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Factors controlling seasonal variations in stable isotope composition of particulate organic matter in a soft water eutrophic lake

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Abstract

Weekly water samples were taken to measure stable isotope composition ($\delta^{13}C$ and $\delta^{15}N$) of particulate organic matter (POM) in Lake Wauberg, Florida, from June 1994 to May 1995. The average $\delta^{13}C$ of POM was −19.3‰, consistent with an autochthonous origin from phytoplankton production, and exhibited a seasonal pattern that coincided with changes in water temperature, pH, CO_2 concentration, and phytoplankton biomass in the surface water. The ^{13}C enrichment in POM was attributed to reduced isotope fractionation due to carbon (C) limitation and the use of an isotopically heavy dissolved inorganic carbon pool supported mainly by atmospheric invasion and anaerobic respiration. Intermittent declines in $\delta^{13}C$ of POM were related to the frequent collapses of phytoplankton blooms and increases in CO_2 concentration resulting from both increased community respiration and terrestrial loading. Average $\delta^{15}N$ of POM was 1.3‰ and varied within a narrow range (−0.1‰ to 2.5‰). No significant correlation between phytoplankton biovolume and the $\delta^{15}N$ of POM was found. The low $\delta^{15}N$ is indicative of strong N_2 fixation, which is in line with the low concentration of dissolved inorganic nitrogen and the presence of high biovolume of N_2-fixing cyanobacteria in the surface water. This study suggests that stable C isotopes are good proxies for surface water CO_2 concentration and primary production, while stable N isotopes can be used to indicate N_2 fixation.

Stable isotope analysis is an excellent tool to study carbon (C) and nitrogen (N) biogeochemical cycles in lacustrine systems. Measurements of stable C isotope ratios ($\delta^{13}C$) of particulate organic matter (POM) have helped gain important insights into sources of organic matter, primary productivity, and CO_2 concentration in the surface water (Quay et al. 1986; Hodell and Schelske 1998; Lehmann et al. 2004). Stable N isotope ratios ($\delta^{15}N$) of POM have been used to understand various N cycling processes (Owens 1987; Teranes and Bernasconi 2000; Lehmann et al. 2004). The $\delta^{13}C$ and $\delta^{15}N$ of POM in lacustrine systems vary over time (Zohary et al. 1994; Gu and Schelske 1996; Lehmann et al. 2004), and these variations are typically related to external loadings, phytoplankton species composition, and primary productivity, as well as source, isotope signature, and concentrations of dissolved inorganic C and N (DIC and DIN) (Rau et al. 1989; Falkowski 1991; Grey et al. 2001). Temporal variations in the $\delta^{13}C$ and $\delta^{15}N$ of POM and their controls must be fully understood before these isotope proxies can be used with confidence. However, few studies have adopted a sampling frequency adequate to capture the detailed seasonal patterns of the $\delta^{13}C$ and $\delta^{15}N$ of POM. Furthermore, compared to the marine system, stable N isotope composition of organic matter in freshwaters has received less attention, although it could be a powerful tool to study the sources and fates of anthropogenic pollution, nitrate uptake, and N_2 fixation (Owens 1987; Van Dover et al. 1992; Montoya et al. 2002).

This study addressed the seasonal variations in $\delta^{13}C$ and $\delta^{15}N$ of POM in a shallow soft water and eutrophic lake in Florida. We employed a weekly sampling scheme over a full annual cycle to obtain 52 weekly samples at two central lake stations from June 1994 to May 1995. To our knowledge, our data represent the most frequent collection of POM for $\delta^{13}C$ and $\delta^{15}N$ determinations in natural waters over an annual cycle reported to date. We also took weekly samples to identify major phytoplankton species composition, measure algal biomass, and describe several physical and chemical variables to aid data interpretation.

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Table 1. Weekly average, minimum (min), maximum (max), and standard deviation (SD) of selected limnological variables and stable C and N isotope ratios from the two central stations in Lake Wauberg, Florida, except rainfall, which was taken from a local weather station. Number of samples is 52 weeks except rainfall data (n = 365 days), Chl *a* (n = 31 weeks), and $\delta^{13}C_{DIC}$ (n = 24 weeks).

Variables	Average	Min	Max	SD
Water temperature (°C)	24.8	13.5	34.0	5.8
Rainfall (cm)	2.1	0.0	9.0	2.5
Secchi depth (m)	0.6	0.3	0.9	0.1
Total biovolume (1×10^6 μm^3 mL^{-1})	38	20	71	14
Cyanobacterial biovolume (1×10^6 μm^3 mL^{-1})	30	11	72	16
N_2 fixer biovolume (1×10^6 μm^3 mL^{-1})	16	0.4	66	17
Chl *a* (μg L^{-1})	92	47	163	33
% cyanobacteria	73	43	100	17
% N_2-fixers	33	2	96	28
pH	8.2	6.9	10.1	0.9
Alkalinity (mg $CaCO_3$ L^{-1})	15.7	14.2	18.3	1.0
DIC (μmol L^{-1})	336	272	472	47
Total N (TN) (μmol L^{-1})	111	51	162	26
DIN (μmol L^{-1})	0.2	0.1	0.7	0.1
Total P (TP) (μmol L^{-1})	3.8	0.9	30	5.0
Soluble reactive P (SRP) (μmol L^{-1})	0.2	0.1	1.6	0.3
Molar TN : TP ratio	38	5	78	12
Molar DIN : SRP ratio	1.1	0.1	4.1	0.8
$\delta^{13}C_{DIC}$ (‰)	−4.0	−16.8	4.3	6.1
$\delta^{13}C_{POM}$ (‰)	−19.3	−22.1	−15.8	1.7
$\delta^{15}N_{POM}$ (‰)	1.3	−0.1	2.5	0.5

The main purpose of this study was to assess the seasonal variability and controls of $\delta^{13}C$ and $\delta^{15}N$ of POM dominated by phytoplankton production. In addition, we also discussed the sources of POM and DIC in the surface water.

Materials and methods

Study site—Lake Wauberg is a small (1.5 km^2), shallow (mean depth = 3.0 m), freshwater ecosystem in north-central Florida (29°31′32″N, 82°18′7″W). The main water sources to the lake are direct rainfall and groundwater (Opper 1982). There is a small outlet to the east into Sawgrass Pond. Lake Wauberg is largely surrounded by a hardwood forest, with the northern shoreline developed for residential and recreation uses. The groundwater contained high phosphorus (P) concentration (Opper 1982). Phytoplankton were the dominant flora, with high annual biomass mainly consisting of cyanobacteria. Aquatic macrophytes were scarce in the lake, possibly because of light limitation. Despite its eutrophic state, Lake Wauberg had low alkalinity and DIC concentration (Table 1). Based on Secchi depth, the trophic state of Lake Wauberg has experienced little change in 60 yr (Carr 1934; Florida Lakewatch 1997).

The lake was sampled weekly at two central lake stations from June 1994 to May 1995. In the field, pH, Secchi depth, and surface water temperature were recorded, and water samples for biological and chemical analyses were taken at a water depth of 0.5 m using a 2.5-liter Niskin bottle between 09:00 h and 11:00 h local time. Phytoplankton samples were fixed with Lugol's solution on site. Water samples for C isotope analysis of DIC ($\delta^{13}C_{DIC}$) were filled into 30-mL Qorpak bottles. Each bottle was injected with 1 mL of saturated $HgCl_2$ solution for preservation. Water samples for stable C and N analysis of POM ($\delta^{13}C_{POM}$ and $\delta^{15}N_{POM}$), alkalinity, nutrients, and chlorophyll *a* (Chl *a*) were collected in 1-liter acid-cleaned polyethylene bottles that were transported to the laboratory within 2 h.

Laboratory analyses—In the laboratory, alkalinity and nutrient concentrations were determined using standard techniques (APHA 1989). Alkalinity was determined with the acidic titration method. Soluble forms of inorganic N and P were analyzed by filtering the samples through 0.45-μm pore size polycarbonate filters (Gelman Supor). Soluble reactive P (SRP) was determined using the ascorbic acid–molybdate blue method. Total P (TP) was determined as SRP after persulfate digestion of whole water samples. Nitrate (NO_3^-) and nitrite (NO_2^-) were determined using the method of cadmium reduction with colorimetric azo dye formation. Ammonium (NH_4^+) and total N (TN) were determined as NO_2^- after persulfate digestion. Nitrite, NO_3^-, and NH_4^+ were reported as DIN. After digestions, all nutrients were analyzed with an autoanalyzer.

