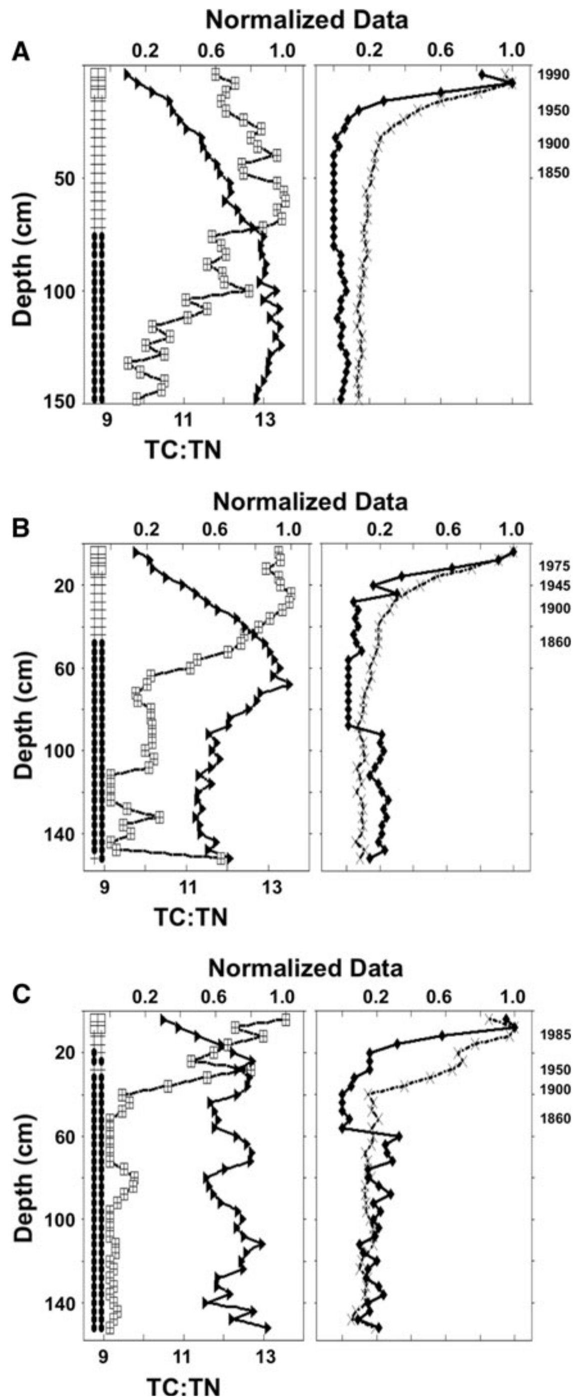

Fig. 7 Sediment total carbon to total nitrogen mass ratios (*dark triangles*), and normalized diatom biogenic silica (*open squares with crosses*), normalized polyphosphate (*dark diamonds*) and normalized total phosphorus (x) concentrations versus depth (cm) for Lake Weir cores WR-1R-99 (**a**), WR-2R-99 (**b**) and WR-3-99 (**c**). Macrophyte (*dark circle*), transitional (*black cross*), and phytoplankton (*open square*) sediment classifications are presented on the depth axis. The left classification is based on normalized polyphosphate, normalized diatom biogenic silica and the total carbon to total nitrogen ratio. The right classification is based on normalized total phosphorus, normalized diatom biogenic silica and the total carbon to total nitrogen ratio. ^{210}Pb dates are plotted on the right axis

Comparison of data from core LH-4-99 with data from the other Lake Harris cores highlights the sensitivity of this statistical analysis and the advantage of using a multi-proxy, multi-core approach. For instance, three samples (52, 56, 68 cm) in LH-4-99 with high concentrations of $BSi_{Diatoms}$ were classified as transitional sediments, but might have been classified as macrophyte-derived, had only TP and TC:TN been considered. This multi-core analysis also demonstrates the site-to-site variability in sediment records from a single lake. The extreme stratigraphic variability seen in Poly-P, $BSi_{Diatoms}$ and $\delta^{13}C$ from core LH-4-99 is not seen in any other core from Lake Harris. This variability may reflect past spatial heterogeneity in the Lake Harris PPCS. Alternatively, it may indicate that LH-4, or the other sites, do not contain reliable paleo-environmental records, despite thick accumulations of soft sediment at all locations. These findings argue for a multi-proxy, multi-core approach to obtain the best historical interpretation.

