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Complex trajectories of aquatic and terrestrial ecosystem shifts caused by multiple human-induced environmental stresses

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Abstract

Large shifts in the isotopic compositions of organic matter (OM) in lake sediments, over the last few hundred years, are commonly interpreted as representing changes in photosynthetic productivity corresponding to eutrophication or in the input of terrestrial OM due to human disturbances. Based on multiple-proxy data (C:N ratio, δ^{13}C and δ^{15}N of OM, δ^{13}C of calcite, lithology and fossil pollen) from a 700-year sediment core at White Lake, New Jersey (USA), we propose a new explanation that relates these large shifts in OM δ^{13}C and δ^{15}N to human-induced changes in aquatic OM producers. Combined records of geochronology, fossil pollen and lithology from White Lake reveal that the upland forest was cleared by European settlers for farmland beginning around 1745 A.D. and has gradually reforested since 1930 after the abandonment of the farmlands. For the pre-agricultural period, OM had relatively constant but extremely low $\delta^{13}C_{VPDB}$ (-35.8 to -34.5‰) and $\delta^{15}N_{Air}$ (-3.5 to -2.5‰) and high atomic C:N ratios (13.7 to 16.7), indicating a stable anoxic lake environment with prominent microbial producers. Following the human disturbance (since 1745), high OM mass accumulation rates and abundances of the green alga *Pediastrum* indicate an increase in aquatic photosynthetic productivity due to enhanced nutrient input from disturbed uplands. However, carbonate δ^{13}C remains constant or even decreases during this period, implying that increasing productivity did not elevate the δ^{13}C of dissolved inorganic carbon and thus cannot explain the observed large increase in OM δ^{13}C (7.4‰) and δ^{15}N (5.8‰) over this period. Instead, δ^{13}C, δ^{15}N and C:N ratios of OM and differences in δ^{13}C between calcite and OM suggest that the large increase in OM δ^{13}C and δ^{15}N can be attributed to a human-induced ecological shift in the predominant organic source from anaerobic bacteria to autotrophic phytoplankton. During the post-agricultural period, mass accumulation rates of OM, carbonate and silicate, and the δ^{13}C of OM and calcite all decreased significantly, corresponding to stabilization of the uplands. However, over the last 70 years, an intensifying aquatic stress from the deposition of ^{15}N-enriched industrial pollutants has resulted in a steady increase of 1.9‰ in δ^{15}N. Proxy records for lake (δ^{13}C and δ^{15}N of OM) and upland conditions (pollen and silicates) at White Lake show complex trajectories of the aquatic and terrestrial ecosystems in response to past human disturbances.
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1. INTRODUCTION

Human impacts on terrestrial and aquatic ecosystems have been readily identified from natural archives, in particular lake sediments, which provide multiple proxies for the reconstruction of past environments (e.g., Fuller et al., 1998; Meyers, 2006). Large shifts in pollen abundance (Fuller et al., 1998) and organic isotopic compositions (Cohen et al., 2005; Köster et al., 2005) widely observed in the uppermost parts of lake sediment sections have been related to anthropogenically induced ecological changes on landscape and in water. These shifts have been attributed to a variety of disturbances including forest clearance, agriculture, urbanization, and raw sewage inputs over the last few hundred years (Ekdahl et al., 2004; Routh et al.,

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2004). In addition, industrial emissions have also played an important role in influencing lake water chemistry via dry and wet atmospheric deposition over the last century (Holland et al., 2005). A recent study of the $\delta^{15}N$ of sediments from alpine lakes in the Colorado Front Range (USA) demonstrated that, whereas these lakes are far removed from industrial activities, the rates and magnitudes of recent ecological shifts responding to the excess loading of agriculturally and industrially derived nitrogen (N) are greater than those of any naturally induced changes over the last 14,000 years (Wolfe et al., 2001). However, such industrial effects are seldom reported, likely because of the difficulty in distinguishing them from other anthropogenic and natural processes based solely on the interpretation of stable isotope data.

The response of ecosystems to human disturbance and their potential for recovery/remediation constitute the basis for environment management and projecting future ecological trends, but the detailed processes are not well understood. For example, the generally accepted interpretative model for agricultural impacts on aquatic ecosystems involves a sequence of events and processes, including increased human-induced erosion of the landscape, elevated nutrient delivery to water bodies, eutrophication and consequent increase in aquatic primary productivity (APP) (Neumann et al., 2002; Routh et al., 2004; Köster et al., 2005). Enhanced APP may increase isotope values of organic matter (OM). Photosynthesis preferentially utilizes light isotopes (^{12}C and ^{14}N) so that the deposition of OM results in enrichments of heavy isotopes in dissolved inorganic carbon (DIC) and dissolved inorganic nitrogen (DIN), thus leading to elevated $\delta^{13}C$ and $\delta^{15}N$ of subsequently produced and deposited OM (McKenzie, 1985; Hodell and Schelske, 1998). Increased APP has been widely invoked to explain the increasing trend of isotope ratios in lacustrine sedimentary components (OM and calcite) formed in the last few hundred years because of its consistency with observed human disturbance history. However, the isotopic compositions of sediments do not always correlate well with APP. For example, a study at Crawford Lake in Ontario (Canada) shows no increase in carbonate $\delta^{13}C$ over the last 130 years despite a large increase in APP as indicated by fossil diatoms and OM mass accumulation rate (MAR) (Ekdahl et al., 2004). Discrepancies such as this suggest that the effect of APP on the isotopic compositions of DIC varies and may sometimes be overridden by other factors. The identification of anthropogenic impacts on lake processes can best be accomplished by the use of multiple proxies with differing sensitivities to the effects of various forcing factors such as changing OM and DIC/DIN inputs from watersheds, eutrophication and changes in rates of primary productivity, and redox change in the water column.

In this study, we carried out a multi-proxy paleolimnological investigation covering the past 700 years from White Lake, New Jersey (USA). The goals were to identify agricultural and industrial impacts on aquatic and terrestrial ecosystems, especially as these can be reconstructed from various lake sediment proxies such as stable isotopes of C and N. To trace the organic sources of lake sediments and possible biogeochemical processes, we employed several independent indicators: fossil pollen as an indicator of the landscape and land use history; *Pediastrum* (a green algae) abundance and MAR of major sedimentary components (OM, carbonate, and silicate) to monitor APP and allogenous detrital deposition; combined $\delta^{13}C$, $\delta^{15}N$ and C:N ratios of OM to distinguish both organic sources (terrestrial vs. aquatic) and internal lake biogeochemical processes; and $\delta^{13}C$ values of carbonate to detect variations in the C isotopic composition of DIC in the lake.

2. STUDY REGION AND SITE

White Lake (41°00′N, 74°55′W; altitude 138 m above sea level) is located in the limestone Paulinskill valley (northwestern New Jersey, USA) of the Valley and Ridge physiographic province, which is underlain by sandstones, shales, limestones, and conglomerates of Ordovician-Silurian ages (Fig. 1a and b; Witte, 2001). This region was glaciated during the last glaciation and is currently covered by hardwood forests dominated by oaks. Based on climate normals (1971–2000) at Belvidere, New Jersey, ~30 km southwest of White Lake, the regional average temperatures are 21.1 °C in the summer (June to August) and −1.5 °C in the winter (December to February), with mean annual precipitation of 1147 mm.

White Lake has a surface area of 0.26 km^2 and a small watershed of ~2 km^2. The maximum depth of the lake is 13.4 m with an average depth of 6.7 m. There is a spring and a small ephemeral inlet at its northeastern end (Fig. 1c). The present water budget of the lake is dominated by groundwater inputs and stream outflow to Paulinskill River (Fig. 1c). White Lake is characterized by relatively high pH (~8.5) and alkalinity (192 mg/L). The summer (May to August) surface-water temperatures recorded in 1997 and 1998 range from 21 to 28 °C (NJDFGW, 1999). The results of our two measurements (25.1 °C on June 23 and 26.6 °C on August 14, 2002) fall within this range. Marl (unconsolidated carbonate-rich sediment) is precipitated during the summer in the lake and visible as a light-colored band in the shallow water (<3 m) around the lake (Fig. 1c).

3. MATERIALS AND METHODS

3.1. Collections of sediment cores

Two parallel sediment cores were retrieved from the deepest part of White Lake in March 2003 using a Glew-type gravity corer (60-cm core WL03-3) and a freeze corer (35-cm core WL03-4; see Fig. 1c and d). Core WL03-3 was cut into 1-cm thick slices. All or selected slices were used for loss-on-ignition (LOI), accelerator mass spectrometry (AMS) ^{14}C dating, stable isotope measurements, and fossil pollen analyses. Core WL03-4 was used only for ^{210}Pb dating to help establish an age model for core WL03-3.