Phytoplankton counts were performed using a Palmer-Maloney cell on an AO Phasestar compound microscope. Ten fields were counted on each of four slides for a total of 40 fields. A magnification of ×300 was used on all counts. Identification was taken to species where possible and to genus for the remaining species. *Microcystis* spp. and *Aphanocapsa* spp. were recorded together because of the difficulty in reliably distinguishing between the two genera. Biovolumes were determined using the closest geometrical shape (Wetzel and Likens 1991).

Chl *a* concentration was determined spectrophotometrically after filtration (Whatman GF/C) and extraction into 90% acetone (APHA 1989). Samples for 1995 were not available for analysis, and monthly measurements of Chl *a* for the same period were obtained from data reports (Florida Lakewatch 1997). Concentrations of DIC were calculated from alkalinity, pH, and water temperature (Wetzel and Likens 1991). Wind speed and rainfall data from Gainesville Regional Airport, approximately 16 km from Lake Wauberg, were obtained from the National Oceanic and Atmospheric Administration.

The $\delta^{13}C_{POM}$ and $\delta^{15}N_{POM}$ were determined on particulates from approximately 100 to 200 mL of lake water filtered onto precombusted (500°C) Whatman QM-A quartz fiber filters (pore size = 1 μm), which were then oven dried at 60°C. Organic matter was scraped off the filters and loaded into tin capsules for mass spectrometer analysis. Procedures for DIC extraction and isotopic determination are from Gu et al. (2004). All samples were analyzed using a VG PRISM II series mass spectrometer for $^{13}C : ^{12}C$ and $^{15}N : ^{14}N$ ratios against internal reference CO_2 and N_2 gases. For every batch of DIC samples, two external standards of potassium bicarbonate ($KHCO_3$) dissolved in CO_2-free deionized water were also analyzed. A secondary standard of organic material was also analyzed for every five POM samples. All isotope values are reported relative to the Vienna PeeDee belemnite standard (V-PDB) or atmospheric N_2. Analytical errors were ±0.1‰ for $\delta^{13}C_{POM}$, ±0.5‰ for $\delta^{13}C_{DIC}$, and ±0.2‰ for $\delta^{15}N_{POM}$.

Results

Physical and chemical variables—Total rainfall in the Lake Wauberg area was 111 cm during the study period, with peaks in the months of July and August and lows in the winter months except January (Fig. 1A). Weekly average water temperature reached a high of 34.0°C in early August and a low of 13.5°C in February (Fig. 1B). Secchi depth ranged from 30 to 93 cm, with the lowest values recorded in the summer and highest in winter (Fig. 1C). pH fluctuated between approximately 7 and 9 from August to April and remained above 8 from May to July (Fig. 1D). Alkalinity ranged from 14.2 to 18.3 mg L^{-1}, while $CaCO_3$ and was highest during the summer and fall and lowest during the winter and spring (Fig. 1E). The low alkalinity and the widely fluctuating pH indicate that Lake Wauberg was a poorly buffered system. Concentration of DIC averaged 336 μmol L^{-1} and was generally low in spring and summer and high in winter (Fig. 1F).

High TN and TP concentrations suggest that Lake Wauberg was a nutrient-rich system (Fig. 2A,C). However, average DIN and SRP concentrations were low (Table 1 and Fig. 2B,D). This may indicate a close coupling between supply and demand of the readily available nutrients for phytoplankton growth. Total N concentrations were low and DIN concentration was high during the winter period, reflecting both low POM concentration and low nutrient demand. Total P and SRP concentrations exhibited small seasonal variations. Similarly, molar TN : TP and DIN : SRP ratios did not show large seasonal variations (Fig. 2E and 2F). The average molar TN : TP ratio was 38 (Table 1), suggesting that Lake Wauberg was P limited. However, the average molar DIN : SRP ratio was only 1.1 (Table 1), a value strongly indicating N limitation. Considering the high biovolume of cyanobacteria capable of N_2 fixation in the water column (Table 1), the molar DIN : SRP ratio appears to be a better indicator for the limiting nutrient in Lake Wauberg and Lake Apopka, another shallow eutrophic lake in Florida (Aldridge et al. 1993).

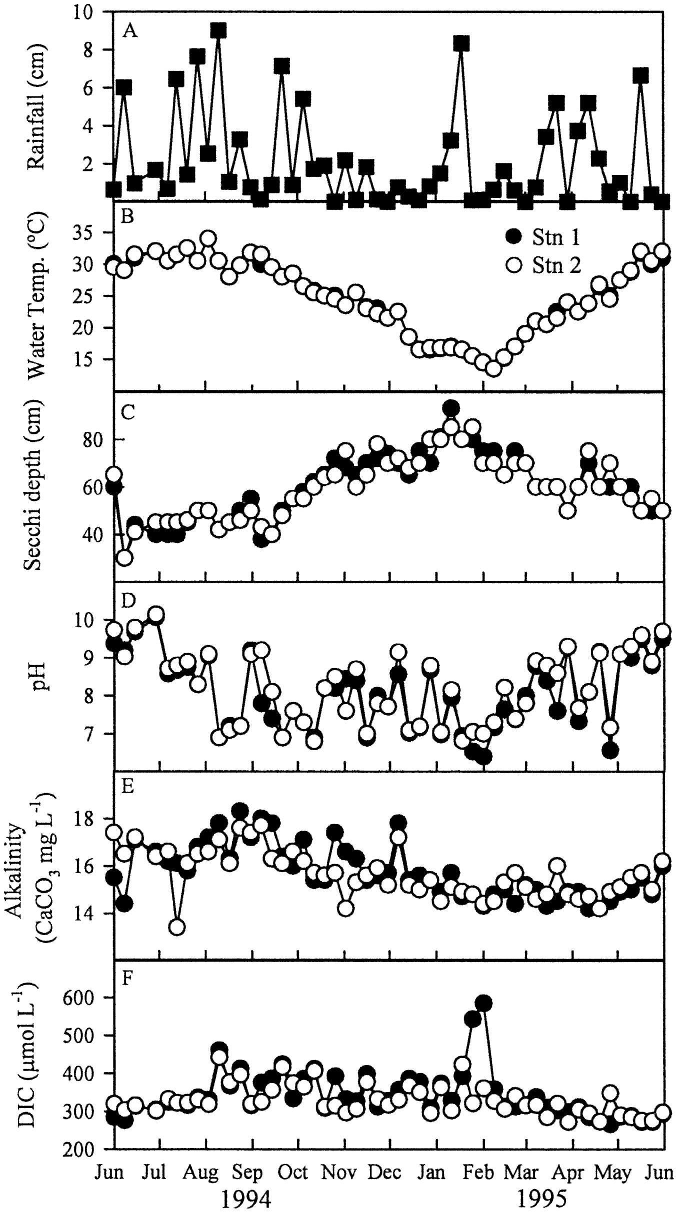

Fig. 1. Seasonal variations in selected physical and chemical variables at two central lake stations. Rainfall data were weekly totals.

