

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

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Abstract

The response of nitrogen isotopic composition of organic matter to changes in nitrate utilization, N-limitation and lake productivity was studied in Baldeggersee, a small eutrophic lake in central Switzerland. Nitrogen isotope ratios were measured on organic matter accumulation in sediment traps, collected daily from March 1995 through October 1996, and on individually sampled light and dark annual laminae from a 108-yr sediment core sequence (1885–1993). Nitrogen accumulation in the sediment traps averaged $0.04 \text{ g N m}^{-2} \text{ d}^{-1}$. $\delta^{15}\text{N}$ values of the sediment trap material increased from 11‰ to 13‰ (atmospheric N_2) as primary productivity decreased surface water $[\text{NO}_3^-]$ from 1.4 to 0.7 mg N L^{-1} during the seasonal stratified periods. Very small amounts of isotopically enriched organic matter ($\delta^{15}\text{N} \sim 15\text{--}20\text{‰}$) of heterotrophic and/or detrital origin accumulated in the winter months.

Nitrogen accumulation in the core sediments average 4 g N m^{-2} per year. $\delta^{15}\text{N}$ values of the sediment core material increased up-core (from $\delta^{15}\text{N} \sim 6\text{‰}$ to $\delta^{15}\text{N} \sim 11\text{‰}$); several abrupt positive isotope shifts ($>2\text{‰}$) occur in the upper part of the record. Comparison between sediment $\delta^{15}\text{N}$ values and surface water $[\text{NO}_3^-]$ measurements for the period of 1976–1993 reveals that the abrupt positive $\delta^{15}\text{N}$ shifts occurred in years where unusually large phytoplankton blooms depleted surface waters nitrate to concentrations of $<0.7 \text{ mg N L}^{-1}$. A 3‰ negative $\delta^{15}\text{N}$ shift, observed between 1973–1975 at the time of maximum anoxic conditions and meromixis, can be attributed to phytoplankton incorporation of ammonia, which was present in concentrations of up to 0.7 mg L^{-1} in the epilimnion.

Preservation of isotopic shifts in the sediment core which are clearly related to water column processes, and the similarity of core top $\delta^{15}\text{N}$ values to the weighted average N-isotopic composition of sediment trap material indicate that the sediment record reliably reflects the surface-generated $\delta^{15}\text{N}$ signal. Our results from sediment trap and uppermost core samples provide the first conclusive evidence that N-isotopes in lacustrine organic matter record the increasing isotopic enrichment of surface water NO_3^- due to its utilization by phytoplankton.

Artificial aeration of the Baldeggersee bottom water since 1982 has effectively reduced water column anoxia. Thus, water column denitrification, which could considerably increase the isotopic composition of residual nitrate, does not occur in the present lake. Even so, present day nitrogen isotopic values in the sediment core data are higher than most all previous periods suggesting that water column denitrification has never been a dominant influence on sediment $\delta^{15}\text{N}$ values. Instead, the up-core 6‰ increase in $\delta^{15}\text{N}$ values better corresponds to the documented history of external N-loading from agricultural runoff in the watershed over the last 100 years. These nitrogen sources have characteristically high $\delta^{15}\text{N}$ values (10–20‰) and could lead to progressive ^{15}N -enrichment of the Baldeggersee dissolved inorganic nitrogen pool.

Organic matter accumulation and its C and N isotopic composition have become valuable tools for reconstructing past productivity and changes in the nutrient availability in surface waters. Temporal increases in organic carbon accumulation and its $^{13}\text{C}/^{12}\text{C}$ ratio have been widely used in lacustrine sediments as an indicator of enhanced aquatic productivity (e.g., Hollander and McKenzie 1991; Hollander et al. 1992; Hodell and Schelske 1998). More recently, the $^{15}\text{N}/^{14}\text{N}$ ratio of sedimentary organic matter has become a complementary productivity proxy in paleoceanographic studies (Calvert et al. 1992; François et al. 1992). Altabet and François (1993) demonstrated that $\delta^{15}\text{N}$ of organic matter is linearly related to the

degree of ocean surface water nitrate utilization in marine environments, where N is a limiting nutrient. Nitrogen assim-

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ilation discriminates between isotopes, favoring the incorporation of ^{14}N over ^{15}N , such that phytoplankton typically have low $\delta^{15}\text{N}$ values relative to NO_3^- (e.g., Fogel and Cifuentes 1993 and refs. therein). As NO_3^- is progressively depleted from the surface waters, its $\delta^{15}\text{N}$ value increases in accordance with Rayleigh fractionation kinetics and produces a subsequent increase in the $\delta^{15}\text{N}$ of newly produced organic matter (Altabet and François 1993, 1994).

Yet, nutrient utilization and paleoproductivity have not been as successfully inferred from N-isotopes in lake sediments. This is primarily because P, and not N, commonly limits primary productivity in lakes. When only a minor portion of the available nitrogen is consumed, the nitrogen isotopic composition of the dissolved inorganic nitrogen (DIN) is never significantly altered. $\delta^{15}\text{N}$ values of the product (organic matter) will reflect a constant $\delta^{15}\text{N}$ signal that is different from the substrate (nitrate) by the fractionation factor. Under these conditions, variations in phytoplankton productivity cannot be readily interpreted from $\delta^{15}\text{N}$ values of sedimenting organic matter.