3.2. ^{210}Pb and ^{14}C dating analyses

A total of 24 sediment slices from the uppermost 33 cm of freeze core WL03-4 were analyzed for ^{210}Pb activities using distillation and alpha-spectrometry methods at the

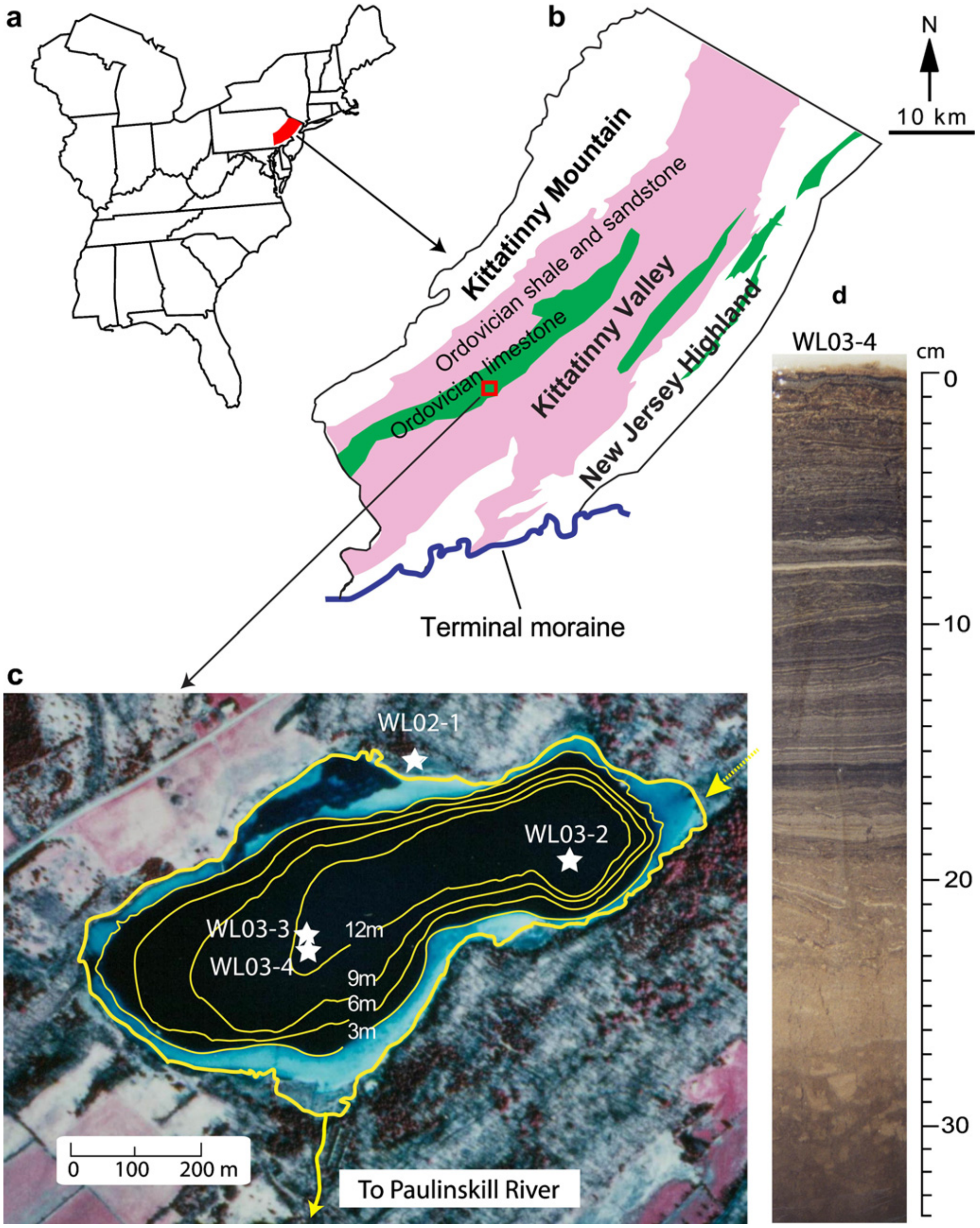

Fig. 1. Location maps and sediment core. (a) Simplified map shows the location of the study region in the eastern USA. (b) Regional geology of northern New Jersey and location of White Lake (square) in a limestone valley (dark green). Note that the study site is to the north of the terminal moraine of last glaciation (Witte, 2001). (c) Air photo and bathymetric map of White Lake (bathymetry from NJDFGW, 1999) showing locations of our studied cores WL03-3 and WL03-4. Also shown are two cores used in previous studies: core WL02-1 from lakeside wetlands for the late-glacial-to-early Holocene climate reconstruction (Yu, 2007), and core WL03-2 from similar depth for mineral-magnetic investigation (Li et al., 2006, 2007). The light-colored band in shallow water around the lake (generally <3 m) is a marl bench formed by seasonal carbonate precipitation. (d) A photo of the freeze core WL03-4 from White Lake. Lithology (from bottom to top) changes from gyttja, through a marl section between 30 and 19 cm, to the laminated sediment.

St. Croix Watershed Research Station of the Science Museum of Minnesota (St. Croix, MN). Dates were determined according to the model of constant rate of supply of excess ^{210}Pb (Appleby and Oldfield, 1978). Because cores WL03-3 and WL03-4 could be well correlated visually by their striking lithologic boundaries and thick marl bands (see Fig. 1d), the ^{210}Pb dating results of core WL03-4 were readily transferred to the upper section of core WL03-3. Terrestrial plant macrofossils (mostly tree anthers, leaves, and needles) from two depths in the lower section of core WL03-3 were used for AMS ^{14}C dating at the University of Arizona (Table 1). Both ^{14}C dates were calibrated based on the CALIB 5.01 program using INTCAL04 calibration data set (Reimer et al., 2004). Linear interpolations of dated intervals were used to derive the age model for core WL03-3 (see Fig. 2).

Table 1
Accelerator mass spectrometry (AMS) ^{14}C dates from core WL03-3, White Lake, northwestern New Jersey, USA

Depth (cm)	Dating material	Sample weight (mg)	δ^{13}C (‰)	AMS Lab #[a]	AMS ^{14}C dates ± 1σ (BP)	Calendar ages Mid-point ± 2σ ranges[b]
45–46	Spruce anthers	2.3	−25.60	AA63243	220 ± 50	1663 ± 44 A.D.[c]
55–58	Leaf fragment, plant stem, needles, anthers	1.3	−27.26	AA63244	500 ± 80	1405.5 ± 116.5 A.D.

[a] AA = University of Arizona AMS lab.

[b] Calibration is based on INTCAL04 calibration data set (Reimer et al., 2004) using calibration program *CALIB* version 5.0.1.

[c] Two possible ages were given from calibration: 1663 ± 44 A.D. with probability of 0.30 and 1772.5 ± 53.5 with probability of 0.41. The age of 1663 ± 44 A.D. was used for the age model because it fits better other age determinations.

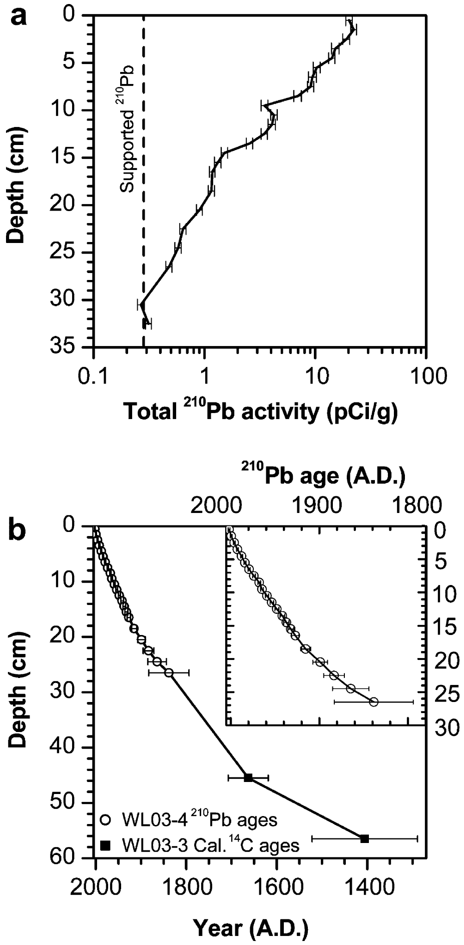

Fig. 2. Age-depth model and chronology at White Lake. (a) Total ^{210}Pb activity and supported ^{210}Pb from core WL03-4. Note that the depth has been adjusted to that of the parallel core WL03-3. (b) Age-depth relationship for core WL03-3. ^{210}Pb dates were transferred from core WL03-4 based on visible lithologic changes. All the error bars represent 2σ ranges.

