

Factors controlling $\delta^{13}\text{C}$ values of sedimentary carbon in hypertrophic Baldeggersee, Switzerland, and implications for interpreting isotope excursions in lake sedimentary records

Jane L. Teranes¹

Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California 92093-0244

Stefano M. Bernasconi

Geological Institute, ETH-Zürich, CH-8092 Zürich, Switzerland

Abstract

We use stable carbon isotope values ($\delta^{13}\text{C}$) in sedimented organic matter and carbonate as proxy indicators of productivity changes in a highly eutrophic to hypertrophic lake. Stable isotope data from a seasonally sampled sediment core recovered from Baldeggersee, Switzerland were compared with direct and inferred total phosphorus (P) concentrations. Carbon isotope values of sedimentary organic matter ($\delta^{13}\text{C}_{\text{org}}$) in both seasonal varves and over the past 100 yr are not linearly related to total P concentrations, nor do they mirror observed trends in carbonate isotope values ($\delta^{13}\text{C}_{\text{CaCO}_3}$). Baldeggersee $\delta^{13}\text{C}_{\text{org}}$ values are influenced by both variations in the relative inputs of eukaryotic biomass, which becomes enriched in ^{13}C with increasing primary productivity, and the contribution of microbial biomass produced in the expanding anoxic bottom waters, which is typically very depleted in ^{13}C . We also examined the fractionation within the organic matter– CO_2 – CaCO_3 system, calculated as $\epsilon_{\text{total organic carbon (TOC)}} = 10^3 \{ [(\delta^{13}\text{C}_{\text{CaCO}_3} + 1,000) / (\delta^{13}\text{C}_{\text{org}} + 1,000)] - 1 \}$. Thresholds within the measured ϵ_{TOC} values represent Baldeggersee trophic status more accurately than $\delta^{13}\text{C}_{\text{org}}$ or $\delta^{13}\text{C}_{\text{CaCO}_3}$ values alone. In alkaline lakes with endogenic carbonate precipitates, ϵ_{TOC} values can facilitate accurate interpretation of values and trends in organic carbon isotope data, and can help to better assess trophic history and lake remediation efforts in lake systems that have been heavily affected by cultural eutrophication.

Stratigraphic variations in carbon accumulation and isotopic compositions ($\delta^{13}\text{C}$) have become standard tools to assess organic matter sources, reconstruct paleoproductivity, and identify changes in nutrient availability in lake environments (e.g., McKenzie 1985; Bernasconi et al. 1997; Hollander and Smith 2001; Meyers and Teranes 2001). Because lakes can undergo major changes in response to augmented nutrient influxes from anthropogenic sources, numerous studies have assessed the applicability of stable isotopes of carbon to trace cultural eutrophication and the impact of lake remediation efforts (Hodell and Schelske 1998; Brenner et al. 1999; Neumann et al. 2002, Lehmann et al. 2004a). Because phytoplankton discriminate against ^{13}C during uptake, sinking organic matter will preferentially remove ^{12}C from the surface water dissolved inorganic carbon (DIC) pool. As supplies of CO_2 in the lake epilimnion are depleted and enriched in ^{13}C by increased productivity, phytoplankton will discriminate less against ^{13}C . Thus, in lake systems where primary productivity is the principle control on the cycling of carbon, organic matter becomes progressively enriched in ^{13}C with increased productivity—both seasonally

and in response to long-term eutrophication. Therefore, for the most part, increases in organic matter accumulation and $\delta^{13}\text{C}_{\text{org}}$ values document an increase in lake trophic levels.

Carbon isotope values in lake sediment may also reflect the input of carbon from sources other than phytoplankton production, including microbial biomass derived from chemoautotrophic processes, particularly in records recovered from anoxic basins in eutrophic systems (Spooner et al. 1994; Hollander and Smith 2001; Neunlist et al. 2002). Carbon isotope values that are significantly depleted in ^{13}C are evidence that bacterially assimilated carbon contributed to the sedimentary carbon biomass, either as coupled or uncoupled to surface water phytoplankton production. A recent isotopic study on sediments from eutrophic Lake Mendota (Wisconsin) illustrated that microbially mediated carbon cycling processes, associated with development of anoxic conditions in the water column, imparted a distinct isotopic signature (i.e., low $\delta^{13}\text{C}_{\text{org}}$ values) to sedimentary carbon (Hollander and Smith 2001). The authors proposed a series of eutrophication models, on the basis of total phosphate concentrations in the water column, to better interpret carbon isotope excursions in terms of the changing influence of ^{13}C -depleted microbial biomass relative to ^{13}C -enriched photoautotrophic biomass. Together, these studies identify the need to reexamine controls on biogeochemical cycling of carbon in response to major changes in nutrient load and water column anoxia, and fully evaluate the usefulness of $\delta^{13}\text{C}$ as a tracer of these processes in eutrophic to hypertrophic systems.

Here we report carbon isotope ratios of sedimentary organic matter and carbonate from a seasonally sampled 108-

¹ Corresponding author (jteranes@ucsd.edu).

Acknowledgments

We thank Maria Dittrich (EAWAG, Kastanienbaum) for providing surface water samples for isotope analyses and for constructive discussions on Baldeggersee. We also thank the associate editor, Mary I. Scranton, and two anonymous reviewers for constructive comments that markedly improved the quality of this paper. We gratefully acknowledge J. A. McKenzie for useful discussions and support during this research project.

yr varved core from Baldeggersee, a small eutrophic lake located in north-central Switzerland. Baldeggersee is ideally suited for a high-resolution study of biogeochemical cycling of carbon because the varved sediment sequence allows collection of seasonally resolved data, and the well-documented history of P concentrations, water column anoxia, and lake remediation efforts allow for accurate comparison of carbon isotope data to environmental conditions over the last century. Thus, we are able to carefully document variations in isotope ratios in the inorganic and organic sedimentary carbon in response to cultural eutrophication and subsequent remediation efforts.

We also consider isotope fractionation between the inorganic and organic carbon as an indicator of the importance of microbial biomass in lake sequences. It is well established that in sedimentary records that contain carbonate and organic carbon, the isotopic difference between the organic matter– CO_2 – CaCO_3 system, $\epsilon_{\text{total organic carbon (TOC)}}$, is more useful than $\delta^{13}\text{C}_{\text{org}}$ or $\delta^{13}\text{C}_{\text{CaCO}_3}$ values alone in interpreting productivity increases and significant organic matter sources (Hayes 1993). In marine sequences, Hayes et al. (1999) developed predictive ranges of ϵ_{TOC} , where ϵ_{TOC} values greater than 32‰ were useful indicators of significant inputs of chemotrophic bacteria biomass in the sedimented carbon. In most cases, discussion and interpretation of $\delta^{13}\text{C}_{\text{org}}$ values alone should be avoided, because $\delta^{13}\text{C}_{\text{org}}$ will increase and decrease with changes in the isotopic composition of ambient DIC (and thus carry a redundant productivity signal) as well as reflecting changes in ϵ_{TOC} (Hayes et al. 1999). We use the carbon isotope data presented here to develop predictive tools to relate ϵ_{TOC} values to relative contributions of ^{13}C -enriched photosynthetic and ^{13}C -depleted microbial biomass. We propose the use of ϵ_{TOC} values in other lake sediment studies, where possible, as an additional proxy to correctly assess the history and extent of cultural eutrophication and the effectiveness of remediation measures.