Phytoplankton biomass and community structure—Phytoplankton biovolume increased from June through early September and decreased through the fall, winter, and early spring, followed by another increase in early May (Fig. 3A,B). Phytoplankton biovolume ranged from 20 × 10^6 to 71 × 10^6 μm^3 mL^{-1}. Chl *a* concentration from our incomplete measurements shows a similar trend to biovolume, with an average of 92 μg L^{-1}, indicating that Lake Wauberg was highly eutrophic. This is in agreement with the monthly data from the Florida Lakewatch (Fig. 3C). The phytoplankton community in Lake Wauberg was dominated by cyanobacteria for most of the year (Fig. 4). Cyanobacteria made up >70% of the total biovolume (Table 1). During the summer months cyanobacteria at times accounted for greater than 95% of the total phytoplankton biovolume. The taxonomic and physiological nature of the cyanobacterial assemblage underwent drastic shifts from non–N_2-fixing species to species capable of fixing N_2 (Fig. 4). On average 33% of the total biovolume was N_2-fixing cyanobacteria (Table 1). The N_2-fixing cyanobacteria included *Cylindrospermopsis raciborskii*, *Planktolyngbya* spp., and *Anabaena* spp. *C. raciborskii* was the most abundant N_2-fixing cyanobacteri-

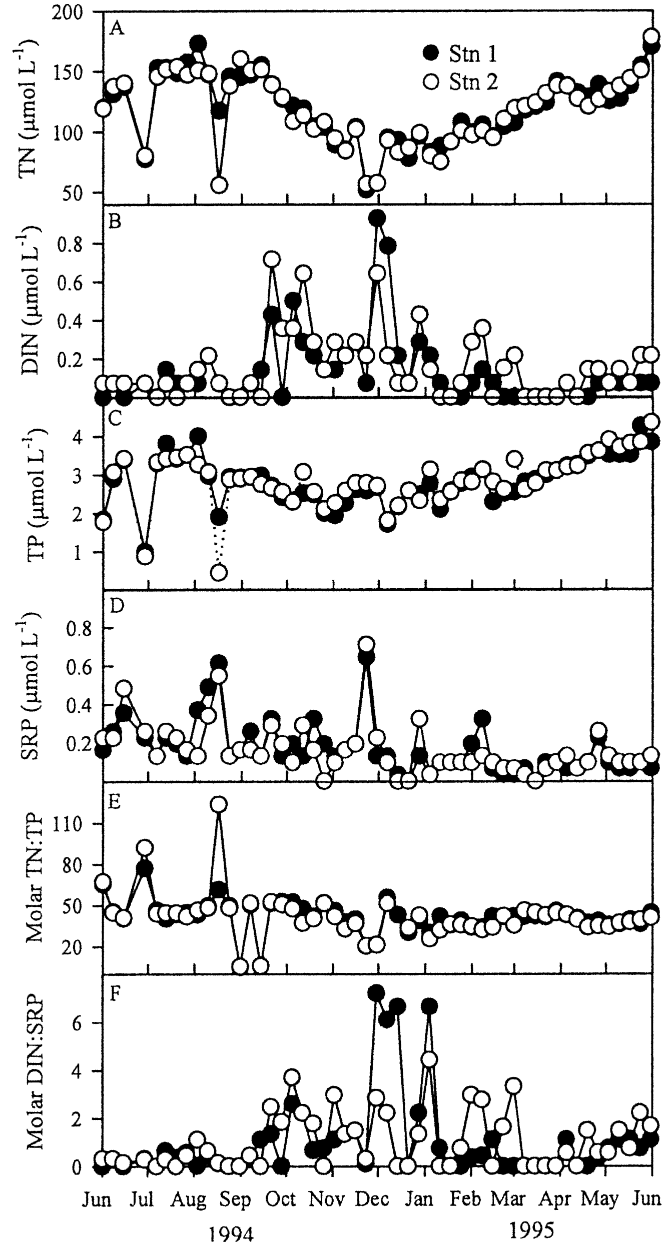

Fig. 2. Seasonal variations in total and dissolved N and P concentrations, molar TN : TP, and DIN : SRP ratios at two central lake stations.

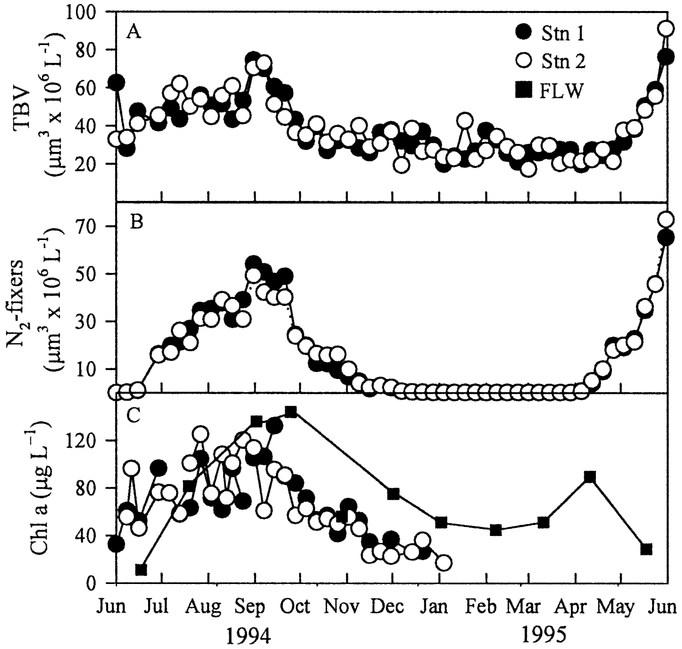

Fig. 3. Seasonal variations in total phytoplankton biovolume (TBV), N_2-fixing cyanobacterial biovolume, and Chl *a* concentration at two central lake stations. FLW = Florida Lakewatch data.

um, at times accounting for over 80% of the total biovolume, but was only present during warmer times of the year (Fig. 4).

Seasonal variations in stable isotopes—Our measurements of C isotopes of DIC ($\delta^{13}C_{DIC}$) were incomplete, with data available only from June to December 1994. The average $\delta^{13}C_{DIC}$ from the two stations was −4.0‰, with values that ranged widely from −16.8 to 4.3‰ (24 samples). $\delta^{13}C_{POM}$ from the two central lake stations tracked each other reasonably well ($r = 0.82$, $p < 0.05$). Thus we used the average from the two stations when discussing the results. Weekly $\delta^{13}C_{POM}$ varied from −22.1‰ to −15.8‰, with an average of −19.3‰, and fluctuated over time (Table 1). Enriched $\delta^{13}C_{POM}$ (~−17‰ to −16‰) typically occurred in the warm months between March and September. With the exception of two relatively high values in November and December, the cold months were dominated by depleted $\delta^{13}C_{POM}$ of ~−21‰ (Fig. 5A). In general, the high $\delta^{13}C_{POM}$ was accompanied by high water temperature, high phytoplankton biovolume, high pH, and low DIC concentration (Fig. 6). Conversely, the low $\delta^{13}C_{POM}$ was typically associated with low water temperature, low biovolume, low pH, and high DIC concentration. However, our weekly sampling revealed occurrences of both high and low $\delta^{13}C_{POM}$ in the warm months (Fig. 5A). Another striking observation is that the high $\delta^{13}C_{POM}$ was often restricted to a single sampling event followed by an immediate decline; conversely, the low $\delta^{13}C_{POM}$ could be maintained for up to 3 consecutive weeks (Fig. 5A).

Like $\delta^{13}C_{POM}$, $\delta^{15}N_{POM}$ from the two lake stations tracked each other closely ($r = 0.70$, $p < 0.05$) and showed small seasonal changes with an average of 1.3‰ and a narrow range from −0.1‰ and 2.5‰ (Table 1 and Fig. 5B). In contrast to $\delta^{13}C_{POM}$, $\delta^{15}N_{POM}$ was generally low in the warm months and high in the cold months (Fig. 5B). However, the maximum and minimum values did not occur in the warmest and the coldest months of the year, respectively. The $\delta^{15}N_{POM}$ was not correlated with any ambient variables, except DIN concentration, which explains only a small portion of the variance ($r^2 = 0.10$, $p < 0.05$).