3.3. Pollen analysis

Sediment sub-samples (0.7 cm^3 in volume) from selected sections of core WL03-3 were prepared for pollen counting according to the modified standard acetolysis procedure, involving treatments of HCl, KOH, HF and acetolysis (Faegri and Iversen, 1989). Pollen sums used for pollen percentage calculations ranged from 225 to 707 grains of terrestrial pollen and spores for each sample. Poaceae (grass) pollen grains were counted as two size classes, with large grass pollen (45–80 μm in diameter) probably representing cereal types and small ones (<45 μm) likely representing both weeds and cereals. The green alga *Pediastrum* was also counted in pollen preparations and used as an indicator of lake productivity (e.g., Cronberg, 1982). A principle component analysis (PCA) was performed on the percentage data of dominant pollen types (21 pollen taxa) to facilitate comparisons of the vegetation shifts with other proxy records for the past 700 years (see Yu, 2003 for description of methods).

3.4. Loss-on-ignition analysis

Sediment sub-samples (0.7 cm^3 in volume) from each slice of core WL03-3 were dried overnight at 100 °C, and then successively combusted at 550 and 1000 °C. Contents of water, OM, carbonate, and silicate were estimated by weight loss in each step and final residues (Heiri et al., 2001). These results were then used, along with the age constraints, to calculate the MAR of OM, carbonate, and silicate.

3.5. δ^{13}C and δ^{15}N of organic matter

Each slice of the upper 38-cm section and every other slice in the lower 22-cm section of core WL03-3 were analyzed for δ^{13}C and δ^{15}N employing sealed-tube methods described by Li and Bebout (2005). Freeze-dried sediment subsamples were reacted with 1 N HCl to remove carbonate. The decalcified samples were freeze-dried again, homogenized, weighed (~3 mg for δ^{13}C analysis and ~20 mg for δ^{15}N analysis) and loaded into quartz tubes (6 mm outer diameter; 4 mm inner diameter) together with Cu–CuO$_x$ reagent. The tubes were then sealed at high vacuum and combusted at 910 °C for 3 h in a programmable furnace. The resulting CO$_2$ and N$_2$ were cryogenically purified and measured for δ^{13}C and δ^{15}N in dual-inlet mode using a Finnigan MAT 252 mass spectrometer at Lehigh

University. The results are reported relative to the Vienna Pee Dee Belemnite (VPDB) standard for $\delta^{13}C$ and atmospheric N_2 for $\delta^{15}N$. The analytical reproducibility is better than 0.1‰ (2σ) for both isotope measurements based on replicate analyses of international and internal standards and individual sediment samples. Carbon (C) concentration was determined by an Hg manometer on the extraction line, whereas N concentration was determined by measuring the m/z-28 signal for calibrated inlet volumes in the mass spectrometer. The uncertainties for duplicate C and N concentration measurements are less than 5% of mean values.

3.6. $\delta^{13}C$ of calcite

Each slice in the upper 36-cm section, where carbonate content is relatively high, was analyzed for carbonate $\delta^{13}C$. Bulk calcite samples from the freeze-dried marl sediments were hand-cleaned by removal of biogenic shells and plant fragments under a stereo microscope. The cleaned samples were then reacted overnight with 100% phosphoric acid in glass vessels held at 25 °C in a water bath (McCrea, 1950). The resulting CO_2 was cryogenically purified and measured for $\delta^{13}C$ and $\delta^{18}O$ in dual-inlet mode using a Finnigan MAT 252 mass spectrometer at Lehigh University. Multiple analyses of lab standards and lake sediment samples show analytical reproducibility of better than 0.1‰ (2σ), and the data are reported relative to the VPDB standard.

4. RESULTS

4.1. Age model and chronology

The excess ^{210}Pb activity in core WL03-4 shows downcore exponential decay (Fig. 2a), and the calculated ages for the upper 27 cm cover the last 165 years (Fig. 2b). Linear interpolation of both ^{210}Pb ages and two calibrated ^{14}C ages (Table 1) were used to develop the age model and chronology of core WL03-3 (Fig. 2b). All ages used in the following discussion are based on this age model and given in calendar years (A.D.), unless otherwise noted.

4.2. Fossil pollen records

The pollen diagram from core WL03-3 shows two pollen zones based on constrained cluster analysis (CONISS; Fig. 3). Zone WL(03-3)-1 spanning from ~1250 to 1745 is dominated by *Quercus* (oak) and other trees such as *Pinus* (pine), *Tsuga* (hemlock), and *Castanea* (chestnut), indicating hardwood-dominant forests. Zone WL(03-3)-2 is characterized by an increase in herb pollen percentages, mostly from *Ambrosia* (ragweed). This zone can be divided into two subzones. Subzone WL(03-3)-2a from 1745 to 1930 is characterized by a continuous upsection increase in pollen percentages of herbs, such as *Ambrosia*, Poaceae (grass) and *Rumex* (sorrel), and an upsection decrease in pollen percentages of trees, such as *Quercus*, *Tsuga*, *Pinus*, and *Betula* (birch), indicating the onset and intensification of deforestation and land clearance for farming after the European settlement. Subzone WL(03-3)-2b since 1930 is characterized by a decrease in herb pollen percentage and an increase in tree (e.g., *Quercus* and *Betula*) pollen percentage, indicating the gradual reforestation following the abandonment of farmland. The decline and near disappearance of *Castanea* since the early 1900s was caused by chestnut blight. Low abundance of large grass grains in Subzone WL(03-3)-2b suggests decreased contribution from cereal crops. The percentage of *Pediastrum* shows a sharp increase at the beginning of Zone WL(03-3)-2 (Fig. 3).

4.3. Sediment lithology and loss-on-ignition results

Three lithologic units were distinguished in both cores (Figs. 1d, 4a and c). From the bottom to the top of the sec-

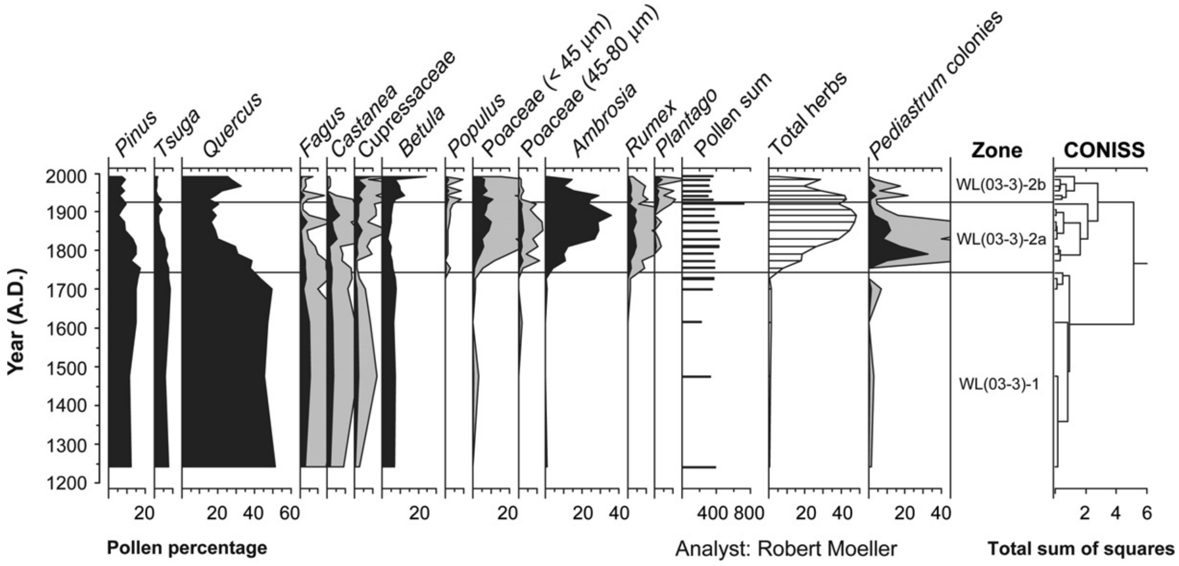

Fig. 3. Summary percentage pollen diagram of 700-year sediment core WL03-3 at White Lake. Gray shading areas represent 5x exaggeration. Only selected taxa shown.