Study site—Baldeggersee is an alkaline, monomictic, hypertrophic lake situated at 463 m above sea level on the Swiss Plateau approximately 60 km northeast of Bern in central Switzerland (47°10'N, 8°17'E). The lake has a mean depth of 33 m, maximum depth of 66 m, volume of 0.173 km³, and a surface area of 5.2 km². The lake is fed by 13 small streams that drain 67.8 km² of catchment area and has one outflow located at the northern end of the lake. The mean hydraulic residence time is 4.3 yr (Lotter et al. 1997).

The annual cycle of water-column stratification and productivity in Baldeggersee is well documented (Teranes et al. 1999a). The water column is typically thermally stratified by late April/early May, when surface water warming and increasing light intensity trigger major algal blooms, consisting largely of centric diatoms. Endogenic calcite production in Baldeggersee is then biologically induced: Photosynthetic utilization of aqueous CO_2 significantly raises the pH to values of over 8.7 in the summer months, inducing calcite precipitation. This spring and summer sediment production results in thick, light-colored sediment layers consisting of calcite (60–80 wt%) and organic matter. These laminations are referred to as spring/summer, or “light”, layers. Algal blooms consisting of pennate diatoms and cyanobacteria

commonly occur again between September and November, also inducing calcite precipitation. The late summer–autumn sedimentation results in thinner, darker laminations with 30–50 wt% calcite, organic matter, and small amounts of detrital material. These laminations are referred to as late summer/autumn, or “dark”, layers (Teranes et al. 1999a, 1999b).

During at least the last 100 yr, Baldeggersee has undergone major changes in productivity, eutrophication, and hypolimnetic oxygen concentration in response to nutrient loading from agriculture and industrialization in the lake's watershed (Teranes and Bernasconi 2000). Concentrations of total phosphate, dissolved inorganic nitrogen, and ammonium concentrations with depth in the water column have been directly measured since 1958 by the Limnological Research Center in Kastanienbaum, Switzerland. Phosphate concentrations from 1885 to 1958 have been inferred from diatom assemblages in the sediment record (Lotter 1998). It is probable that inferred P concentrations in 1885 already reflected eutrophic conditions, due to nutrient influx from agricultural sources. P concentrations increase steadily throughout the record, reaching a maximum value of almost 0.6 mg L⁻¹ in 1974. Government restrictions on P influx into natural waters, initiated in 1974, decreased phosphate concentrations to present levels of <0.1 mg L⁻¹. An internal lake restoration program, consisting of a bubble plume of oxygen during summer and injection of compressed air during winter, was initiated in 1982 in an attempt to oxygenate the lake bottom waters and to force mixing of the water column (Wehrli et al. 1997). Despite these measures, internal P cycling in the lake continues, primary productivity has not decreased significantly, and the sediment–water interface has remained anoxic (Gächter and Wehrli 1998).

Materials and methods

In October 1993, three freeze cores (BA93-A, B, C) were recovered from the deepest part of Baldeggersee at a water depth of 66 m. Details of the varve chronology and sampling techniques are provided in Lotter et al. (1997) and Teranes et al. (1999b). Sinking particulate material was also collected daily, from March 1995 until October 1996, with a TECHNICALAP (Markasub© Basel, Switzerland) sediment trap device deployed at 60 m water depth in Baldeggersee, approximately 6 m above the lake bottom. Accumulation rates of organic and inorganic C and isotopic values of inorganic C for core and sediment trap samples are given in Teranes et al. (1999a) and Teranes et al. (1999b), respectively. Accumulation rates of organic nitrogen, $\delta^{15}\text{N}$ data, and C:N atomic ratios from core and sediment trap samples are reported in Teranes and Bernasconi (2000).

Sediment core and sediment trap samples for C-isotopic analysis were first decarbonated in dilute hydrochloric acid, rinsed with copious amounts of distilled water, and then freeze-dried on a vacuum line. Approximately 0.5–2.0 mg of carbonate-free sediment was then loaded into tin sample capsules and measured on a Carlo-Erba CNS[®] analyzer with autosampler coupled to a Fisons Optima mass spectrometer in the ETH stable isotope laboratory. C isotope composition is reported in the conventional delta notation with respect to PDB (Pee Dee Belemnite). We measured light and dark samples for every year back to 1909, and every 3 yr from 1908

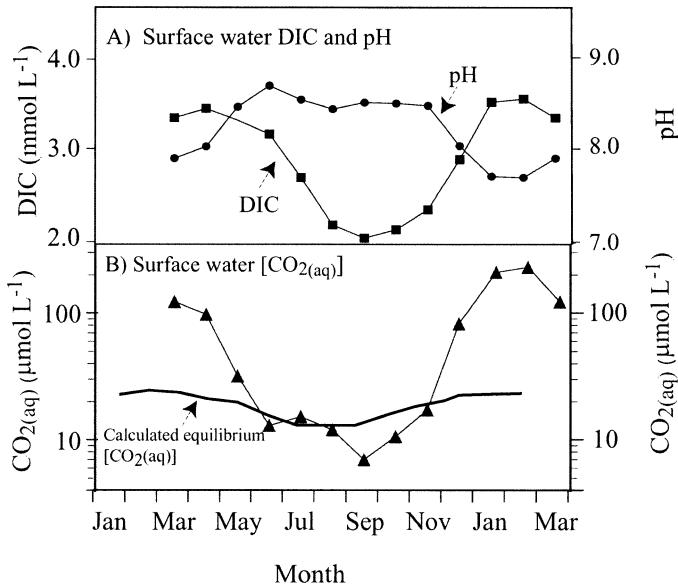


Fig. 1. Generalized seasonal cycle of surface water carbonate chemistry cycle in Baldeggersee including (A) DIC concentration and pH, and (B) surface water $[\text{CO}_2(\text{aq})]$. Data represent long-term surface-water (0–7.5 m) averages from the years 1981–1993. Data collected by EAWAG Lake Research Laboratory-Kastanienbaum. Also see Teranes et al. 1999a and 1999b. Calculated equilibrium $[\text{CO}_2(\text{aq})]$ is based on surface-water temperature averages and an assumed atmospheric pCO_2 value of 360 ppm.

to 1885. Analytical reproducibility for $\delta^{13}\text{C}$, determined on repeat analysis of NBS-22, is $\pm 0.1\text{‰}$.

Surface waters (2.5 m) were collected at approximately biweekly intervals from April through July 1999 for determination of $\delta^{13}\text{C}$ composition of the DIC throughout the period of the most intensive primary productivity. Surface waters were collected by filtration through 0.2- μm glass fiber filters into 50-ml glass bottles, poisoned with CuCl_2 , and then sealed with a rubber stopper and a crimp top seal. $\delta^{13}\text{C}$ ratios were determined on the CO_2 liberated from the water after acidification with phosphoric acid on a vacuum extraction line. The overall precision of $\delta^{13}\text{C}$ determination of the DIC, on the basis of repeat analyses of a laboratory water standard, was better than 0.3‰.