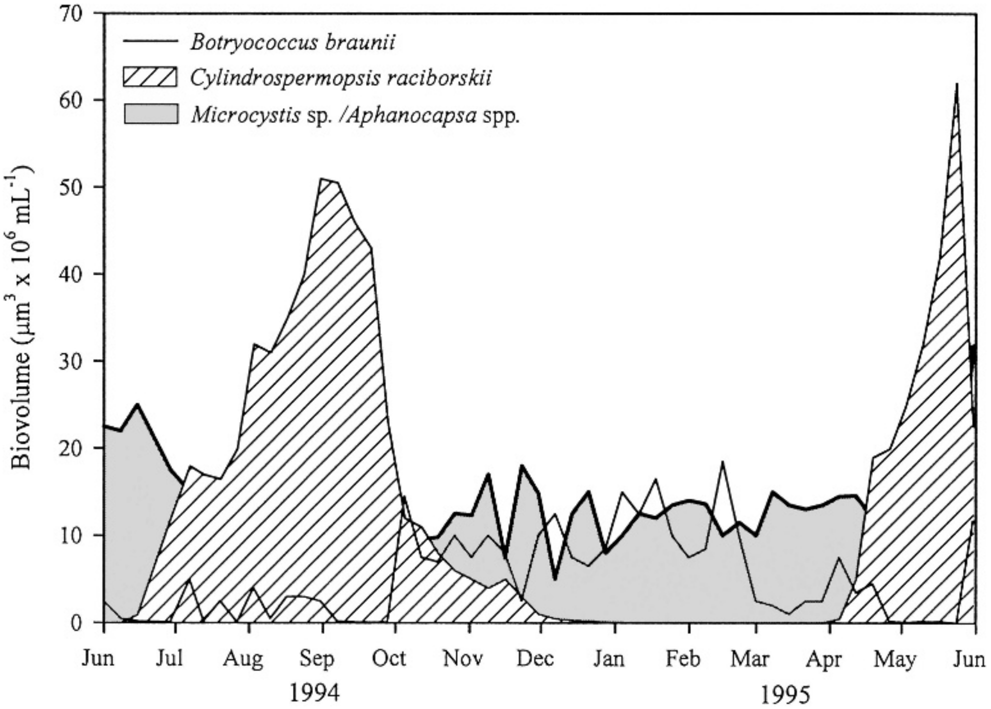

Fig. 4. Seasonal variations in biovolume for major phytoplankton species. Values were averages of two central lake stations.

Discussion

Origin of POM—Organic matter in lacustrine surface water is typically derived from in situ production, terrestrial loading, sediment mixing, or a combination of some or all of these sources. Several lines of evidence indicate that the POM in Lake Wauberg originated largely from autochthonous production. First, changes in $\delta^{13}C_{POM}$ generally tracked the seasonal variation in total phytoplankton biovolume. Previous studies also linked the changes in C isotopes of POM to autochthonous production when they covaried over time (Hollander and McKenzie 1991; Hodell and Schelske 1998; Lehmann et al. 2004). Second, the average $\delta^{13}C_{POM}$ is also indicative of phytoplankton-derived production and suggests few contributions from other sources. A recent study in Lake Wauberg reveals isotopic depletion in terrestrial (−27‰) and sediment (−24‰) organic matter (Shumate 2004). The $\delta^{13}C_{POM}$ depletion in surface waters is often attributed to substantial inputs from terrestrial C (Grey et al. 2001; Martineau et al. 2004). Finally, ancillary data, such as high phytoplankton biovolume and Chl *a*, as well as the lack of both aquatic macrophyte coverage and permanent surface flow, also pointed to the dominance of POM by water-column production.

Magnitude for annual $\delta^{13}C_{POM}$ variation—C isotope composition of POM in lacustrine systems varies over an annual cycle (*see* summaries by Zohary et al. 1994 and Gu and Schelske 1996). The magnitude of this variation is typically driven by external physical forces such as temperature and photoperiod that affect phytoplankton growth rates and isotope fractionation (Fogel et al. 1992; Lehmann et al. 2004). In general, eutrophic lakes in the low latitude region show relatively narrow ranges of $\delta^{13}C_{POM}$. For example, the range of $\delta^{13}C_{POM}$ in Lake Apopka, a shallow subtropical lake located approximately 100 km from Lake Wauberg, was <3‰ (Gu and Schelske 1996). Conversely, eutrophic lakes in the temperate and subarctic regions typically show larger variations in $\delta^{13}C_{POM}$ (Hollander and McKenzie 1991; Zohary et al. 1994; Gu et al. 1999). Lake Wauberg is located in a transition zone between subtropical and temperate regions and is characterized by small seasonal changes in climate and relatively high winter water temperature (Beaver et al. 1981). Phytoplankton in Lake Wauberg were able to maintain high biomass in the cold months. The range of $\delta^{13}C_{POM}$ (6‰) in Lake Wauberg is correspondingly smaller than that reported for subarctic and temperate lakes.

Mechanisms for $\delta^{13}C_{POM}$ seasonality—Seasonal variations in $\delta^{13}C_{POM}$ may be related to allochthonous loading (Grey et al. 2001), phytoplankton species composition (Falkowski 1991; Zohary et al. 1994), productivity (Rau et al. 1989; Fogel et al. 1992), and DIC pool size and isotopic composition (Hollander and McKenzie 1991; Lehmann et al. 2004). The phytoplankton community in Lake Wauberg was overwhelmingly dominated by cyanobacteria, although a number of other species existed. There are no close correlations among $\delta^{13}C_{POM}$ and biovolume of total cyanobacteria, biovolume of N_2-fixing cyanobacteria, or biovolume of other phytoplankton species (all $p > 0.05$). Periods with peak biovolume of *Microcystis* or *Cylindrospermopsis* did not show unique $\delta^{13}C$ from the periods when

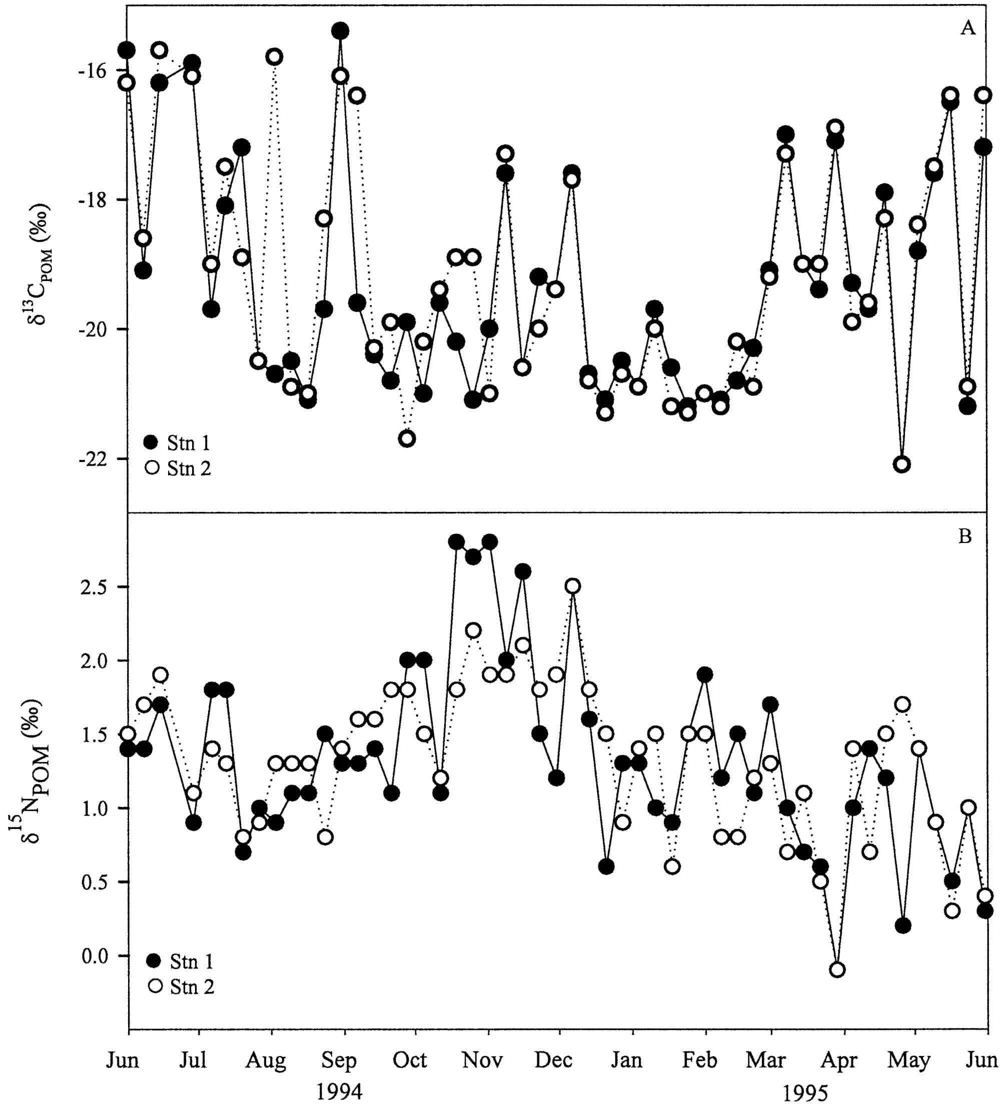

Fig. 5. Seasonal variations in (A) $\delta^{13}C_{POM}$ and (B) $\delta^{15}N_{POM}$ at two central lake stations.

these species were not abundant. Therefore, it is unlikely that the $\delta^{13}C$ seasonality in Lake Wauberg was controlled by the changes in phytoplankton species composition.