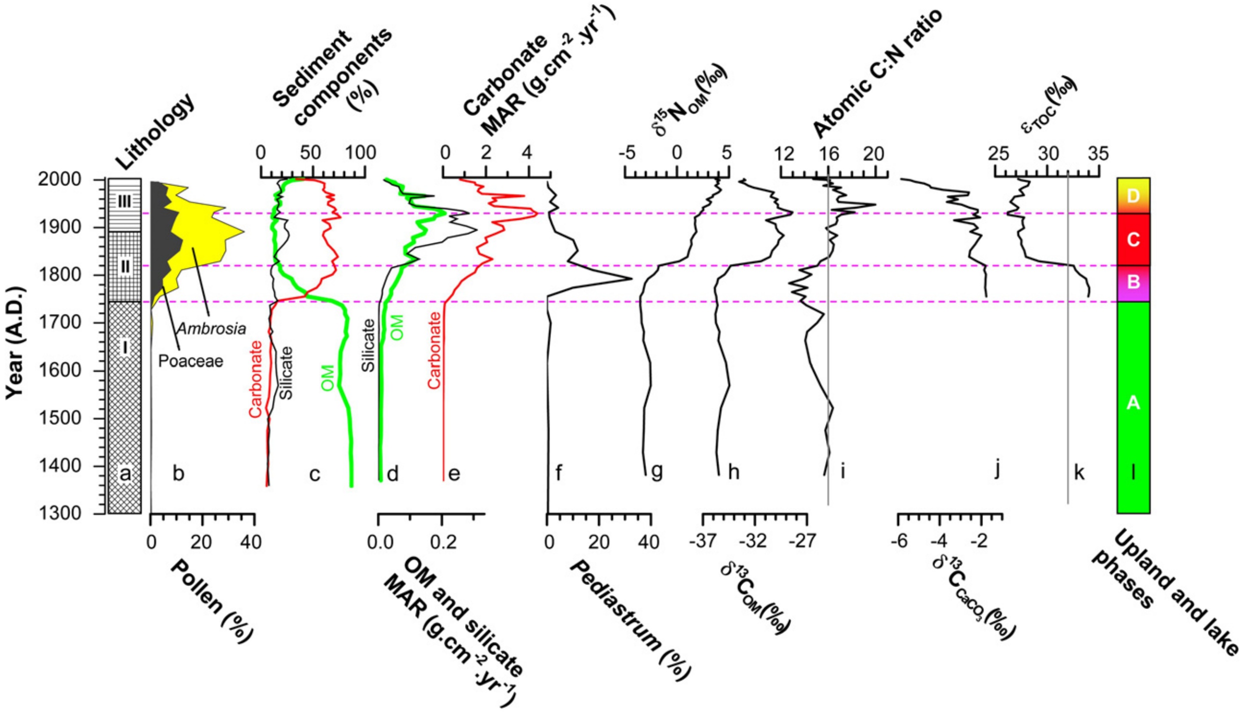

Fig. 4. Multiple-proxy records from core WL03-3 for the last 700 years. (a) sediment lithology: I—gyttja, II—marl, and III—laminated sediments, (b) pollen percentages of *Ambrosia* and Poaceae, (c) concentrations of sediment components, (d) mass accumulation rates (MAR) of OM and silicate, (e) carbonate MAR, (f) *Pediastrum* percentage, (g) $\delta^{15}N$ of organic matter, (h) $\delta^{13}C$ of organic matter, (i) atomic C:N ratio of organic matter-gray vertical line marks the stable-state average value of ~16, (j) $\delta^{13}C$ of calcite, (k) $\delta^{13}C$ difference between calcite and OM-values greater than +32‰ (gray vertical line) suggest significant microbial contribution (Hayes et al., 1999), (l) upland and lake environmental phases based on the variations of pollen, sediment lithology, and isotopes: A—pre-agricultural, B—early-agricultural, C—peak-agricultural, and D—post-agricultural phases.

tion, they are: (I) a gyttja (OM-rich mud) section before 1745 containing relatively constant OM (85%), carbonate (7%) and silicates (8%), with slightly low OM and high silicate between 1500 and 1700; (II) a marl section from 1745 to 1895 with 10–20% OM, 55–80% carbonate, and 5–25% silicate content; and (III) laminated sediments (light carbonate and dark OM layers) from 1895 to the present with 10–30% OM, 50–75% carbonate, and 15–25% silicate content.

4.4. $\delta^{13}C$, $\delta^{15}N$ and atomic C:N ratios of organic matter

The C and N concentrations and isotopic compositions of the decalcified sediments are presumed to represent those of OM. The low contents of silicate in the sediments reduce the potential contribution of structurally bound NH_4^+ (in clay minerals) to negligible levels (see Fig. 4c). $\delta^{13}C$, $\delta^{15}N$, and C:N ratios of OM display significant variability over the last 700 years (Fig. 4g–i). During the period from ~1350 to 1745, OM was constant in its $\delta^{13}C$ (about −36‰) and $\delta^{15}N$ (about −3.5‰), except a period of slightly higher $\delta^{13}C$ and higher $\delta^{15}N$ between 1500 and 1700 (Fig. 4g and h). Organic C:N ratios were also relatively constant before 1500, with slightly lower values between 1500 and 1700, but rapidly decreased by ~3 from 1720 to 1745. During the period from 1745 to 1930, $\delta^{13}C$ and $\delta^{15}N$ rapidly increased at ~1820 and gradually increased before and after that time. During this period, the overall increases in the isotope values for OM reach 7.4‰ for $\delta^{13}C$ (from −35.8 to −28.4‰) and 5.8‰ for $\delta^{15}N$ (from −3.5 to +2.3‰). C:N ratios show a sawtooth pattern with relatively low values for the period of 1745 to 1820 and an increase from 15.3 to 18.7 for the period of 1820 to 1930. After 1930, both $\delta^{13}C$ and C:N ratios decreased rapidly, from −28.4 to −33.1‰ and from 20.8 to 14.9, respectively; however, $\delta^{15}N$ gradually increased from +2.3‰ in 1930 to about +4‰, before leveling off at ~1980 (Fig. 4g–i).

4.5. $\delta^{13}C$ of authigenic calcite

In core WL03-3, C isotopic ratios of carbonate were obtainable only for samples formed after 1745 when carbonate content was high. Because this study is focused on discussion of human disturbances and ecosystem responses and $\delta^{18}O$ values of carbonate mostly reflect climate changes, the $\delta^{18}O$ data are not presented here. In fact, the variation in the $\delta^{18}O$ of carbonate from White Lake shows patterns similar to those in the climate-controlled $\delta^{18}O$ records from some other lakes in the northeastern USA (e.g., Cronin et al., 2003), further suggesting that the $\delta^{13}C$ data reported in this study indeed represent authigenic carbonate. $\delta^{13}C$ values are uniform at −1.8‰ for the period of

1745 to 1820, fluctuate around −2.2‰ with a trend of decrease for the period of 1820 to 1930, and show a large decrease of 3.7‰ (from −2.2 to −5.9‰) for the period of 1930 to 2003 (Fig. 4j).

5. DISCUSSION

On the basis of combined records from sediment lithology, fossil pollen and isotopic compositions of OM and calcite, we divide the profile into four distinct terrestrial and aquatic environmental phases for White Lake over the last 700 years (Fig. 4l): (A) pre-agricultural phase (before 1745), (B) early-agricultural phase (1745–1820), (C) peak-agricultural phase (1820–1930), and (D) post-agricultural phase (1930–2003).

5.1. Nature of terrestrial and aquatic ecosystems in the pre-agricultural period

During the pre-agricultural period, the pollen record shows relatively constant tree abundances (Fig. 3), indicating a mature and stable hardwood-forest landscape. Similarly, MAR of OM, carbonate and silicate and $\delta^{13}C$, $\delta^{15}N$ and C:N ratios of OM are relatively invariable for this period except for slight variations in $\delta^{13}C$, $\delta^{15}N$ and C:N ratios for the period of 1500–1700 (Fig. 4g–i), suggesting a stable aquatic environment in White Lake. The low carbonate content (∼7%) in the sediment indicates that the lake, or at least the bottom water, was less alkaline than at present. Compared to non-disturbed Holocene sediments in other lakes (see the reviews by Meyers and Ishiwatari, 1995; Talbot, 2001), White Lake sediments are characterized by low $\delta^{13}C$ values (−35.8 to −34.5‰), low $\delta^{15}N$ values (−3.5 to −2.5‰), and high OM C:N ratios (13.7–16.7). These $\delta^{13}C$ and $\delta^{15}N$ values are among the lowest data reported to date for Holocene lacustrine sedimentary OM (e.g., Hammarlund et al., 1997; Mayer and Schwark, 1999; Teranes and Bernasconi, 2005).