Results

Surface water carbon chemistry data—Figure 1 presents the generalized seasonal changes in the surface water carbonate chemistry cycle. Surface water pH increases to values of 8.7 in the summer months, and DIC concentrations drop dramatically by mid-summer because of progressive photosynthetic removal of CO_2 and subsequent carbonate precipitation (Fig. 1A). Figure 1B compares measured seasonal changes in the surface water $[\text{CO}_2(\text{aq})]$ concentrations with calculated equilibrium $[\text{CO}_2(\text{aq})]$ concentrations on the basis of $\text{pCO}_2(\text{atm})$ and surface water temperature measurements. Surface waters are oversaturated with respect to $[\text{CO}_2(\text{aq})]$ from winter until early spring. Primary productivity utilization depletes surface water $[\text{CO}_2(\text{aq})]$ to concentrations below calculated equilibrium values by late summer to autumn (Fig. 1B).

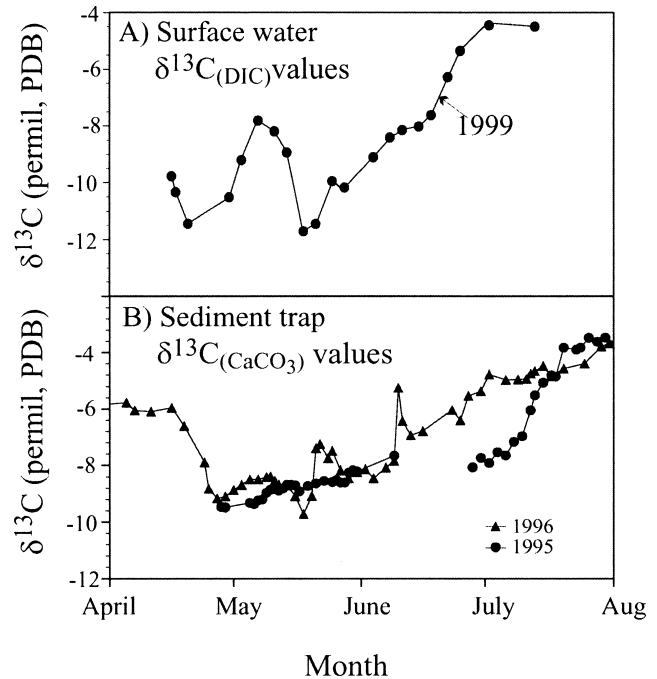


Fig. 2. Representative seasonal variations in carbon isotope values from (A) surface-water DIC pool (2.5 m) in 1999, and (B) carbonate in daily sediment trap samples from 1995–1996. Also see Teranes et al. 1999a. Although $\delta^{13}\text{C}$ measurements of the DIC were not made in the same years that sediment trap samples were collected, the values presented here are representative of the extent of seasonal variability.

Figure 2A plots the $\delta^{13}\text{C}$ of DIC from water samples collected biweekly at 2.5 m depth over the main part of the seasonal productivity cycle in 1999. As in most small lakes, surface water $\delta^{13}\text{C}$ values are significantly modified by seasonal biological activity, varying by $\sim 7\text{‰}$ over an annual cycle. In early spring, before water column stratification, $\delta^{13}\text{C}$ values are as low as -12‰ , reflecting incorporation of ^{13}C -depleted DIC, derived from the hypolimnion, during seasonal mixing. During seasonal photosynthetic productivity, as ^{12}C is preferentially incorporated into organic matter, the surface water DIC reservoir becomes progressively enriched in ^{13}C . This can be observed as a progressive isotopic enrichment of the surface water reservoir throughout the summer. By mid-summer, the water column is stratified and $\delta^{13}\text{C}$ values have increased to -4.6‰ . The brief period of elevated $\delta^{13}\text{C}$ values that occurred in early May 1999 is a predicted response to an early warming event and a corresponding phytoplankton bloom.

Figure 2B plots $\delta^{13}\text{C}$ values from carbonate collected in daily sediment trap samples over the productivity period in 1995 and 1996 (Teranes et al. 1999a). This data set offers a view, in unparalleled resolution, of the seasonal increase in $\delta^{13}\text{C}$ values of epilimnion carbonate precipitate as related to the annual changes in the $^{13}\text{C}:^{12}\text{C}$ ratios of surface-water DIC due to C-isotope fractionation during in situ biosynthesis. Together Figs. 1 and 2 document the close coupling of C-isotope dynamics with the annual cycle of primary productivity controlling CO_2 drawdown in surface waters. This

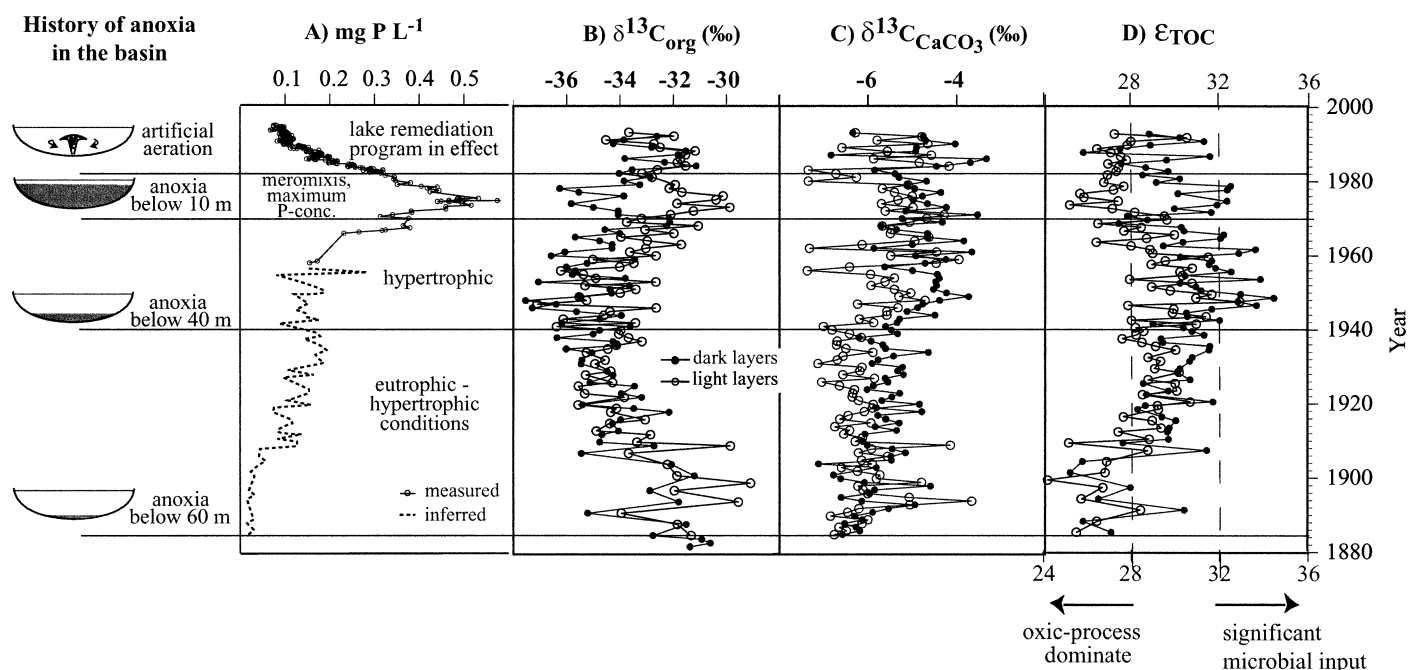


Fig. 3. Summary diagram showing the development of historical hypolimnion anoxia in Baldeggersee (adapted from Niessen and Sturm 1987). (A) Inferred and measured total phosphate concentrations throughout the study period, and measurements from the Baldeggersee laminated sequence including (B) organic matter $\delta^{13}\text{C}_{\text{org}}$ values, (C) carbonate $\delta^{13}\text{C}_{\text{CaCO}_3}$ values, and (D) ϵ_{TOC} values calculated from $\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{13}\text{C}_{\text{org}}$ values. Results from the light and dark laminae are plotted separately. P data are from EAWAG Lake Research Laboratory-Kastanienbaum and represent water column concentrations after seasonal overturn when the water column concentrations are relatively constant. Inferred P concentrations from Lotter (1998).

is important to the present study, as it demonstrates that carbonate precipitate accurately reflects changes in surface-water DIC, as related to DIC sources and seasonal surface-water primary production.