Comparison with results from previous studies

Comparing phytoplankton- and macrophyte-derived sediments from all 17 cores in this study, we found that the shift from macrophyte to phytoplankton dominance was associated with about a 9-fold increase in Poly-P concentration and about a 5-fold increase in TP concentration. These changes exceed those found previously in the Harris chain of lakes (Kenney et al. 2001). In Lake Apopka (mean depth = 1.6 m), there was a ~6-fold increase in Poly-P concentrations and a ~3-fold increase in TP concentrations associated with the shift from macrophyte to phytoplankton dominance (Kenney et al. 2001). The larger relative increase in P concentrations in the lakes of the current study occurred because predisturbance sediment P concentrations were lower in these lakes than in Lake Apopka (Kenney et al. 2001). This may reflect, in part, differences in lake morphometry. If predisturbance, areal P loading were relatively constant in the Upper Ocklawaha River Basin, then one might expect the relatively deeper lakes of the current study to have

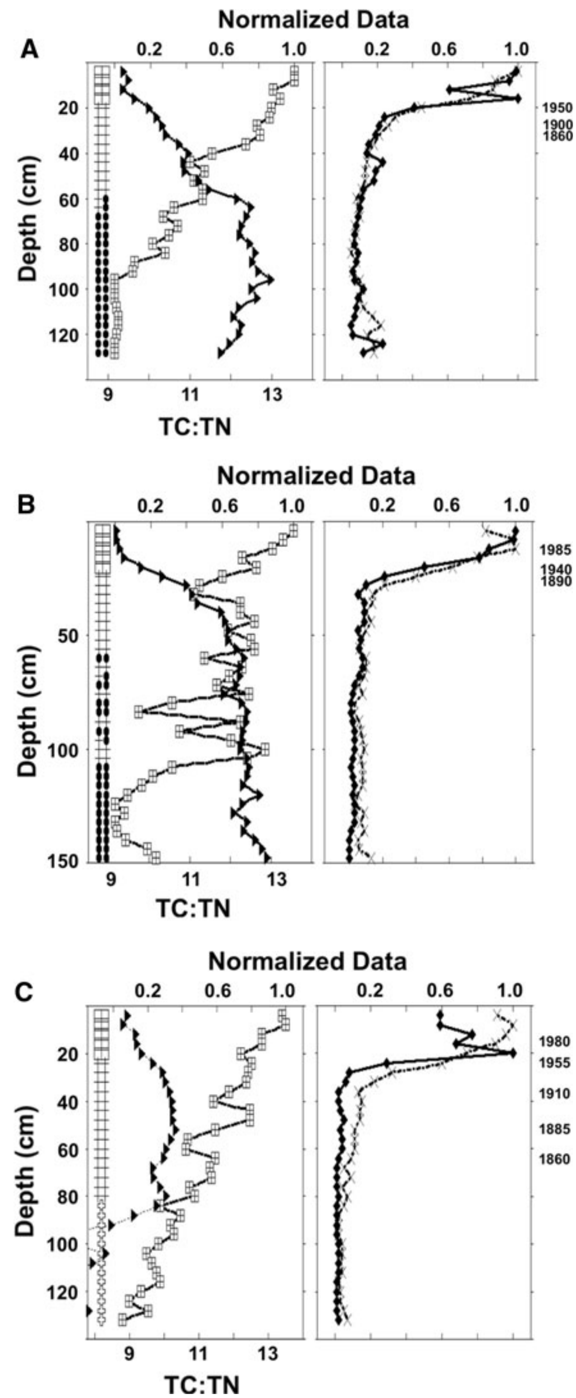

Fig. 8 Sediment total carbon to total nitrogen mass ratios ▶ (*dark triangles*), and normalized diatom biogenic silica (*open squares with crosses*), normalized polyphosphate (*dark diamonds*) and normalized total phosphorus (x) concentrations versus depth (cm) for Lake Yale cores LY-1-99 (**a**), LY-2-99 (**b**) and LY-3-99 (**c**). Macrophyte (*dark circle*), transitional (*black cross*), and phytoplankton (*open square*) sediment classifications are presented on the depth axis. The left classification is based on normalized polyphosphate, normalized diatom biogenic silica and the total carbon to total nitrogen ratio. The right classification is based on normalized total phosphorus, normalized diatom biogenic silica and the total carbon to total nitrogen ratio. Samples with large and variable total nitrogen (*open cross*) were considered outliers as described in the text. ^{210}Pb dates are plotted on the right axis

had lower limnetic P concentrations and produced sediments with lower P concentrations than shallower Lake Apopka.

In a previous study of shallow Florida lakes, TP, TC:TN and $BSi_{Sponges}$ were used in cluster analysis to differentiate sediment types (Kenney et al. 2002). In the current study, $BSi_{Diatoms}$ was more informative than $BSi_{Sponges}$ to identify clusters, which may reflect the fact that these lakes are deeper, and in their undisturbed state supported fewer macrophytes per unit water column volume than the very shallow lakes of the earlier study. Of the four lakes in the present study, only the smallest, Lake Beauclair, has a mean depth < 3.5 m. Of the five lakes in the previous study (Kenney et al. 2002), only the smallest, Little Lake Jackson has a mean depth > 3.0 m.