Generally, the isotopic compositions and C:N ratios of sedimentary OM in a lake depend on the organic source (aquatic vs. terrestrial) and can be affected by diagenetic processes. Most of the photosynthetic OM produced by phytoplankton through uptake of DIC and DIN in the oxic photic zone has $\delta^{13}C$ values of −30 to −20‰ and $\delta^{15}N$ values of 2 to 10‰ with atomic C:N ratios less than 10 (Meyers, 1994). At eutrophic conditions, N_2-fixing processes (Junium and Arthur, 2007) or biological uptake of ammonium (preferentially $^{14}NH_3$) generated by the decomposition of OM (e.g., Takahashi et al., 1995; Présing et al., 2001) can produce biomass characterized by $\delta^{15}N$ of −4 to +1‰ (Minagawa and Wada, 1986; MacGregor et al., 2001; Struck et al., 2001). The assimilation by heterotrophic bacterial communities of ^{13}C-depleted methane produced during diagenetic processes can yield biomass with extremely low $\delta^{13}C$ (Gong and Hollander, 1997; Hollander and Smith, 2001; Bastviken et al., 2003; Teranes and Bernasconi, 2005). Terrestrial C3 plants have $\delta^{13}C$ similar to that of typical phytoplankton but with higher C:N ratios (>20), whereas terrestrial C4 plants show higher $\delta^{13}C$ values of −15 to −10‰ and C:N ratios of >30 (Meyers, 1994).

The source signatures may be significantly affected under anoxic conditions, where most of the N-rich and ^{13}C- and ^{15}N-enriched labile organic compounds (e.g., amino acid) are preferentially removed by diagenetic processes such as denitrification (Deines, 1980; Harvey et al., 1995; Lee et al., 2000; Van Mooy et al., 2002), causing an increase in C:N ratios (Twichell et al., 2002; Meyers and Bernasconi, 2005) and a decrease in $\delta^{13}C$ and $\delta^{15}N$ of residual sediment OM (Sweeney and Kaplan, 1980; Nakatsuka et al., 1997; Lehmann et al., 2002). Under oxic environments, both labile and refractory organic compounds (e.g., lipid, lignin) can be decomposed, so the shift in C:N ratio is not significant. However, kinetic isotopic effects (i.e., preferential loss of light isotopes ^{12}C and ^{14}N) accompanying the partial decomposition of OM can lead to increases in $\delta^{13}C$ and $\delta^{15}N$ (Freudenthal et al., 2001; Macko and Estep, 1984; Lehmann et al., 2002). The magnitude of this isotopic increase is small when OM MAR is high, but can reach 3–5‰ when OM MAR is low (François et al., 1997; Altabet et al., 1999). On the other hand, microbial biomass may be relatively resistant to diagenesis (Ogawa et al., 2001).

The high C:N ratios of OM in the White Lake sediments could be attributed to (1) significant contribution of lignin- and cellulose-rich terrestrial OM (characterized by C:N ratios > 20; Meyers, 1994), (2) N limitation in the lake, or (3) selective degradation of N-rich components of aquatic OM. Possibility (1) can be excluded because the extremely low $\delta^{13}C$ values of the OM in the sediments differ significantly from the $\delta^{13}C$ of terrestrial plants; the latter are characterized as having much higher values (e.g., −14 to −10‰ for C4 plants and −30 to −20‰ for C3 plants; our two measurements of the terrestrial plant remnants in the core gave $\delta^{13}C$ of −25.6 and −27.3‰; Table 1). Possibilities (2) and (3) are difficult to distinguish from each other. Selective degradation mostly occurs in anoxic aquatic environments, where N is often limited because of denitrification. Therefore, both (2) and (3) could be responsible for the high OM C:N ratios. However, neither (2) nor (3) can explain the extremely low $\delta^{13}C$ and $\delta^{15}N$ values observed in White Lake. Nitrogen limitation may result in less biological discrimination of isotopes and thus produce high $\delta^{15}N$ values. On the other hand, selective degradation can only shift the isotope ratios of OM by a relatively small magnitude (e.g., 1–2‰) and thus cannot yield the observed negative $\delta^{15}N$ values, presuming that the OM is mostly from phytoplankton typically with $\delta^{15}N$ greater than 2‰ (Talbot, 2001). In previous studies, the $\delta^{15}N$ values near or lower than 0‰ are mostly attributed to N_2 fixation or uptake of ^{15}N-depleted ammonium (Waser et al., 1998; Montoya et al., 2002). These processes mostly occur in eutrophic lakes or in anoxic waters where nitrate is unavailable due to denitrification. N_2 fixation has been proposed to explain the low $\delta^{15}N$ values of OM in the sapropels from the Eastern Mediterranean Sea (Calvert et al., 1992; Meyers and Bernasconi, 2005) and the marine shales formed during the Aptian–Albian and Cenomanian–Turonian Oceanic Anoxic Events (Kuypers et al., 2002; Junium and Arthur, 2007). In the case of the Oceanic Anoxic Events, the key role of N_2-fixing cyanobacteria has been demonstrated by molecular-fossil investigation (Kuypers et al., 2004). Therefore, the low

$\delta^{15}N$ values of sedimentary OM in White Lake, coupled with high C:N ratios, are diagnostic of an anoxic aquatic environment during the pre-agricultural period. This anoxic environment would have been established and maintained in the deeper water column during periods of thermal stratification by progressive oxygen consumption during the decomposition of sinking particulate OM. Denitrification in this lower anoxic water layer could have transformed nitrate in groundwater (presumably input from the lower part of the lake) to N_2 before upwelling into the photic zone, optimizing the process of N_2 fixation in the upper water layer. At the same time, ammonium assimilation could be an important process in the lower anoxic zone. Preferential uptake of ^{14}N from recycled ammonium, by algae or bacteria, may contribute to the low $\delta^{15}N$ of bulk OM in the sediments. Given the fact that the water column is only ~13 m deep, it is also possible that the lower anoxic zone may in part overlap with the photic zone, facilitating N_2 fixation by cyanobacteria as well as ammonium uptake by phytoplankton.

Carbon cycling under anoxic conditions may also entail the production and deposition of ^{13}C-depleted microbial biomass. Both conceptual models (Hollander and Smith, 2001) and field measurements (Blumenberg et al., 2007) indicate that methanotrophy and/or methane oxidation processes are important in and above anoxic zones. As examples of significant microbial contribution to the sediments, $\delta^{13}C$ values of −30 to −45‰ have been reported for the bacterial biomarkers from the anoxic depocenter of the Santa Monica Basin, California (Gong and Hollander, 1997) and from eutrophic Lake Mendota, Wisconsin (Hollander and Smith, 2001), as well as for bulk OM from Baldeggersee, Switzerland (Teranes and Bernasconi, 2005). In White Lake, the carbonate $\delta^{13}C$ values for the early-agricultural period (Fig. 4j) are similar to those for the early Holocene (Yu, 2007) and show relatively uniform and typical values around −2‰. Because the C-isotope fractionation between calcite and DIC is relatively constant under normal water temperatures, calcite $\delta^{13}C$ is a reliable indicator of the isotopic variation of DIC. Thus the relatively constant carbonate $\delta^{13}C$ values suggest a relatively constant and typical isotopic composition of DIC in the lake in these periods. Therefore, sedimentary OM $\delta^{13}C$ values as low as −36‰ in White Lake cannot be explained by ^{13}C-depletion of DIC resulting from hydrologic change and enhanced input of soil-respired CO_2, as in the case of Lake Tibetanus in northern Sweden (Hammarlund et al., 1997). Instead, these extremely low OM $\delta^{13}C$ values more likely reflect significant contribution from microbial biomass possibly produced through methanotrophy.

The secondary peaks in $\delta^{13}C$, $\delta^{15}N$ and decreasing C:N ratios for the period of 1500–1700 may correspond to the Little Ice Age (Cronin et al., 2003; Pederson et al., 2005). During this period, colder climate and lowered nutrient influx into the lake could have resulted in a decrease in APP as inferred from the slight decrease of *Pediastrum* abundance (Fig. 3), alleviating the oxygen deficiency in the water column. In response to this less anoxic environment, selective degradation of the N-rich and isotopically heavy labile compounds decreased, leading to slight increase in $\delta^{13}C$ and $\delta^{15}N$ but decrease in C:N ratios of OM (Fig. 4g–i).