Core sediment carbon isotope values—Figure 3 compares the known history of P concentrations and anoxia in the Baldeggersee water column to the sediment core carbon isotope data, including $\delta^{13}\text{C}_{\text{org}}$ values, $\delta^{13}\text{C}_{\text{CaCO}_3}$ values, and the isotopic fractionation between the two, ϵ_{TOC} , calculated as:

$$\epsilon_{\text{TOC}} = 10^3 \left\{ \left[\frac{(\delta^{13}\text{C}_{\text{CaCO}_3} + 1,000)}{(\delta^{13}\text{C}_{\text{org}} + 1,000)} \right] - 1 \right\} (1)$$

At the start of our record, inferred P concentrations already classify the lake as eutrophic (where eutrophic is defined by P concentrations between 0.035 mg L⁻¹ and 0.100 mg L⁻¹; OECD 1982), most likely as a result of early agricultural activity surrounding the lake. By 1900 Baldeggersee has become hypertrophic (P concentrations >0.100 mg L⁻¹; OECD 1982) and stays hypertrophic until after 1990.

Measured $\delta^{13}\text{C}_{\text{org}}$ values, plotted in Figure 3B, vary between -30‰ and -37‰. These very negative values are lower than most reported lacustrine algal matter and lake sediment values (Meyers and Teranes 2001). $\delta^{13}\text{C}_{\text{org}}$ values generally decrease from the beginning of the record ($\delta^{13}\text{C}_{\text{org}} \sim -31‰$) until 1940–1950 when $\delta^{13}\text{C}_{\text{org}}$ values reach -35‰ to -37‰. Starting in 1960, $\delta^{13}\text{C}_{\text{org}}$ values show an increasing trend and return to values of -33‰ by 1970. In general, dark-layer $\delta^{13}\text{C}_{\text{org}}$ values are more negative than light-layer $\delta^{13}\text{C}_{\text{org}}$ values throughout the record; particularly 1970–1982, when dark-layer $\delta^{13}\text{C}_{\text{org}}$ values are up to 6‰

lower than light-layer values for the corresponding year. Since the beginning of the lake remediation program in 1982, light- and dark-layer $\delta^{13}\text{C}_{\text{org}}$ values oscillate between approximately -34‰ to -32‰, yet never completely increase to values noted at the very beginning of the record.

$\delta^{13}\text{C}_{\text{CaCO}_3}$ values, varying between -7.4‰ and -3.5‰, record progressive changes in the isotopic composition of the surface-water DIC pool and, for the most part, are distinct from the observed trends in $\delta^{13}\text{C}_{\text{org}}$ values (Fig. 3C). $\delta^{13}\text{C}_{\text{CaCO}_3}$ values show a slight 1‰ increase from the beginning of the record until 1940–1950, with the trend being more pronounced in the dark layer values. Throughout the upper part of the core, $\delta^{13}\text{C}_{\text{CaCO}_3}$ values fluctuate significantly around average values of -5.5‰ and -4.8‰ for light and dark layers, respectively. During this period the light-layer $\delta^{13}\text{C}_{\text{CaCO}_3}$ values show occasional and abrupt negative excursions to $\delta^{13}\text{C}_{\text{CaCO}_3}$ values of <-7‰. Dark-layer $\delta^{13}\text{C}_{\text{CaCO}_3}$ values show occasional positive excursions to $\delta^{13}\text{C}_{\text{CaCO}_3}$ values of >-4. Since the beginning of the lake remediation program in 1982, light- and dark-layer $\delta^{13}\text{C}_{\text{CaCO}_3}$ values continue to oscillate significantly between -3‰ and -7‰, without displaying any clear trends.

Calculated ϵ_{TOC} values vary between 24‰ and 35‰ (Fig. 3D), and are slightly greater than other reported values for the isotope enrichment between organic matter and DIC sources (typically 25.3‰; Fogel and Cuifentes 1993; Popp et al. 1998).

Discussion

Comparison of Baldeggersee data with existing eutrophi-

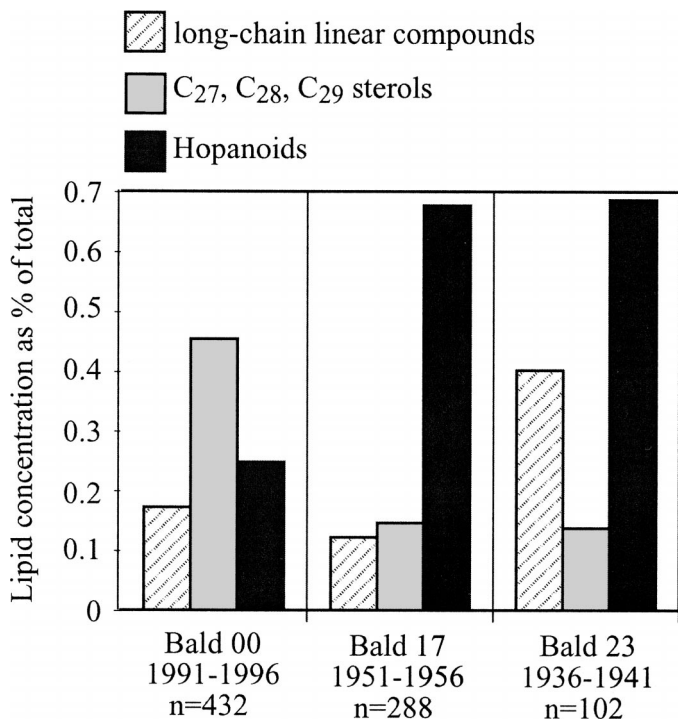


Fig. 4. Lipid concentrations for Baldeggersee sediment samples at three different intervals. Concentrations are plotted as percentage of total where n = total amount of analyzed lipids in micrograms per gram dry weight. Data are from Neunlist et al. (2002). Here we plot lipid concentrations in three groups, according to the most probable source organisms. Long-chain linear compounds, including long-chain n-alkanes, long-chain n-alkanols, and long-chain n-fatty acids, are mainly attributed to plant waxes and microalgae. Sterols are attributed to algae, microalgae, higher plants, zooplankton, and animals. Hopanoids are attributed to bacteria and cyanobacteria. See Neunlist et al. (2002) for further discussion and references. The data show a higher percentage of hopanoids during times of higher trophic level and more severe anoxia.