The general seasonal pattern for $\delta^{13}C_{POM}$ in Lake Wauberg was consistent with the changes in water temperature, phytoplankton biomass, and DIC concentration. Primary productivity is a fundamental factor affecting aqueous inorganic C dynamics and isotope fractionation of organic matter. Although we did not measure phytoplankton growth rate, the high biovolume and Chl *a* concentration in the warm months were undoubtedly the result of increased phytoplankton productivity. Similarly, low biovolume and Chl *a* concentration in the cold months reflected reduced phytoplankton growth. During C uptake, phytoplankton preferentially assimilate ^{12}C, leaving the DIC pool enriched with ^{13}C. In spring, phytoplankton photosynthesis in Lake Wauberg increased as water temperature increased, resulting in low dissolved nutrients and DIC concentration. Phytoplankton show less isotope fractionation during periods of high growth, leading to more ^{13}C accumulated in organic matter than periods of slow growth. The increases in $\delta^{13}C_{POM}$ from March to August reflected high CO_2 uptake rates and decreased isotope fractionation. In early September, a decrease in water temperature led to lower phytoplankton growth. As a result, $\delta^{13}C_{POM}$ decreased along with the decreases in biovolume, Chl *a*, and increases in DIN and DIC concentrations. This period of low phytoplankton biomass and $\delta^{13}C_{POM}$ lasted from September to February despite two small bounces in $\delta^{13}C_{POM}$. However, the significant, but relatively weak correlation between phytoplankton biomass and $\delta^{13}C_{POM}$ (Fig. 6C) implies that biovolume is not an ideal indicator for phytoplankton productivity, and it is possible that other factors also affected the $\delta^{13}C_{POM}$ in this lake.

Biological C isotope fractionation also depends on DIC pool size. Lake Wauberg is a poorly buffered system with low DIC concentration and low alkalinity. It is expected that any significant increases in C demand will deplete the DIC pool. Because phytoplankton use CO_2 as their

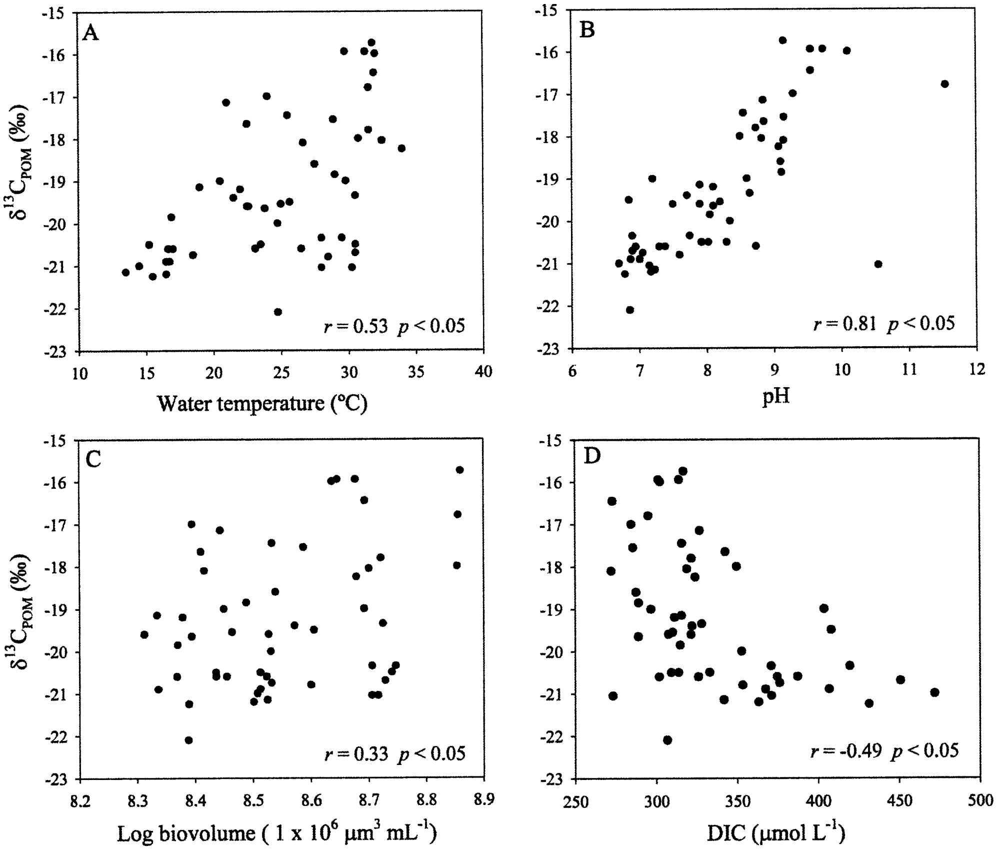

Fig. 6. Correlations between $\delta^{13}C_{POM}$, and (A) water temperature, (B) pH, (C) biovolume, and (D) DIC concentration. Biovolume was log-transformed before correlation analysis was performed.

primary C source, we calculated CO_2 concentration from DIC concentration, pH, and ambient water temperature to assess the effect of CO_2 pool size on $\delta^{13}C_{POM}$. The close relationship between CO_2 concentration and $\delta^{13}C_{POM}$ (Fig. 7A) suggests that $\delta^{13}C_{POM}$ is an ideal indicator for surface water CO_2 concentration. In fact, such a relationship has been used as a proxy for past atmospheric and oceanic CO_2 concentrations (Rau et al. 1989; Hollander and McKenzie 1991). The magnitude of the apparent isotope fractionation (ε_{app}), defined as $[\delta^{13}C_{CO_2} + 1{,}000)/(\delta^{13}C_{POM} + 1{,}000) - 1] \times 10^3$ (Farquhar et al. 1989), generally increased with increasing CO_2 concentration (Fig. 7B). The ε_{app} values were small from June and early August when phytoplankton productivity was high and CO_2 concentration was near zero (<1 μmol L^{-1}) and increased from mid-August to September and remained similarly high to December, reflecting reduced C demands and increased respiration at lower temperatures (Fig. 8A). Because the maximum isotope fractionation could be as high as 29‰ when fully expressed (Roeske and O'Leary 1984), the average ε_{app} (15‰) indicates reduced isotope fractionation and increased CO_2 limitation due to intense phytoplankton blooms and low CO_2 concentration in Lake Wauberg.

Increasing biological pumping often decreases the ambient CO_2 concentration. This is especially true for Lake Wauberg, with its small DIC pool and intense phytoplankton blooms. A high rate of CO_2 uptake leads to increases in pH and a switch in the C balance from CO_2 to HCO_3^- dominance. During the spring and summer periods, pH was typically maintained around 9; at such a pH level, HCO_3^- was the major form of DIC. The phytoplankton community in Lake Wauberg was dominated by cyanobacteria, which are capable of using HCO_3^-. Because $\delta^{13}C$ of HCO_3^- is on average 8‰ higher than that of dissolved free CO_2 (Mook et al. 1974), phytoplankton are enriched with ^{13}C when using HCO_3^- as their C source. Furthermore, under C limitation, phytoplankton tend to use DIC more efficiently via active transfer instead of passive diffusion (Farquhar et al. 1989; Fogel et al. 1992). This will also result in less isotope fractionation and greater ^{13}C enrichment in POM. Our data reveal an average $\delta^{13}C_{POM}$ of -18.2‰ ± 1.5‰ when the dissolved CO_2 concentration was less than 10 μmol L^{-1} (average = 2.2 μmol L^{-1}). By contrast, the average $\delta^{13}C_{POM}$ was -21.1‰ ± 1.1‰ when the dissolved CO_2 concentration was above 10 μmol L^{-1} (average = 96 μmol L^{-1}). The 3‰ difference in $\delta^{13}C_{POM}$ is significant (unpaired Student's t-test, $p < 0.01$) and likely partly reflects the use of different forms of DIC by phytoplankton under CO_2 deplete and replete conditions.