5.2. Ecological responses to deforestation and landscape disturbance

At the beginning of pollen zone WL(03-3)-2a at ~1745, the increase in pollen percentages of *Ambrosia*, Poaceae, *Rumex* and other herbs and the decrease in *Quercus* and *Pinus* tree pollen reflect forest clearance and agricultural activities after the initial settlement of Europeans in the region (Fig. 3). *Ambrosia* and other weeds proliferated in disturbed lands and around agricultural fields. The strong correlation between these fossil pollen changes and silicate MAR (Fig. 4b and d) indicates that the silicate deposited in White Lake was mostly eroded from the upland, consistent with our preliminary results of biogenic-silica analyses indicating that only 5–20% of silica is biogenic in origin. Following the deforestation for farming and also possible human-induced hydrologic change, silicate MAR increased by more than an order of magnitude within 150 years (from 1745 to 1895), exceeding the rate at any earlier time (Fig. 4d). These large inputs of detrital minerals would have been accompanied by nutrients, in dissolved as well as particulate forms, which would have shifted the lake chemistry from moderately hardwater to distinctly alkaline and also increased APP. Enhanced photosynthetic production after 1745 is indicated by accelerated OM MAR and increased *Pediastrum* abundance, along with a corresponding decrease in C:N ratio (Fig. 4d, f, and i). In this hardwater lake, the elevated rates of CO_2 uptake by photosynthesis and removal of OM from the water column would increase the pH and shift the DIC equilibrium, favoring the precipitation of carbonate (Hodell et al., 1998). In addition, deforestation and resultant reduction in evapotranspiration would have increased groundwater flow and bicarbonate inputs to the lake, which would further stimulate carbonate precipitation in the lake. These changes resulted in the major lithologic change from gyttja to marl starting at ~1745 (Figs. 1d, 4a and c) and thus showed no obvious time lag.

Peak abundance of ragweed pollen between 1820 and 1930 indicates maximum forest clearance and agricultural activities in the region (Fig. 4b). Large Poaceae (grass) pollen reflects cereal cultivation on nearby ploughed soils (Fig. 3). Enhanced eutrophication would have caused water column anoxia to expand into shallower depths and/or over longer periods of the year in response to the greater consumption of oxygen by settling OM. In this increasingly anoxic-water environment, the summer calcite production could have been preserved as distinct seasonal layers because of the lack of bioturbation by bottom-living organisms at the water-sediment interface (Lotter et al., 1997; Gruber et al., 2000), explaining the laminated sediments after 1895 in White Lake.

One possible geochemical effect of enhanced photosynthesis is to increase $\delta^{13}C$ and $\delta^{15}N$ values of DIC and DIN and successively produced OM (McKenzie, 1985; Hodell and Schelske, 1998). In this case, a covariation of $\delta^{13}C$ between OM and authigenic carbonate is expected in calcareous lakes (Hammarlund et al., 1997; Hodell et al., 1998); however, this was not observed in the White Lake records for the agricultural periods (Fig. 4h and j). The $\delta^{13}C$ values of calcite from White Lake remain constant during the period of 1745–1820 and show a slightly decreasing trend from 1820 to 1930 (Fig. 4j), indicating that the enhanced lake eutrophication had little effect on the δ^{13}C of DIC during this period. This may be due to the deforestation-induced elevated DIC inputs. The deforestation could have enhanced dissolution of the limestone bedrock and accelerated groundwater flow, resulting in the transport of large amounts of DIC into the lake. If the biologically assimilated C is only a small part of the lake DIC budget, δ^{13}C of DIC may not be significantly shifted with the removal of OM even in eutrophic lakes. The trend of decreasing carbonate δ^{13}C (up to 1.5‰) for the period of 1820 to 1930—most of it at ~1820—cannot be fully explained by exchange between lake DIC and atmospheric CO_2 (a decrease of only ~0.3‰ in δ^{13}C over this period; Francey et al., 1999), but can be attributed to greater contribution from a ^{13}C-depleted source (e.g., enhanced production, upwelling and oxidation of methane).

To evaluate the microbial effect, Hayes et al. (1999) proposed using the index of δ^{13}C difference between carbonate and OM ($\varepsilon_{\text{total organic C }(TOC)} = \delta^{13}\text{C}_{\text{carbonate}} - \delta^{13}\text{C}_{\text{OM}}$), where ε_{TOC} values larger than +32‰ imply significant incorporation of ^{13}C-depleted bacterial biomass into the sediment. This index has been applied to probe the microbial contribution to the sedimentary OM in Baldeggersee, Switzerland (Teranes and Bernasconi, 2005). Early-agricultural sediments from White Lake show ε_{TOC} values consistently larger than +32‰ with slight decrease between 1745 and 1820 (Fig. 4k), implying that the microbial contribution, although slowly decreasing, was significant in the sedimentary OM. Given the essential constancy of OM δ^{13}C between this time and the end of the pre-agricultural period, we suggest that the low OM δ^{13}C values for the pre-agricultural period are also related to microbial biomass. A rapid decrease in ε_{TOC} from +32‰ to +28‰ occurred around 1820, indicating a dramatically diminished microbial contribution. The shift partly reflects dilution of microbial biomass by accelerating deposition of phytoplankton OM, but a short-lived decrease in the microbial populations (methanotrophic and N_2-fixing bacteria) may have caused the abruptness of the shift (see below).

Sedimentary OM shows large variations in δ^{13}C, δ^{15}N and C:N ratios in response to the anthropogenic aquatic environmental changes during the agricultural periods (Fig. 4g–i). Organic δ^{13}C and δ^{15}N during the early-agricultural period show small increases, likely attributable to a relative decrease in microbial contributions, due to dilution by increasing phytoplankton OM. The C:N ratios of OM for the 1745 to 1820 period of initial settlement and forest clearance vary from 12 to 14, lower than those in both the pre-agricultural and peak-agricultural periods (Fig. 5), suggesting that (1) the effect of differential degradation was reduced from that prevailing during the pre-agricultural period, and (2) any increase in terrestrial OM input was more than offset by the increase in photosynthetic OM produced in the lake. During the peak-agricultural period, OM C:N ratios are independent from MAR of both OM and silicate and show similar values to those in the post-agricultural period (Fig. 5), suggesting an insensitivity to terrestrial inputs, and resumption of more selective degradation under increasingly anoxic conditions.

The transition into the peak-agricultural period at ~1820 is marked by significant shifts in the isotope ratios. Large increases in δ^{15}N (~2‰) and δ^{13}C of OM (~4‰) coincide with a small downshift in δ^{13}C (~0.8‰) of carbonate. Following these abrupt isotope shifts around 1820, positive trends in δ^{15}N and δ^{13}C of OM continue through the peak-agricultural period, but at much reduced rates (Fig. 4). These shifts and trends can be effectively examined in context of the steadily increasing MAR of OM (Figs. 4 and 6). Assuming plausible δ^{13}C values for methane-derived bacteria (−40‰) and for phytoplankton (−23‰), we calculate that eutrophication through the pre- and

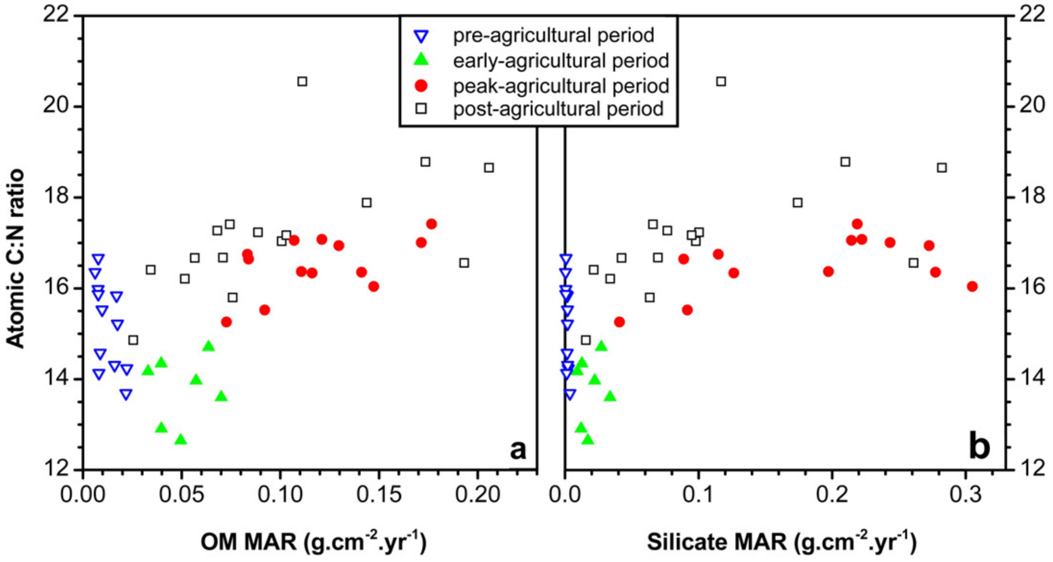

Fig. 5. Scatter plots showing (a) atomic C:N ratio of OM vs. OM accumulation rate (MAR) and (b) silicate MAR during different time periods. No obvious covariation exists for any period, suggesting that terrestrial OM input to the sediments is not important.