cation models—Primary productivity in the epilimnion is most often considered the dominant biogeochemical control on $\delta^{13}\text{C}$ of organic matter in lake environments. Phytoplankton preferentially incorporate ^{12}C during DIC uptake; the degree of isotope fractionation will vary with the form of DIC assimilated ($\text{CO}_{2(\text{aq})}$ vs. HCO_3^-). Export of organic matter out of the photic zone enriches the epilimnion DIC pool in ^{13}C , at least on a seasonal basis, until oxidation of the sinking organic matter returns the ^{12}C to the surface waters during autumn/winter overturn. If enough organic matter accumulates on the lake bottom, or supplies of surface-water DIC become seasonally depleted through increased productivity, $\delta^{13}\text{C}$ values of the remaining DIC pool increase and produce a subsequent increase in the $\delta^{13}\text{C}$ values of newly produced organic matter. Increases or decreases in sedimented organic matter and its stable isotopic signature, therefore, have been widely interpreted as indicative of increases or decreases in productivity in response to eutrophication and remediation measures (Hodell and Schelske 1998; Brenner et al. 1999; Neumann et al. 2002). In systems where primary productivity dominates, inorganic and organic carbon will display parallel trends in $\delta^{13}\text{C}$ values as carbon precipitated in the

epilimnion from a DIC reservoir becoming progressively enriched in ^{13}C with increases in productivity. A recent sediment trap study in eutrophic Lake Lugano, Switzerland by Lehmann et al. (2004a) documents a significant negative correlation between phosphorus concentrations (range 0.030–0.120 mg L^{-1}) and $\delta^{13}\text{C}$ values of the epilimnetic organic matter. This Lake Lugano study demonstrates that $\delta^{13}\text{C}$ values primary photosynthate can correlate to variations in P concentrations, even at relatively high levels of eutrophication.

Recent work in modern sedimentary environments has identified microbial biomass as an additional and important source of organic matter to the total sedimentary carbon reservoir (Spooner et al. 1994; Kelley et al. 1998; Hollander and Smith 2001). Biogenic methane production, occurring through fermentation of sinking or recently deposited organic carbon at the sediment–water interface, and methane oxidation by methanotrophic bacteria are other important controls on carbon cycling in anoxic portions of the water column. Biomass originating from methanotrophic bacteria have very low $\delta^{13}\text{C}$ values, because these organisms fractionate -16‰ to -30‰ during biosynthesis (Summons et al. 1994) from a biogenic methane carbon source that is already depleted in ^{13}C ($\delta^{13}\text{C}$ values of -50 to -70‰ ; Whiticar 1999). Lehmann et al. (2004b) have documented the formation of particulate organic matter with $\delta^{13}\text{C}$ values as low as -60‰ at the oxic–anoxic interface in the benthic nepheloid layer in Lake Lugano, Switzerland. Synthesis of bacterial biomass at the anoxic–oxic interface has also been documented in meromictic Lake Cadagno, Switzerland. Bernasconi and Hanselmann (1995) measured $\delta^{13}\text{C}$ values of -41.5‰ in the particulate organic matter at the chemocline, and Behrens et al. (2000) measured $\delta^{13}\text{C}$ values of -46‰ in a bacterial biomarker for purple sulfur bacteria.

Using $\delta^{13}\text{C}$ data from two highly productive lakes, Lake Mendota (Wisconsin) and Lake Greifen (Switzerland), Hollander and Smith (2001) derived new eutrophication models to incorporate the importance of microbially mediated carbon cycling processes as related to the intensification of cultural eutrophication. Notably, their models predict parallel trends in $\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{13}\text{C}_{\text{org}}$ records. At relatively low P concentrations ($<0.05 \text{ mg L}^{-1}$), their model predicts that primary productivity processes will dominate and the DIC reservoir will become progressively enriched in ^{13}C , with increases in productivity such that inorganic and organic carbon will display parallel increasing trends in $\delta^{13}\text{C}$ values. During periods of moderate to severe eutrophication, defined as $0.05 \text{ mg L}^{-1} < \text{P} < 0.18 \text{ mg L}^{-1}$, their models predict expansion of bottom-water anoxia and increased importance of microbial processes. The addition of microbial biomass would produce a ^{13}C -depletion trend in sedimentary organic carbon records. Also, the shallowing of the oxic–anoxic interface could contribute the ^{13}C -depleted dissolved CO_2 from oxidation of biogenic methane directly to the epilimnion DIC reservoir during seasonal stratification. Assimilation of DIC by photoautotrophic plankton and epilimnion carbonate precipitation would result in ^{13}C -depleted organic carbon and inorganic carbon in the sediment record. Their model predicts that photoautotrophic processes will again dominate when $\text{P} > 0.18 \text{ mg L}^{-1}$ and progressive increases of P above

this threshold will produce positive isotopic trends in sedimentary carbon.

We suggest that primary productivity and the addition of microbial biomass are both important considerations when interpreting the Baldeggersee carbon isotope records. For example, $\delta^{13}\text{C}_{\text{org}}$ values initially show a negative shift (from -31‰ to -36‰) in response to early hypertrophic conditions (1900–1950 Fig 3B), most likely due to the addition of microbial biomass to the sediments. From approximately 1960 to 1972, under increasingly hypertrophic conditions (Fig. 3A), $\delta^{13}\text{C}_{\text{org}}$ values begin to increase. This is consistent with the models of Hollander and Smith (2001) that predict a changing influence from ^{13}C -depleted microbial biomass to ^{13}C -enriched photoautotrophic biomass as P concentrations gradually increase above approximately 0.2 mg L^{-1} . Finally, during the period of maximum P concentrations and meromixis (1970–1982), $\delta^{13}\text{C}_{\text{org}}$ values show a distinct seasonal offset, with dark-layer values up to 6‰ more negative than light-layer values (Fig. 3B). If primary productivity alone influenced the isotopic composition of organic carbon in the sediment, then higher $\delta^{13}\text{C}_{\text{org}}$ values should be associated with sediment deposited when the surface-water DIC concentrations were lowest (i.e., the dark layers, deposited in late summer and autumn). Instead, our data suggest a depleted organic carbon source to the sediment that is dominant during the late summer and fall, especially when the anoxic bottom waters are most expanded.

In the case of Baldeggersee, the most plausible source of ^{13}C -depleted organic carbon to the sediments is microbial biomass resulting from expansion of chemoautotrophic and methanotrophic microbial communities in the anaerobic portions of the Baldeggersee hypolimnion and metalimnion, in response to increasing cultural eutrophication. Although this cannot be confirmed by the data presented here, the presence of microbial biomass in the Baldeggersee sediments has been confirmed by a previous study of biomarker compounds from the same Baldeggersee sediment core (Neunlist et al. 2002). Their study looked at biomarker compounds at three different stratigraphic intervals in the Baldeggersee sediment core: 1936–1941 (hypertrophic conditions), 1951–1956 (severe hypertrophic conditions), and 1991–1996 (period of lake aeration). Their analyses found hopanoid biomarkers, lipid compounds from bacterial and cyanobacterial sources, in all three periods sampled, with the highest concentrations, by far, noted in the 1951–1956 sample (Fig. 4; Neunlist et al. 2002). Their study confirms a large presence of microbial biomass in the sediments, with the highest concentrations occurring during the most anoxic of the sampled intervals. This data supports our observations that negative trends in Baldeggersee $\delta^{13}\text{C}_{\text{org}}$ values reflect the expansion of microbial communities in the anoxic part of the water column and the addition of the ^{13}C -depleted microbial biomass to the sediment.