The greater importance of phytoplankton in the relatively deeper lakes of this study is also suggested by the TC:TN data (Table 5). Furthermore, the TC:TN of macrophyte-derived sediments in this study was lower than the TC:TN of macrophyte-derived sediments in the previous study. The latter finding indicates a greater relative contribution from phytoplankton to the sediments of the deeper lakes even under a macrophyte-dominated state. Likewise, TC:TN of phytoplankton sediments in this study was lower than the TC:TN of phytoplankton-derived sediments in the previous study. Lower TC:TN in phytoplankton-derived sediments from the current study indicates an even smaller contribution from macrophytes during the period of phytoplankton domination in these deeper lakes. All other factors being equal, regardless of what plants dominate the PPCS, sedimentation of phytoplankton-derived OM relative to macrophyte-derived OM is greater in the relatively deeper lakes.

The smaller contribution of macrophytes to the sediments of the deeper lakes in this study, compared to the very shallow lakes of Kenney et al. (2002), may explain the different responses of the two lake groups to human-induced P enrichment. Shallower lakes have a relatively greater area of lake bottom

Table 5 Results from the current study compared to the results of Kenney et al. (2002)

		n	Phytoplankton Sediments	*n*	Transitional Sediments	*n*	Macrophyte Sediments
Normalized	This Study	76	0.88 (0.12)	256	0.30 (0.17)	227	0.19 (0.14)
Total Phosphorus	Kenney et al. (2002)	105	0.79 (0.18)	95	0.48 (0.17)	33	0.31 (0.13)
Total Carbon: Total	This Study	76	9.2 (0.4)	256	10.7 (0.7)	227	12.1 (0.7)
Nitrogen	Kenney et al. (2002)	105	10.6 (0.8)	95	11.8 (0.7)	33	13.7 (0.7)
Normalized Sponge	This Study	76	0.26 (0.18)	256	0.46 (0.24)	227	0.48 (0.28)
Biogenic Silica	Kenney et al. (2002)	105	0.40 (0.15)	95	0.74 (0.14)	33	0.74 (0.20)
Diatom	This Study	76	76.2(23.2)	256	81.0 (27.6)	227	15.6 (15.5)
Biogenic Silica (mg/g)	Kenney et al. (2002)	105	71.9 (23.1)	95	41.8 (20.0)	33	25.0 (11.0)

Cluster means are listed followed by the standard deviation in parentheses

that can be colonized by macrophytes and thus are able to assimilate and sequester small increases in P loading into the macrophyte biomass, without an increase in phytoplankton production (Schelske et al. 2005). As P loading continues to increase, however, macrophyte communities in the shallower lakes are not competitive and are replaced by phytoplankton (Phillips et al. 1978). Such a PPCS shift was documented well in Lake Apopka (Schelske et al. 2010; Kenney et al. 2002). Deeper lakes of the current study had a smaller relative area that could be colonized by macrophytes, and the macrophyte community was less able to assimilate the added P that came with early cultural eutrophication. Consequently, there was an early increase in phytoplankton biomass and a shift to the transitional state. As P loading continued to increase, the nutrient was utilized by the existing phytoplankton community, but the shift to complete phytoplankton dominance in these larger-volume lakes was slower than that observed in the shallower lakes (Kenney et al. 2002).

Conclusions

Geochemical analyses of short sediment cores from four relatively shallow Florida lakes indicated that $BSi_{Diatoms}$, TC:TN, Poly-P and TP displayed clear stratigraphic trends that reflect a recent shift in the primary producer community. Using these sediment variables in k-means cluster analysis, we identified samples as macrophyte-derived, transitional, or phytoplankton-derived sediments. All four lakes displayed a predisturbance, macrophyte-dominated state, but entered a transitional state by the late 1800s. The lakes became phytoplankton-dominated by the middle of the twentieth century. The Poly-P and TP data indicate that the shift to phytoplankton dominance was attributable to increased phosphorus loading. Geochemical data from multiple sediment cores collected in Lake Harris indicated spatial differences in sedimentation patterns, arguing for multi-core analyses in such studies. Our results indicate that multiple geochemical measures, used in combination with multivariate statistical analyses, provide a powerful tool for identifying the source of sediment organic matter in shallow lakes.

Acknowledgments We thank the late Martha Love and Brandy DeArmond for administrative and technical assistance. Financial support was provided in part by the St. Johns River Water Management District, the University of Florida Foundation, Carl S. Swisher Endowment, and the University of Florida Land Use and Environmental Change Institute (LUECI).

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