Another factor that could influence the $\delta^{13}C_{POM}$ in Lake Wauberg is the isotope composition of the DIC pool. In

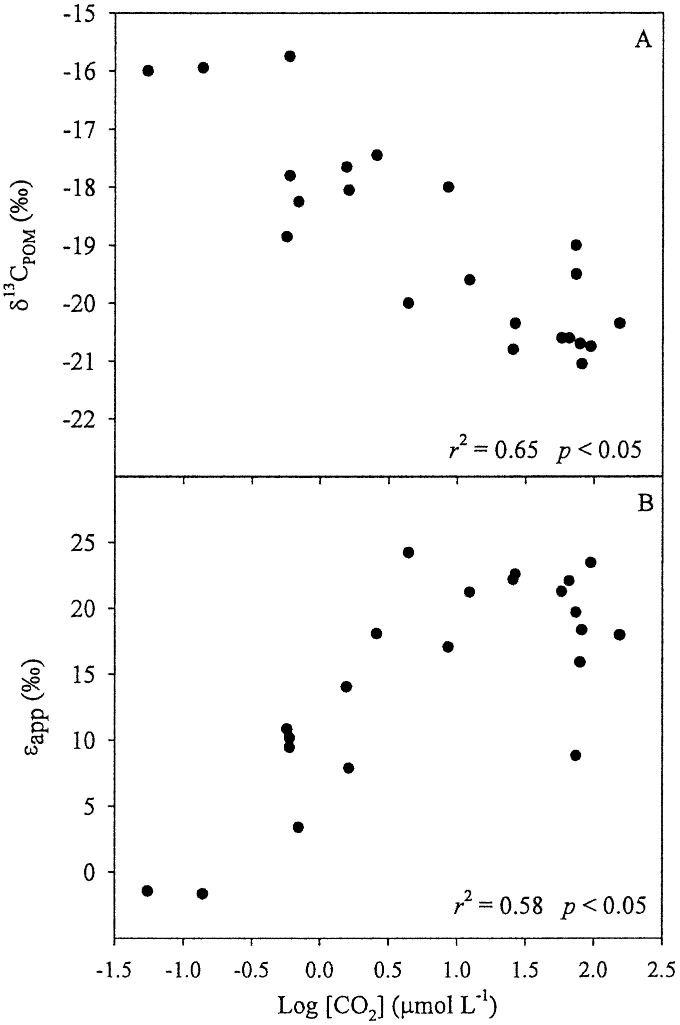

Fig. 7. Correlations between logarithmic CO_2 concentration and (A) $\delta^{13}C_{POM}$ and (B) apparent isotope fractionation (ε_{app}) between $\delta^{13}C_{POM}$ and $\delta^{13}C_{CO_2}$. $\delta^{13}C_{CO_2}$ and ε_{app} were calculated following Shumate (2004) and Farquhar et al. (1989), respectively.

fact, the relatively high $\delta^{13}C_{POM}$ reflected the use of an isotopically heavy DIC source (−4‰). However, the $\delta^{13}C_{DIC}$ had a range of 20‰, compared to the only 6‰ change in $\delta^{13}C_{POM}$. The temperature effect on isotope fractionation only accounts for less than 3‰ of the variation in $\delta^{13}C_{POM}$ (Mook et al. 1974). There are two striking phenomena associated with isotope composition of DIC in Lake Wauberg: $\delta^{13}C_{DIC}$ decreased with the increases in $\delta^{13}C_{POM}$ ($r = -0.65$, $p < 0.05$) and increased with increases in DIC concentration ($r = 0.38$, $p < 0.05$). The low $\delta^{13}C_{DIC}$ is likely related to terrestrial runoff with DIC input from the C-3 plants-dominated watershed during the warm growth months (Fig. 8B). $\delta^{13}C_{DIC}$ increased sharply during the fall turnover and remained high throughout the remaining cold months in 1994 (Fig. 8B). The high $\delta^{13}C_{DIC}$ from September to December likely reflected reduced terrestrial runoff as a result of less precipitation during the winter period. Furthermore, diffusion and mixing of the isotopically heavy CO_2 from anaerobic respiration at the water-column–sediment interface might also contribute to the ^{13}C enrichment in the surface water DIC pool, which will be discussed later. Thus, the phytoplankton in Lake Wauberg used an isotopically light DIC pool during the fast growth period and a heavy DIC pool during the slow growth period. The seasonal trend for $\delta^{13}C_{POM}$ suggests that phytoplankton productivity and DIC concentration, not $\delta^{13}C_{DIC}$, dictated the isotope composition of POM in Lake Wauberg.

Controls for intermittent $\delta^{13}C_{POM}$ variations—The $\delta^{13}C_{POM}$ in Lake Wauberg showed strong weekly fluctuations, especially during the spring and summer periods. What caused these fluctuations? Water temperature did not show large short-term (weekly) variation and hence cannot explain the frequent temporal variations in $\delta^{13}C_{POM}$ (Fig. 9A). Further analysis indicates that rapid changes in phytoplankton biomass and the rain-induced terrestrial loading were the driving forces behind these episodic changes. Periodic collapses of the intense blooms resulted in high CO_2 concentration and low pH. After a decline, increased growth again led to low CO_2 and high pH in the surface water. The periodic changes in phytoplankton growth are supported by large fluctuations in weekly biovolume and Chl *a*, especially during the spring and summer periods. Interweek changes in Chl *a* were as high as 20–50 $\mu g\ L^{-1}$ (Fig. 3C). Some of these changes were consistent with the changes in $\delta^{13}C_{POM}$. For example, biovolume and $\delta^{13}C_{POM}$ closely tracked each other with only a few mismatches between September and January (Fig. 9B). However, this relationship was not found in other months. We attributed this discrepancy partly to the inability of our biovolume measurements to accurately predict the dynamic changes in $^{13}C_{POM}$, pointing to the necessity of using a more appropriate indicator such as in situ measurements of phytoplankton growth to explain the changes in $\delta^{13}C_{POM}$. Furthermore, this discrepancy hints that other factors may also have important influences on $\delta^{13}C_{POM}$ variability in Lake Wauberg.

The weekly variation in $\delta^{13}C_{POM}$ is closely correlated with CO_2 concentration in the surface water (Fig. 9C). A plot of the weekly rainfall data against pH reveals significant drops in pH (≥1 pH unit) during or after a major rainfall event (Fig. 10), which may be caused by increases in the CO_2 concentration during the episodic terrestrial runoff triggered by rainfalls. Terrestrial runoff may have double effects on $\delta^{13}C_{POM}$. First, rain-driven CO_2 flux brought isotopically light C into the lake, which may be as low as −27‰, because Lake Wauberg is surrounded by a dense forest of C-3 plants. Second, terrestrial runoff may lead to increases in water-column CO_2 concentration, which in turn lead to decreases in phytoplankton isotope fractionation. However, the influences of terrestrial flux on CO_2 concentration, pH, and $\delta^{13}C_{POM}$ were restricted to the major rain events because of the lack of permanent surface flow and the poor buffering capacity of the lake. This is supported by the subsequent declines in CO_2 concentration after major rainfalls (Fig. 10). High CO_2 concentration was associated with several major rain events, but not all major rain events led to high CO_2 (Fig. 10), suggesting that terrestrial input was