Rather than paralleling $\delta^{13}\text{C}_{\text{org}}$ trends, however, the Baldeggersee $\delta^{13}\text{C}_{\text{CaCO}_3}$ record is mostly consistent with the productivity models that suggest that surface water photoautotrophs are the most important factor in determining trends in the carbon isotope composition of the DIC, and therefore $\delta^{13}\text{C}_{\text{CaCO}_3}$, on both seasonal and longer-term bases. For example, the Baldeggersee $\delta^{13}\text{C}_{\text{CaCO}_3}$ record shows a general

increase upcore until 1940–1950, as cultural eutrophication intensifies (Fig. 3C). This positive $\delta^{13}\text{C}_{\text{CaCO}_3}$ trend is especially prominent in the dark layers, when the surface-water DIC concentrations are lowest and relatively enriched in ^{13}C toward the end of summer. Even during the period of most severe anoxia in the lake (1970–1982) when the anoxic–oxic interface had moved up to just 10 m water depth, $\delta^{13}\text{C}_{\text{CaCO}_3}$ values are not consistently more negative than the rest of the record (Fig. 3C), indicating that surface-water DIC during stratification dominantly reflects primary productivity.

On longer-term time scales, we do note that $\delta^{13}\text{C}_{\text{CaCO}_3}$ values are lower, on average, than calculated equilibrium values with atmospheric CO_2 . This is true of DIC and $\delta^{13}\text{C}_{\text{CaCO}_3}$ values in most small lakes, and can be attributed to biological activity. Oxidation of sinking organic matter will return ^{12}C to the water column, and this will be mixed into the surface waters during autumn/winter overturn. Additionally, oxidation of biogenic methane, which is produced in anoxic portions of the water column, could seasonally add significant quantities of ^{13}C -depleted CO_2 to the epilimnion during any mixing event. Evidence for the addition of ^{12}C during overturn is recorded in early spring surface water $\delta^{13}\text{C}_{\text{DIC}}$ values (as low as -12‰ , Fig. 2A) and sediment trap $\delta^{13}\text{C}_{\text{CaCO}_3}$ values (as low as -10‰ , Fig. 2B). Occasionally, low $\delta^{13}\text{C}$ values after overturn are significant enough to be recorded as prominent negative excursions in the light-layer sediment $\delta^{13}\text{C}_{\text{CaCO}_3}$ record. These are recorded $\delta^{13}\text{C}_{\text{CaCO}_3}$ values as low as -7.4‰ in 1956, 1962, 1980, and 1982 (Fig. 3C). Clearly the degree to which DIC will be influenced by oxidation of biogenic methane over longer time scales is dependent on the degree of lake stratification, quantity of ^{13}C -depleted CO_2 added to the epilimnion, and the degree to which DIC is modified by primary productivity both seasonally and over longer terms.

Thus, in Baldeggersee, the inorganic and organic carbon systems are fundamentally independent; $\delta^{13}\text{C}_{\text{CaCO}_3}$ trends respond mainly to surface-water productivity, whereas $\delta^{13}\text{C}_{\text{org}}$ trends reflect incorporation of microbial biomass. The chemoautotrophic biomass is formed largely at the anoxic–oxic interface or anoxic part of the water column (hypolimnion and occasionally metalimnion), whereas light limitation confines photoautotrophic activity, and hence carbonate precipitation, to the epilimnion. The contribution of microbial biomass in the sediment is most prominent in the dark layers (i.e., late summer and winter) when stratification and anoxia are most well developed.

Comparisons with other lake data—Despite the conceptual usefulness of any eutrophication model, attempting to apply any one model to widely different sedimentary sequences inevitably reveals inadequacies. Eutrophication models that are based on degree of primary productivity best explain the carbon-cycling processes in the epilimnion. These models are most appropriate in lakes that are essentially phosphorus-limited over the disturbance period. For example, lake sediment records from Lake Erie and Lake Ontario (Schelske and Hodell 1995, Hodell and Schelske 1998) and several lakes in Florida (Brenner et al. 1999) show a straightforward increase in photoautotrophic productivity in response to increasing P concentrations. Eutrophication models that rec-

ognize the importance of chemoautotrophic and methane oxidation processes seem to be most useful in lakes that are heavily disturbed and overenriched with phosphate. Lake Mendota and Lake Greifen (Hollander and Smith, 2001), Lake Lugano (Lehmann et al. 2004b), and Baldeggersee (this study) are examples of hypertrophic lakes with significant seasonal water column anoxia. In such systems it is important to recognize that microbial processes can significantly influence carbon cycling and produce distinct trends in sedimentary carbon.

Yet, even with these general guidelines it is still difficult to estimate the overall contribution of microbial processes on carbon cycling in lake systems. For example, some characteristics of the Baldeggersee $\delta^{13}\text{C}_{\text{org}}$ data agree quite well with the thresholds of P concentrations as outlined in Hollander and Smith (2001). Photoautotrophic processes are dominant when P concentrations are low, and microbial processes are most prevalent in the $0.1 \text{ mg L}^{-1} < \text{P} < 0.2 \text{ mg L}^{-1}$ range (as noted by trends in the $\delta^{13}\text{C}$ data when compared with known lake conditions). However, most of the Baldeggersee $\delta^{13}\text{C}_{\text{org}}$ data are significantly more negative, over a wider range of P concentrations, than the gradients suggested by Hollander and Smith (2001), and the models tend to overemphasize the influence of microbial activity on DIC isotope compositions. Obviously, other factors, in addition to total phosphate, are important in the determination of biomass sources and the $\delta^{13}\text{C}$ response. The degree of water column anoxia—and hence the expansion of the microbial biomass—may be the most important primary control, yet this is only weakly approximated by phosphate concentrations. Basin morphology, local hydrology, and mixing conditions are all additionally important.

To alleviate some deficiencies in both models, we can consider isotope fractionation between the inorganic and organic carbon as an additional tool to aid prediction of the importance of microbial biomass in lake sedimentary sequences. It is well established that the isotopic difference between two carbon species is more meaningful than either isotopic value on its own (Hayes, 1993). Hayes et al. (1999) recommended using records of the isotopic fraction between sedimentary carbonate and sedimentary organic carbon, $\Delta\delta^{13}\text{C}$ (defined as $\delta^{13}\text{C}_{\text{CaCO}_3} - \delta^{13}\text{C}_{\text{org}}$), as a useful approximation of ϵ_{TOC} (the average isotopic fractionation between C_{org} and ambient DIC) and suggested that $\Delta\delta^{13}\text{C}$ values are preferable over $\delta^{13}\text{C}_{\text{org}}$ data alone for discussion and interpretation of paleo-productivity and organic matter sources. Hayes et al. (1999) applied this concept to interpretation of marine sedimentary sequences and offered threshold values for indication of microbial sources. These thresholds were based on calculated ϵ_{TOC} ranges from marine phytoplankton assimilation of carbon (Popp et al. 1998) over a wide range of ambient temperature and CO_3^{2-} concentrations. Hayes et al. (1999) concluded that ϵ_{TOC} values greater than 32‰ are indicative of significant inputs from chemoautotrophic bacteria; ϵ_{TOC} values between 28 and 32‰ are either caused by maximal fractionation of carbon isotopes by phytoplanktonic producers or by lesser levels of input from chemoautotrophs; and ϵ_{TOC} values of less than 28‰ primarily reflect phytoplanktonic producers with a reduction of primary fractionation due to conditions of the growth environment and cell physiology.