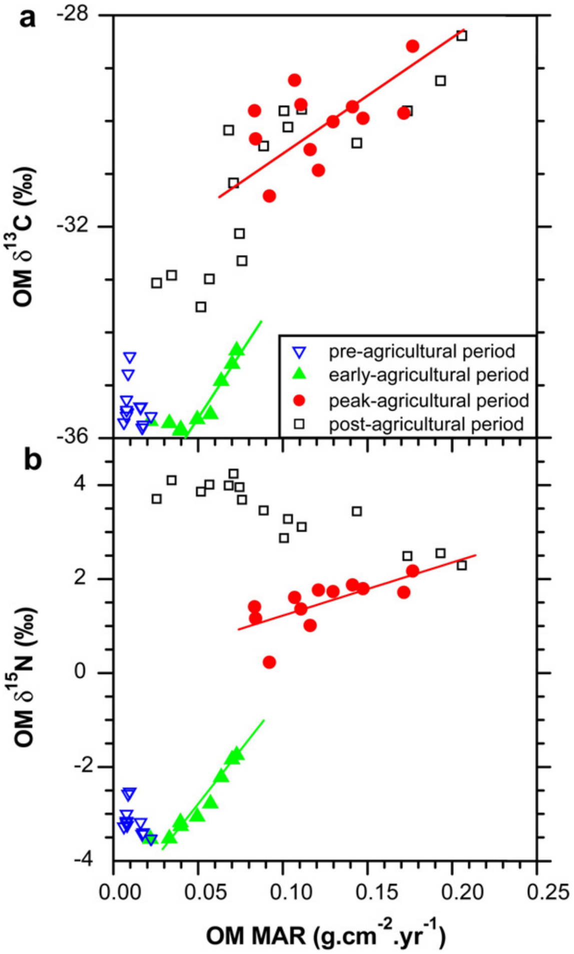

Fig. 6. Variation of organic $\delta^{13}C$ (a) and $\delta^{15}N$ (b) with OM accumulation rate (MAR) during different time periods. With the continuous increase of OM MAR, both $\delta^{13}C$ and $\delta^{15}N$ show different slopes during the early- and peak-agricultural periods and a gap (abrupt shift) between these two periods, suggesting that the increase in organic $\delta^{13}C$ and $\delta^{15}N$ is an integrated effect of enhanced influx of phytoplankton OM and changing contribution from bacteria communities.

peak-agricultural periods shifted the sediment OM from predominantly bacteria-derived (OM $\delta^{13}C$ of −35.7‰, or 75% bacterial) to predominantly phytoplanktonic (OM $\delta^{13}C$ of about −29‰, or 35% bacterial). Since the MAR of OM increased 5-fold during these periods, it is evident that deposition of methanotrophically derived OM must have increased, though at a slower rate than that of phytoplankton OM. It is logical that methane production should increase with higher OM deposition and increasing anoxia. The abruptness of isotopic shifts from the early-agricultural to peak-agricultural periods, shown as large isotopic jumps on the OM MAR vs. isotope diagram (Fig. 6), suggests a short-lived episode of reduced MAR of bacterial OM. It is precisely at this time that the $\delta^{13}C$ of carbonate decreased slightly, perhaps reflecting a greater amount and proportion of methane upwelling into the surface waters, concomitant with reduced sedimentary deposition of methanotrophic bacterial OM.

5.3. "Recovery" from human-induced landscape disturbance and industrial stress on aquatic ecosystems

Starting at ~1930, rapid decrease in Poaceae and *Ambrosia* pollen percentages and increase in *Quercus* pollen percentage (Fig. 3) indicate abandonment of some agricultural fields and reforestation in the region. The 30-fold decrease in silicate MAR since 1930 to a level similar to that of the pre-agricultural period suggests rapid reforestation and stabilization of landscapes (Fig. 4d). Corresponding to the reduced inputs of terrestrial nutrients and detritus, the MAR of OM and carbonate also decreased rapidly towards pre-agricultural levels (Fig. 4d and e). The $\delta^{13}C$ values of OM and calcite decreased by 4.7‰ and 3.7‰, respectively, from 1930 to 2003 (Fig. 4h and j), indicating a large decrease in the $\delta^{13}C$ of DIC. Again, this decrease cannot be explained by the decrease in $\delta^{13}C$ of atmospheric CO_2 in the last 70 years because the magnitude of atmospheric decrease (<1‰; Francey et al., 1999) is too small to account for the ~4‰ shift in the $\delta^{13}C$ values of the OM and calcite. Although the $\delta^{13}C$ shift toward values for pre-agricultural OM might suggest the return to a bacterial-dominated source for sedimentary OM, the parallel shift in $\delta^{13}C$ of DIC seems to require a different interpretation. Because the production of methane may have declined with the decrease in APP during this period, we speculate that methane oxidation may not be the cause of this large $\delta^{13}C$ decrease of DIC. Instead, the $\delta^{13}C$ shifts of the OM and carbonate may be caused by a decrease in the $\delta^{13}C$ of the groundwater DIC source due to the increasing organic respiration in soil related to the reforestation and soil C accumulation (Richter et al., 1999).

In contrast with $\delta^{13}C$, OM $\delta^{15}N$ shows constant increase since 1930. A strong correlation exists between NO_x emissions from the eastern United States (USEPA, 1996) and the $\delta^{15}N$ of OM from White Lake for the last 100 years (Fig. 7), implying that addition of ^{15}N-enriched pollutants from industrial combustion of fossil fuels (e.g., coal) may be responsible for the $\delta^{15}N$ increase during this period. The industrial source of organic N is also supported by N isotopes. Generally, the $\delta^{15}N$ of nitrate from the burning of fossil fuel (e.g., coal) is high (+6 to 13‰; Heaton, 1990). Recent studies have shown that, in Pennsylvania and surrounding area, the $\delta^{15}N$ of nitrate can be as high as +3.2‰ in wet deposition (Elliott et al., 2007a) and significantly higher (>+10‰) in dry deposition (Elliott et al., 2007b). Mixture of these two components can easily produce the intermediate $\delta^{15}N$ values observed in the White Lake sediments. However, the relative importance of these two sources is difficult to quantify due to their large seasonal isotope variations (Elliott et al., 2007b). The industrial signal may be strong in White Lake sediments for two reasons. First, industrial N is loaded, by either dry or wet atmospheric deposition, directly into the upper oxic water layer and thus avoids denitrification, promoting nitrate uptake in the photic zone. Second and perhaps more importantly, the diminishing N demand of the upland forest with its gradual maturation may decrease the retention of atmospheric N in the forest (Murdoch and Stoddard, 1992), significantly increasing the industrial N influx into

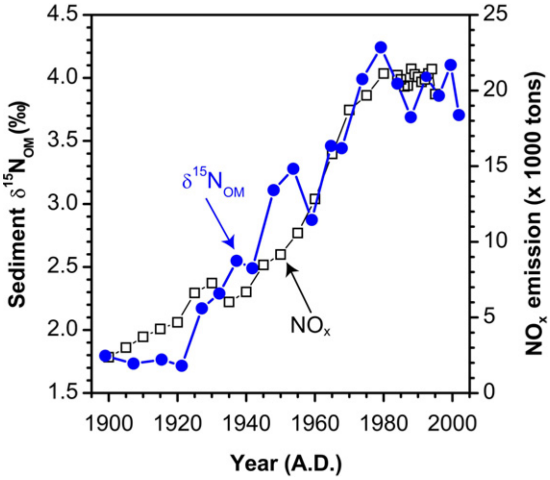

Fig. 7. Comparison between $\delta^{15}N$ values of sedimentary organic matter in White Lake and nitrogen oxides (NO_x) emissions in the eastern United States for the last 100 years (NO_x data from USEPA, 1996).