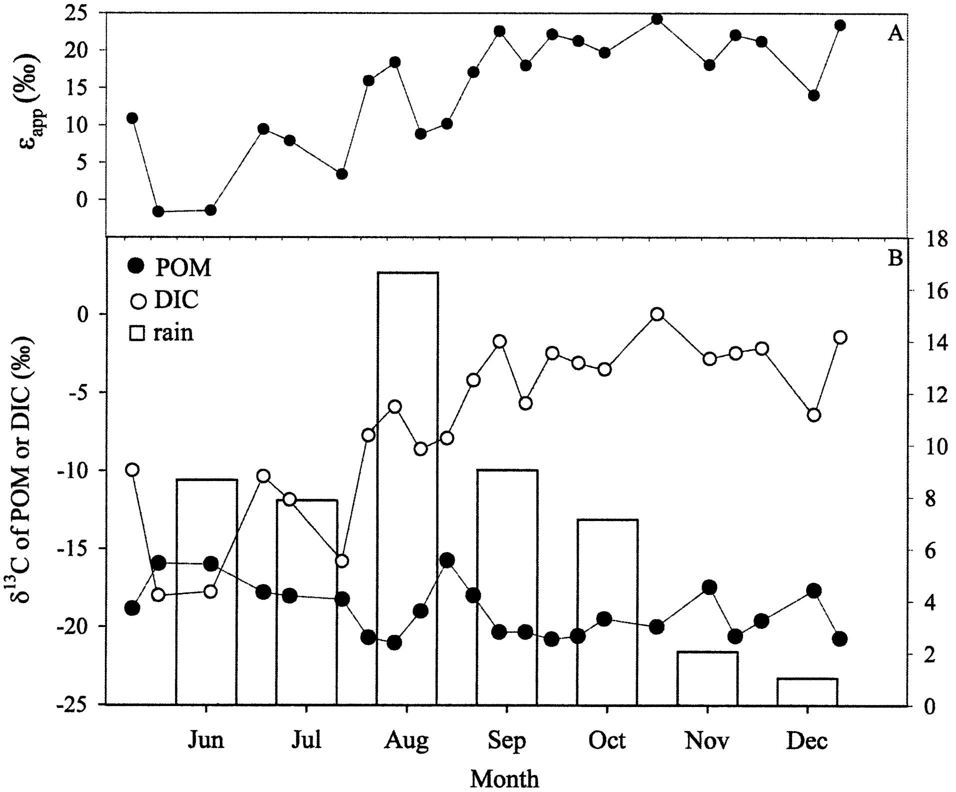

Fig. 8. Seasonal variations in (A) apparent isotope fractionation (ε_{app}) and (B) carbon isotopes of POM and DIC, and monthly total rainfall. Data for $\delta^{13}C_{DIC}$ were only available from June to December 1994.

not always the cause for high CO_2 in Lake Wauberg. Since high CO_2 was typically found during the fall and winter periods when biovolume and Chl *a* concentration were low, reduced phytoplankton growth, increased respiration, and water-column mixing can also lead to high water-column CO_2 concentration. Although the high CO_2 in April 1995 did not occur concurrently with the major rain events, moderate rains (2–3 cm) in the previous 3 weeks might still account for the high CO_2 and the sudden drop of pH (Fig. 10). However, major rainfalls did not result in high CO_2 in several summer months (May to July), indicating that during the intense summer blooms there was a close coupling between CO_2 supply and phytoplankton demand.

Sources of the water-column DIC pool—Despite the large isotope variation, the DIC pool in Lake Wauberg was enriched with ^{13}C. DIC loading from the watershed was expected to be isotopically depleted and was only significant to the lake during the major rain events. DIC derived from oxidation of phytoplankton and sediment organic matter would produce isotopic signatures similar to their sources (−19‰ and −24‰, respectively). Another possible source of DIC was groundwater input. A recent study from Lake Apopka reveals ^{13}C depletion in the groundwater (Gu et al. 2004). Atmospheric CO_2 flux could provide an important source of DIC to Lake Wauberg. The small DIC pool and persistent phytoplankton blooms suggested that CO_2 invasion from the atmosphere to the lake's surface water was possible. An estimate of dissolved free CO_2 partial pressure (pCO_2) for Lake Wauberg using Henry's law yielded an average pCO_2 of 15.3 Pa, which was undersaturated relative to the atmospheric pCO_2 (36.5 Pa). An average CO_2 flux can be calculated as $[CO_{2(atm)} - CO_{2(aq)}]$) $\times$ D/z where $CO_{2(atm)}$ and $CO_{2(aq)}$ are air and water CO_2 concentrations, respectively; D is a diffusion coefficient of CO_2 (1.9×10^{-5} cm^{-2} s^{-1}); z is the thickness of the stagnant boundary layer (0.013 cm), which is a function of wind speed (Kling et al. 1992). This estimate yielded an average CO_2 flux to the lake water as 9 mmol m^{-2} d^{-1} without considering chemical enhancement (Schindler et al. 1972). This calculation indicates that atmospheric invasion provided an important source of DIC to Lake Wauberg. Support of primary production from atmospheric CO_2 invasion to eutrophic lakes has long been recognized. For example, Schindler et al. (1972) demonstrated that atmospheric CO_2 invasion was essential to maintain primary production in the artificially eutrophic Canadian Shield lakes. Stable C isotope measurements also show a high flux of CO_2 to a soft water lake during an intense phytoplankton bloom period (Herczeg and Fairbanks 1987). Recently, Gu et al. (2004) have shown that nearly half of the C fueling phytoplankton production in Lake Apopka was provided by atmospheric flux.

The average $\delta^{13}C$ for atmospheric CO_2 is −8‰, lower than that (average = −4‰) of water-column DIC. In addition to atmospheric invasion, there must have been another DIC source highly enriched with ^{13}C to the water

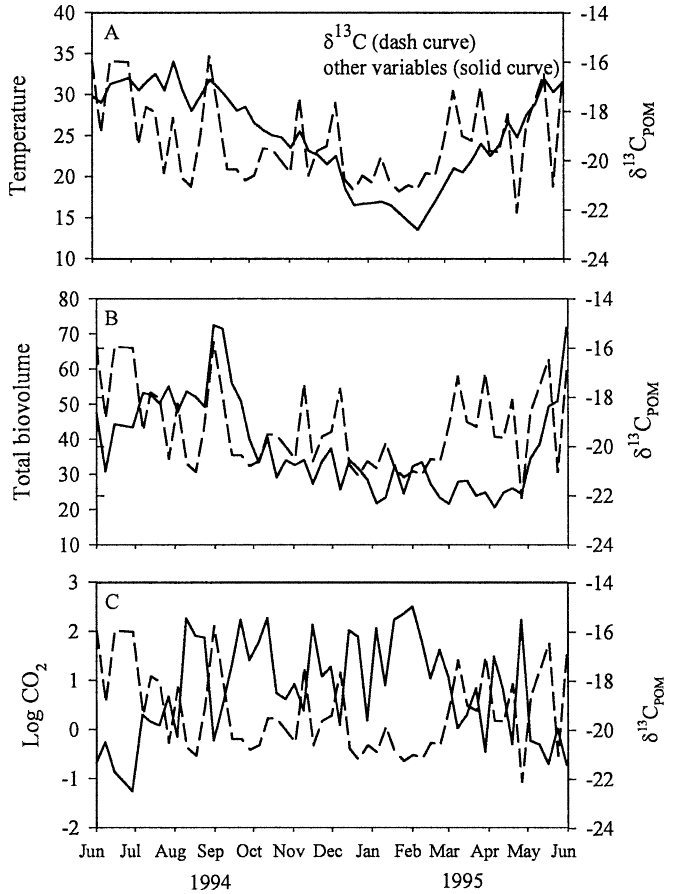

Fig. 9. Time series of $\delta^{13}C_{POM}$ versus (A) water temperature, (B) total biovolume, and (C) logarithmic CO_2 concentration. Values represented monthly averages of two central lake stations. Units of measurement are the same as those presented in previous figures.

column. Recent data indicate that the isotope composition of the sediment organic matter from Lake Wauberg ranged from −25.7‰ to −22.4‰ (Shumate 2004). Oxidation of sediment organic matter produces CO_2 with an isotope signature similar to its substrate. However, anaerobic respiration via methanogenesis can produce CO_2 with extreme ^{13}C enrichment (Stiller and Magaritz 1974; Games and Hayes 1976). Shumate (2004) found high $\delta^{13}C_{DIC}$ (mean = 4‰) in the surface water of Lake Wauberg and speculated that diffusion and mixing of porewater with CO_2 produced by sediment methanogenesis isotopically enriched the water-column DIC pool. Similarly, Wachniew and Różański (1997) suggested that increased supply of methanogenesis-derived CO_2 ($\delta^{13}C$ = ∼15‰) was responsible for the elevated epilimnetic $\delta^{13}C_{DIC}$ in a Polish lake. Gu et al. (2004) also reported extreme ^{13}C enrichments in the water column (9‰) and sediment porewater (26‰) from Lake Apopka. Therefore, the DIC pool from Lake Wauberg water column must have received several important contributions, mainly from atmospheric flux during the intense bloom period, terrestrial runoff during the major rain events, and sediment anaerobic respiration during the mixing periods. In general, atmospheric invasion and sediment flux of anaerobic respiration dominated the DIC supplies to the water column.