Below we provide an analysis of measured ϵ_{TOC} values in Baldeggersee in light of the well-documented trends in water column P concentrations, anoxia, and sedimentary records of organic and inorganic carbon.

Threshold ϵ_{TOC} values and implications for eutrophication models—There are three brief historical periods when ϵ_{TOC} values are consistently less than 28‰ (Fig. 3). The first period occurs at the very beginning of the sequence, when $\text{P} < 0.08 \text{ mg L}^{-1}$ and bottom water anoxia was never severe enough or persistent enough for development of extensive microbial activity. Another period occurs during the lake restoration phase, when the lake hypolimnion was artificially aerated to promote mixing during the winters, and oxygen was pumped into the bottom waters during the summer. Finally, ϵ_{TOC} values are consistently less than 28‰ in spring/summer (i.e., the light layers) of the most severe period of eutrophication (Fig. 3). The first two periods are characterized by oxic bottom water conditions when anaerobic microbial processes would have been limited and photosynthetic biomass would have dominated the sedimentary record. The third period occurred when lake meromixis prevented seasonal mixing of the water column.

There are also at least two periods in the Baldeggersee sequence when ϵ_{TOC} values in the dark layers are often $>32\%$ (Fig. 3). This is the case for most of the period of severe eutrophication (i.e., from 1940 to 1969) when P concentrations ($0.18\text{--}0.35 \text{ mg L}^{-1}$) and the anoxic bottom water mass are both steadily increasing, and during late summer/autumn (i.e., the dark layers) of the period of maximum eutrophication (i.e. from 1970 and 1982). During both of these periods the anaerobic portions of the hypolimnion are highly developed or significantly expanding (or both), which would result in increased anaerobic microbial activity and corresponding sedimentation of ^{13}C -depleted microbial biomass.

Anaerobic microbial processes and sedimentation should be most prominent from late summer to winter, when seasonal stratification and expansion of the anaerobic hypolimnion is more pronounced, accounting for the generally higher ϵ_{TOC} values in dark layers (compared to light layers from the same year). Between 1970 and 1982, when Baldeggersee experienced the most severe anoxic conditions, the seasonal offset $\delta^{13}\text{C}_{\text{org}}$ and ϵ_{TOC} values are most pronounced (Fig. 3) probably because of significant input of ^{13}C -depleted microbial biomass to the sediment during deposition of the dark layer. The seasonal offset during this period also indicates how bacterially assimilated carbon can be uncoupled to surface phytoplankton production: Light-layer ϵ_{TOC} values plot consistently below 28‰, demonstrating that ^{13}C -enriched photoautotrophic biomass flux during the spring and summer is sufficient to overwhelm all other carbon sources in the sedimentary record. Dark-layer ϵ_{TOC} values reach 30‰ and above, consistent with an increase in relative contribution of ^{13}C microbial biomass to the sedimentary carbon record when photoautotrophic productivity wanes.

Although initiation of artificial aeration in 1982 did effectively mix the lake enough to restore circulation and oxygen to the bottom waters, Baldeggersee most certainly has not recovered completely and can still be considered a eutrophic system. Despite decreased P concentration, internal phos-

phate cycling is about the same (Gächter and Wehrli 1998) and productivity and sedimentation rates of organic matter have remained high (Teranes and Bernasconi 2000), particularly in the form of large phytoplankton blooms, which record even higher biomass levels than before the lake restoration efforts (Buergi and Stadelmann 2000). ϵ_{TOC} values often are high during this period; in particular, marked abrupt positive shifts in the dark layers are noted in 1985 and 1990–1991 (Fig. 3D). In both cases the high ϵ_{TOC} values are due to high $\delta^{13}\text{C}_{\text{CaCO}_3}$ values of the dark layers, which, in turn, are attributed to years of high productivity blooms that would deplete the surface-water DIC in ^{13}C by late summer/fall.

Overall our lake record of ϵ_{TOC} values agrees with the thresholds as proposed by Hayes et al. (1999). Although there are obvious differences in applying thresholds for this parameter that were established on long time scales in marine sediments to lakes, our analyses do provide compelling evidence that the ϵ_{TOC} proxy may provide insight on organic matter sources and aid in the interpretation of sedimentary sequences.

However, despite the potential usefulness of the ϵ_{TOC} proxy, a significant portion of the Baldeggersee sequence is characterized by ϵ_{TOC} values between 28‰ and 32‰ where the interpretation is inconclusive. These intermediate values can be caused either by lower but increasing levels of chemoautotroph input, as in the period from 1900 to 1940 when $\delta^{13}\text{C}_{\text{org}}$ values display a decreasing trend, or by maximal fractionation of carbon isotopes by phytoplanktonic producers, as in the light layers from 1940 to 1970 when $\delta^{13}\text{C}_{\text{org}}$ values display an increasing trend. Although ϵ_{TOC} values between 28‰ and 32‰ are not particularly useful in pinpointing organic matter sources, they do serve to signify that bacterial sources could be present. In such cases, additional proxies for expanding bottom water anoxia should be pursued to aid the interpretation of carbon isotope trends.

Data from high-resolution Baldeggersee samples presented here are evidence that the isotopic composition of sedimentary carbon (inorganic and organic) has a distinct seasonal signal, and that long-term isotopic trends are not simply coupled to historical records of nutrient loading and abatement. The $\delta^{13}\text{C}$ record reflects several related variables including P concentrations, degree of seasonal stratification, modification of the water column chemistry, bottom water anoxia, and variations in the importance of photoautotrophic and microbial biomasses. Published data from other lakes reveal that the relative importance of these variables on $\delta^{13}\text{C}_{\text{org}}$ will be system specific, and cannot be related definitively to water column P concentrations alone. In some lake basins, such as Baldeggersee, bottom water anoxia and the related functioning of microbial processes may play a more significant role than absolute nutrient concentrations in determining the quality and quantity of sedimentary organic matter.

We propose that, in alkaline lake systems with endogenic carbonate precipitates, calculating ϵ_{TOC} values can facilitate accurate interpretation of values and trends in organic carbon isotope data. ϵ_{TOC} values will provide a more accurate representation of lake status than $\delta^{13}\text{C}_{\text{org}}$ values alone, as $\delta^{13}\text{C}_{\text{org}}$ changes with both the isotopic composition of the DIC pool

and change in the fractionation factor ϵ_{TOC} . On the basis of data from Baldeggersee, we suggest that ϵ_{TOC} values of >28‰ in lake sequences signify the possible addition of microbial biomass, and ϵ_{TOC} values of >32‰ indicate significant input of microbial biomass to the sedimentary record. Both cases indicate that care should be used when interpreting trends in carbon isotope values in terms of past nutrient availability or assessing cultural eutrophication or lake remediation efforts.