White Lake. The $\delta^{15}N$ values leveled off or slightly decreased after ~1980, corresponding to stabilized NO_x emissions following implementation of the 1970s Clean Air Act in the USA. This close correlation suggests sensitive biogeochemical response of lake ecosystems to industrial pollution and environmental regulation. It is interesting to note that, based on the evidence of the MAR and $\delta^{13}C$ of OM in the sediments, the large industrial N input did not result in any increase in lake productivity, perhaps cancelled out by the rapid recovery from the agriculture-induced eutrophication and increasing limitation of APP by phosphorus. The discordance between changes in the $\delta^{15}N$ and the $\delta^{13}C$ of OM shows that the lake has been experiencing a new anthropogenic environmental stress from industrial pollutants in the last several decades during its recovery from earlier agricultural perturbation. Similar patterns of decreasing $\delta^{13}C$ and increasing $\delta^{15}N$ over the last 100 years, especially during the "recovery" period after the 1970s, were also observed in sediments at Walden Pond, Massachusetts, USA (Köster et al., 2005), suggesting a possible regional effect of industrial pollution on lake ecosystems in the northeastern USA.

5.4. Shifting trajectories of terrestrial and aquatic environmental changes

Scatter plots of pollen PCA data and isotopic compositions of OM were used to illustrate the trajectories of terrestrial and aquatic environment changes during the last 700 years in the upland and in the lake. The PCA results (Fig. 8a) of pollen samples reflect the trends in the pollen diagram (Fig. 3). The first PCA axis (accounting for 50.9% of total variance in pollen data) mostly separates the pre-agricultural forest phase (A; containing *Quercus*, *Pinus*, and *Tsuga*) from the early- and peak-agricultural impact phases (B and C; including herbs *Ambrosia*, Poaceae, and *Rumex*). In addition, the second axis separates post-agricultural phase D from peak-agricultural phase. The vegetation around White Lake changed from oak forest in the pre-agricultural phase, through a transition in the early-agricultural phase, to ragweed-dominated herb zone in the peak-agricultural phase, and finally to birch-oak woodland in the post-agricultural or "recovery" phase (Fig. 8a). This U-shaped trajectory suggests either a successional lag of vegetation recovery or even an irreversible change in terrestrial vegetation after the anthropogenic disturbance, reflecting altered soil nutrient conditions (excess nitrate) as well as introductions or losses (*Castanea*) of plant species from the regional species pool.

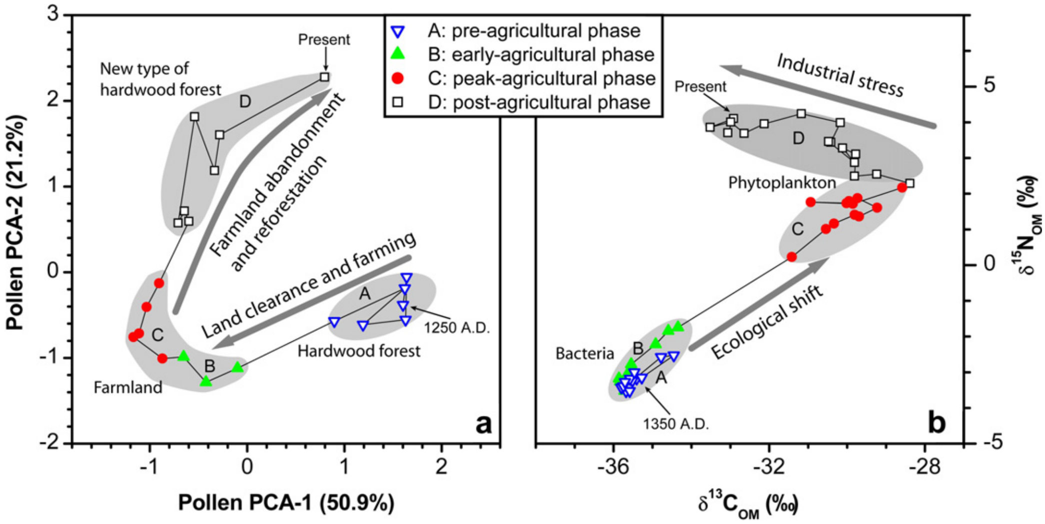

Fig. 8. Trajectories of terrestrial and aquatic environmental changes at White Lake. (a) PCA plot of pollen records, and (b) isotopic compositions of organic matter. The diagrams show consistent environmental phases: (A) pre-agricultural phase before ~1745, (B) early-agricultural phase from 1745 to 1820, (C) peak-agricultural phase from 1820 to 1930, and (D) post-agricultural or "recovery" phase from 1930 to the present. The trajectories indicate that both terrestrial and aquatic ecosystems shifted to new states after human disturbance.

Isotopic compositions of sedimentary OM also illustrate the environmental history of White Lake over the last 700 years. According to the OM $\delta^{13}C$ and $\delta^{15}N$ records, four lake phases can also be distinguished (Fig. 8b). The initial isotopic compositions of OM in the pre-agricultural period (phase A) are characterized by extremely low $\delta^{13}C$ and $\delta^{15}N$ values within a narrow range, suggesting a relatively stable aquatic environment with strong contribution to the residual sediment OM from methanotrophs and other anerobic bacterial processes. The early-agricultural phase (B) has indistinguishable $\delta^{13}C$ and $\delta^{15}N$ values relative to the pre-agricultural phase, likely reflecting the resilience of the aquatic ecosystem due to negative feedbacks operating during the initial stage of the anthropogenic effect. Eutrophication during the peak-agricultural phase (C) shifted the sediment OM source strongly to phytoplankton, reducing the relative contribution from bacterial processes, and resulting in rapid and large increases in both $\delta^{13}C$ and $\delta^{15}N$. During the post-agricultural phase (D), $\delta^{13}C$ and $\delta^{15}N$ show decoupled variations due to a new human-induced stress (i.e., industrial emission) on the aquatic ecosystems. The trajectories of $\delta^{13}C$ and $\delta^{15}N$ suggest that the aquatic environment is shifting to a new state (Fig. 8b). The human-induced regime shifts of aquatic ecosystems during the recovery of lakes from eutrophication have been observed in some other lakes (Ibelings et al., 2007). In White Lake, the aquatic environmental phases correspond well to the upland environmental phases, demonstrating that human-induced shifts of terrestrial environments have strong impacts on aquatic ecosystems.

6. CONCLUSIONS AND IMPLICATIONS

(1) Sedimentary organic matter from White Lake in northern New Jersey shows uniform but extremely low $\delta^{13}C$ and $\delta^{15}N$ values and relatively high C:N ratios for the period before human disturbance (before ~1745), indicating a relatively stable aquatic environment with a large microbial contribution to the sedimentary organic matter.

(2) Initial European settlement and land clearance in ~1745 induced an immediate lithologic change from organic-rich gyttja to carbonate-rich marl, by shifting the lake hydrology, water chemistry and carbonate precipitation equilibrium. Eutrophication and subsequent productivity increase in the lake during the period of peak disturbance led to greatly increased sedimentary deposition of phytoplankton OM, intensification of anoxic conditions and the preservation of laminated sediment after ~1895.

(3) This study demonstrates that the application of several proxies, especially multiple isotopes, helps to distinguish between the terrestrial and aquatic processes potentially responsible for the observed changes. A combination of the $\delta^{13}C$ of OM and carbonate and the OM C:N ratios indicates that the large increase in OM $\delta^{13}C$ and $\delta^{15}N$ in the peak-agricultural period (from 1820 to 1930) was caused by a shift in the source organic matter from bacteria- to phytoplankton-dominated origins. This interpretation differs from the conventional interpretation invoking productivity-induced increases in the $\delta^{13}C$ of lake DIC.

(4) Comparison of the $\delta^{15}N$ and $\delta^{13}C$ values for the most recent 70 years allows separation of the effects of industrial pollution and agricultural activities. The strong correlation of $\delta^{15}N$ with industrial NO_x emissions in the eastern USA suggests sensitive responses of aquatic ecosystems to industrial pollutants and to the implementation of environmental regulations.

(5) Fossil-pollen and isotope data from White Lake show that both terrestrial and aquatic systems are following trajectories to states different from those before the agricultural disturbance, implying that these perturbed ecosystems take long periods of time to recover, if ever, from past and ongoing human impacts.

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