$\delta^{15}N_{POM}$ *and* N_2 *fixation*—N_2 fixation is an important pathway for primary production in lakes with low DIN concentration and with phytoplankton dominated by N_2-fixing cyanobacteria. Isotopically light $\delta^{15}N_{POM}$ is typically associated with N_2 fixation because, by definition, the $\delta^{15}N$ of N_2 fixers is close to 0‰ when they use N_2 as their sole N source and because they show little isotope fractionation during N_2 fixation (Hoering and Ford 1960; Delwiche and Steyn 1970). Low $\delta^{15}N_{POM}$ during high N_2 fixation has been reported from pure culture (Hoering and Ford 1960; Minagawa and Wada 1986), terrestrial (Shearer and Kohl 1986; Boddey et al. 2000), marine (Montoya et al. 2002; Pantoja et al. 2002), and lacustrine systems (Gu and Alexander 1993; Lehmann et al. 2004). Conversely, lakes with high DIN concentrations typically show little N_2 fixation and high $\delta^{15}N_{POM}$. For example, Ferber et al. (2004) found high $\delta^{15}N$ of cyanobacteria in a small shallow lake with low N_2 fixation and high DIN uptake rates.

By contrast to the C isotope values of POM, $\delta^{15}N_{POM}$ was generally low in the warm months and high in the cold months, although some low values were also found in the cold months. This pattern is consistent with the dominance of N_2-fixing cyanobacteria during the growth period. Previous research indicated that the N isotope composition of *Anabeana cylindrica* did not change with growth rate in a pure culture (Minagawa and Wada 1986). This can be explained by (1) an ample supply of N_2, (2) constant $\delta^{15}N$ in the dissolved N_2, and (3) little isotope fractionation during N_2 fixation. Under the field conditions, $\delta^{15}N_{POM}$ can be influenced by phytoplankton composition, as well as sources, concentrations, and utilization pathway of DIN. Aside from a weak but significant correlation with DIN concentration, $\delta^{15}N_{POM}$ did not follow the changes in other ambient variables and indeed varied little over time. We have already eliminated terrestrial contribution as a major nutrient source and do not expect any effect of phytoplankton biomass on $\delta^{15}N_{POM}$ because isotope fractionation is irrelevant to growth rate during N_2 fixation (Minagawa and Wada 1986). However, we are surprised by the lack of correlation between phytoplankton composition and $\delta^{15}N_{POM}$. We expect a change in $\delta^{15}N_{POM}$ with increasing or decreasing N_2-fixing cyanobacterial biovolume, which affects the amount of N_2 incorporated into the community biomass. One explanation is that the DIN and N_2 might share similar isotope composition. The water-column DIN pool could be fed by regenerated N derived partly from previous N_2 fixation. Gu and Alexander (1993) also speculated in their estimate of N_2 fixation by *Anabaena flosaquae* from a subarctic lake that the uptake of isotopically light N released during bacterial decomposition of the cyanobacterial bloom was responsible for the seemingly high N_2 contribution during the late bloom period when other techniques pointed to low N_2 fixation rate.

Our weekly sampling and analysis revealed moderate seasonal variation in stable C isotopes of the water-column POM. This pattern of change was driven by a combination

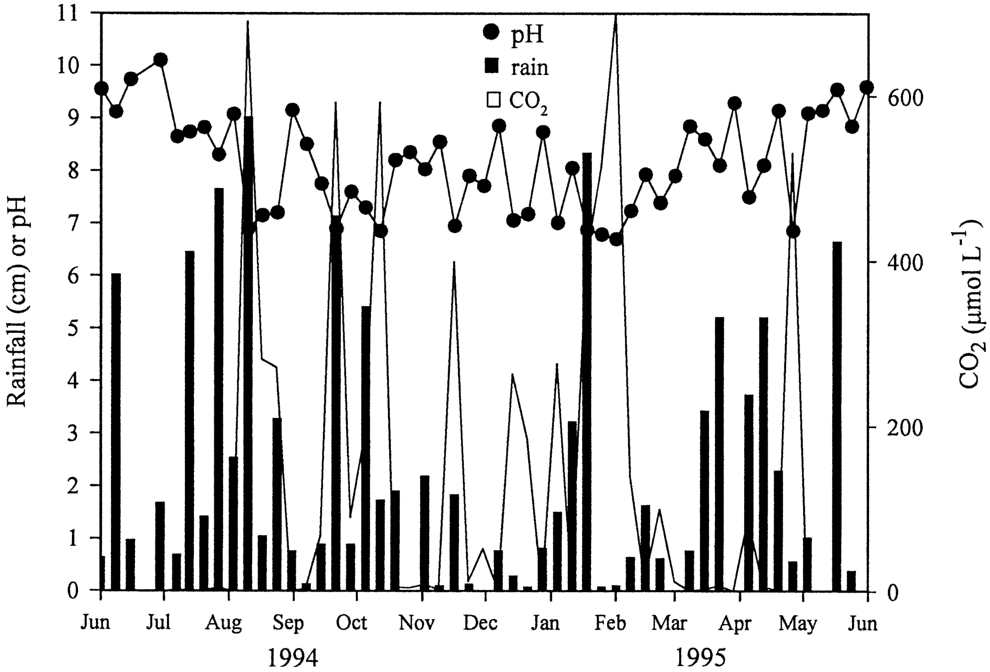

Fig. 10. Responses of pH and CO_2 to seasonal variations in weekly total rainfall over the study period. Values for pH and CO_2 concentration represented monthly averages of two central lake stations.

of CO_2 concentration, pH, and phytoplankton productivity. Frequent collapses of the intense blooms and the episodic terrestrial runoff with high CO_2 concentration and depleted $^{13}C_{DIC}$ dictated the frequent $\delta^{13}C_{POM}$ variations in our weekly samples. Carbon limitation in Lake Wauberg is evidenced by the reduced isotope fractionation and low CO_2 concentration. This study demonstrates the usefulness of $\delta^{13}C_{POM}$ as a proxy for predicting CO_2 concentration and system productivity. Multiple lines of evidence indicate that POM in the surface water was derived principally from autochthonous production. This is not surprising given the high phytoplankton biomass in the lake and the lack of terrestrial inputs from the watershed.

Because the water-column DIC pool was enriched with ^{13}C relative to the potential sources from oxidation of terrestrial and sediment organic matter, contributions to this pool must be dominated by DIC sources also enriched with ^{13}C. The terrestrial loading with depleted $\delta^{13}C$ cannot be a major DIC supply to Lake Wauberg due to the absence of a continuous surface flow to the lake. High CO_2 concentration and depleted $\delta^{13}C_{DIC}$ during major rain periods suggested that C flow from the episodic runoffs brought a large amount of DIC to the surface water. However, these C pulses did not have lasting effects on the isotope composition of POM because the lake only maintained a small DIC pool because of its poor buffering capacity. Excessive CO_2 from the surface water must have been quickly lost to atmosphere. Carbon dioxide produced from anaerobic respiration of sediments was considered a major DIC source to the water column in Lake Wauberg. This was accompanied by atmospheric CO_2 invasion due to the low pCO_2 in the surface water and the intense annual phytoplankton blooms.

The seasonal pattern of $\delta^{15}N_{POM}$ was inverse to the C isotopes of POM but varied little on the absolute scale. The low and relatively consistent $\delta^{15}N_{POM}$ in the growth period, the presence of high biomass of N_2-fixing cyanobacteria, and the low molar DIN : SRP ratios suggest that atmospheric N_2 was an important N source to the lake. The low $\delta^{15}N_{POM}$ in the winter period probably indicates the use of recycled N derived from N_2 fixation. The nonlinear relationship between phytoplankton biomass and $\delta^{15}N_{POM}$ prohibits us from using N isotope composition as a proxy for system productivity on an annual basis. However, low $^{15}N_{POM}$ from water column and sediment samples often indicates nitrate depletion and N_2 fixation. Further research is warranted to gain more insights of stable N isotope biogeochemistry in freshwater lakes.

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