References

- BEHRENS, A., P. SCHAEFFER, S. BERNASCONI, AND P. ALBRECHT. 2000. Mono- and bicyclic squalene derivatives as potential proxies for anaerobic photosynthesis in lacustrine sulfur-rich sediments. *Geochim. Cosmochim. Acta.* **64**: 3327–3336.
- BERNASCONI, S. M., A. BARBIERI, AND M. SIMONA. 1997. Carbon and nitrogen isotope variations in sedimenting organic matter in Lake Lugano. *Limnol. Oceanogr.* **42**: 1755–1765.
- , AND K. HANSELMANN. 1995. The influence of bacterial activity at the chemocline on particulate organic matter fluxes and nutrient cycling in meromictic Lake Cadagno. *In* J. O. Grimalt and C. Dorronsoro [eds.], *Organic geochemistry: Developments and applications to energy, climate, environment and human history*. Donostia-San Sebastian A.I.G.O.A.
- BRENNER, M., T. J. WHITMORE, J. H. CURTIS, D. A. HODELL, AND C. L. SCHELSKE. 1999. Stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) signatures of sedimented organic matter as indicators of historic lake trophic state. *J. Paleolimnol.* **22**: 205–221.
- BUERGI, H. R., AND P. STADELMANN. 2000. Change of phytoplankton diversity during long-term restoration of lake Baldegger (Switzerland). *Proc. Int. Ass. Theor. Appl. Limn.* **27**: 574–582.
- FOGEL, M. L., AND L. A. CIFUENTES. 1993. Isotope fractionation during primary production, p. 73–98. *In* M. H. Engel and S. A. Macko [eds.], *Organic geochemistry: Principles and applications*. Plenum Press.
- GÄCHTER, R., AND B. WEHRLI. 1998. Ten years of artificial mixing and oxygenation: No effect on the internal phosphorus loading of two eutrophic lakes. *Environ. Sci. Tech.* **32**: 3659–3665.
- HAYES, J. M. 1993. Factors controlling ^{13}C contents of sedimentary organic compounds: Principles and evidence. *Mar. Geol.* **113**: 111–125.
- , H. STRAUSS, AND A. J. KAUFMAN. 1999. The abundance of ^{13}C in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800 Ma. *Chem. Geol.* **161**: 103–125.
- HODELL, D. A., AND C. L. SCHELSKE. 1998. Production, sedimentation and isotopic composition of organic matter in Lake Ontario. *Limnol. Oceanogr.* **43**: 200–214.
- HOLLANDER, D. J., AND M. A. SMITH. 2001. Microbially mediated carbon cycling as a control on the $\delta^{13}\text{C}$ of sedimentary carbon in eutrophic Lake Mendota (USA): New models for interpreting isotopic excursions in the sedimentary record. *Geochim. Cosmochim. Acta.* **65**: 4321–4337.
- KELLEY, C. A., R. B. COFFIN, AND L. A. CIFUENTES. 1998. Stable isotope evidence for alternative bacterial carbon sources in the Gulf of Mexico. *Limnol. Oceanogr.* **43**: 1962–1969.
- LEHMANN, M. F., S. M. BERNASCONI, A. BARBIERI, M. SIMONA, AND J. A. MCKENZIE. 2004a. Interannual variation of the isotopic composition of sedimenting organic carbon and nitrogen in Lake Lugano: A long-term sediment trap study. *Limnol. Oceanogr.* **49**: 839–849.
- , S. M. BERNASCONI, J. A. MCKENZIE, A. BARBIERI, M. SIMONA, AND M. VERONESI. 2004b. Seasonal variation of the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of particulate and dissolved carbon and nitrogen in

- Lake Lugano: Constraints on biogeochemical cycling in a eutrophic lake. *Limnol. Oceanogr.* **49**: 415–429.
- LOTTER, A. F. 1998. The recent eutrophication of Baldeggersee (Switzerland) as assessed by fossil diatom assemblages. *Holocene* **8**: 395–405.
- , M. STURM, J. L. TERANES, AND B. WEHRLI. 1997. Varve formation since 1885 and high-resolution varve analyses in hypereutrophic Baldeggersee (Switzerland). *Aquat. Sci.* **59**: 304–326.
- MCKENZIE, J. A. 1985. Carbon isotopes and productivity in the lacustrine and marine environment, p. 99–118. *In* W. Stumm [ed.], *Chemical processes in lakes*. Wiley.
- MEYERS, P. A., AND J. L. TERANES. 2001. Sediment organic matter, p. 239–269. *In* W. M. Last and J. P. Smol [eds.], *Tracking environmental change using lake sediments*, vol. 2: Physical and geochemical methods. Kluwer.
- NEUMANN, T., A. STÖGBAUER, E. WALPERSDORF, D. STÜBEN, AND H. KUNZENDORF. 2002. Stable isotope in recent sediment of Lake Arendsee NE Germany: Response to eutrophication and remediation measures. *Palaeogeog. Palaeoclim. Palaeoecol.* **178**: 75–90.
- NEUNLIST, S., C. RODIER, AND P. LLOPZ. 2002. Isotopic biogeochemistry of the lipids in recent sediment of Lake Bled (Slovenia) and Baldeggersee (Switzerland). *Org. Geochem.* **33**: 1183–1195.
- OECD. 1982. *Eutrophication of waters, assessment and control*. OECD, Paris.
- POPP, B. N., E. A. LAWS, R. R. BIDIGARE, J. E. DORE, K. I. HANSON, AND S. G. WAKEHAM. 1998. Effect of phytoplankton cell geometry on carbon isotopic fractionation. *Geochim. Cosmochim. Acta* **62**: 69–77.
- SCHELSKE, C. L., AND D. A. HODELL. 1995. Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie. *Limnol. Oceanogr.* **36**: 961–975.
- SPOONER, N., G. RIELEY, J. W. COLLISTER, M. LANDER, P. A. CRANWELL, AND J. R. MAXWELL. 1994. Stable carbon isotopic correlations of individual biolipids in aquatic organisms and a lake bottom sediment. *Org. Geochem.* **21**: 823–827.
- SUMMONS, R. E., L. L. JAHNKE, AND Z. ROKSANDIC. 1994. Carbon isotopic fractionation in lipids from methanotrophic bacteria: Relevance for interpretation of the geochemical record of biomarkers. *Geochim. Cosmochim. Acta.* **58**: 2853–2863.
- TERANES, J. L., AND S. M. BERNASCONI. 2000. The record of nitrate utilization and productivity limitation provided by $\delta^{15}\text{N}$ values in lake organic matter—a study of sediment trap and core sediments from Baldeggersee, Switzerland. *Limnol. Oceanogr.* **45**: 801–813.
- , J. A. MCKENZIE, S. M. BERNASCONI, A. F. LOTTER, AND M. STURM. 1999b. Stable isotope response to lake eutrophication: Calibration of a high-resolution lacustrine sequence from Baldeggersee, Switzerland. *Limnol. Oceanogr.* **44**: 320–333.
- , ———, A. F. LOTTER, AND M. STURM. 1999a. A study of oxygen isotopic fractionation during bio-induced calcite precipitation in eutrophic Baldeggersee, Switzerland. *Geochim. Cosmochim. Acta* **63**: 1891–1989.
- WEHRLI, B., A. F. LOTTER, T. SCHALLER, AND M. STURM. 1997. The high-resolution varve project in Baldeggersee (Switzerland): Project overview and limnological background data. *Aquat. Sci.* **59**: 285–294.
- WHITICAR, M. J. 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chem. Geol.* **161**: 291–314.

Received: 13 November 2003

Amended: 31 December 2004

Accepted: 2 January 2005