In fact, factors other than primary productivity often more strongly influence the N isotopic composition of lacustrine organic matter. For example, external nitrate loading from agricultural runoff and sewage will progressively increase the nitrogen isotopic composition of DIN in lakes, as nitrate derived from human and animal waste is enriched in ^{15}N ($\delta^{15}\text{N} = 10$ to 25‰ ; Kendall 1998). Also, water column denitrification in anoxic basins will considerably enrich the residual DIN in ^{15}N . A 6‰ linear increase in organic matter $\delta^{15}\text{N}$ values (1840—present) in a core recovered from Lake Ontario has been interpreted as the possible isotopic signature of increased denitrification rates accompanying increased bottom water anoxia (Hodell and Schelske 1998).

Shifts in phytoplankton species composition or addition of heterotrophs can also influence the $\delta^{15}\text{N}$ of sedimenting organic matter. An increase in abundance of N-fixing cyanobacteria, which directly fix atmospheric N_2 ($\delta^{15}\text{N}_{\text{AIR}} = 0\text{‰}$), would decrease $\delta^{15}\text{N}$ values in sedimenting organic matter (Fogel and Cifuentes 1993). In contrast, addition of heterotrophic organic matter will increase the $\delta^{15}\text{N}$ of organic matter because $\delta^{15}\text{N}$ increases by 3–4‰ with each trophic transfer (Deniro and Epstein 1981; Minagawa and Wada 1984; Peterson and Fry 1987). For example, sedimenting organic matter in Lake Ontario displays a 6‰ seasonal difference in $\delta^{15}\text{N}$ due to a shift between dominantly isotopically light phytodetritus during summer and isotopically heavy organic matter from heterotrophic or detrital sources during winter (Hodell and Schelske 1998).

In this study, we present surface water nitrate concentrations and nitrogen isotopic data from sedimenting organic matter in Baldeggersee, a small lake located in central Switzerland, to quantitatively document and evaluate the usefulness of $\delta^{15}\text{N}$ as a tool to reconstruct nutrient utilization and N-limitation in lacustrine environments. Baldeggersee provides an ideal system for this calibration because it has experienced dramatic changes in nutrient loading and productivity during this century, providing a variety of well-monitored environmental conditions. Seasonal $\delta^{15}\text{N}$ trends are constructed from sediment trap data collected daily over a two-year period; down-core $\delta^{15}\text{N}$ trends are con-

structed from individually sampled light and dark laminations from the biochemically varved sediment core. $\delta^{15}\text{N}$ trends are compared with well-documented variations in surface water nitrate concentrations, phytoplankton blooms, primary productivity, and bottom-water anoxia in the lake.

Site characteristics—Baldeggersee is a monomictic eutrophic lake situated at 463 m a.s.l. on the Swiss Plateau approximately 60 km northeast of Bern in central Switzerland ($47^\circ 10'\text{N}$, $8^\circ 17'\text{E}$; Fig. 1). The lake has a maximum depth of 66 m, a volume of 0.173 km^3 , and a surface area of 5.2 km^2 (Wehrli et al. 1997). The lake is fed by 13 small streams that drain 67.8 km^2 of catchment area and has one outflow located at the northern end of the lake. The mean hydraulic residence time is 4.3 yrs.

Primary productivity, thermal stratification, and sediment production in Baldeggersee respond strongly to seasonal cycles (Teranes et al. 1999a). Thermal stratification of the water column typically begins in late April/early May. Warming of the surface waters and increasing light intensity trigger major algal blooms, consisting mainly of centric diatoms, cyanobacteria, chlorophyta, and chrysophyta (Buergi and Stadelmann 2000). Photosynthetic utilization of aqueous CO_2 significantly raises the pH, inducing calcite precipitation. Spring and summer sediment production results in thick, light-colored, calcite-rich (60–80 wt% calcite) sediment layers, referred to as the spring/summer, or “light” layers the sediment core. Algal blooms consisting mainly of pennate diatoms and cyanobacteria commonly occur between September and November, again inducing calcite precipitation. The late summer-autumn sedimentation results in thinner, darker laminations with lesser amounts of calcite (30–50 wt%), organic matter, and small amounts of detrital material. These laminations are referred to as late summer/winter, or “dark” layers in the sediment core (see Teranes et al. 1999a,b).

History of nutrient loading, eutrophication and anoxia in baldeggersee—During the last 100 years, Baldeggersee has undergone major changes in productivity, eutrophication, and hypolimnic oxygen concentration in response to nutrient loading from agriculture and industrialization in the lake’s watershed (Wehrli et al. 1997; Lotter 1998). Depth-averaged concentrations of phosphate, DIN, and ammonium concentrations have been directly measured from 1958 until present by the Limnological Research Center in Kastanienbaum, Switzerland (Fig. 2). Before the 1950s, concentrations of phosphate have been inferred from diatom assemblages in the sediment records (Lotter 1998).

Augmented P influx began in the late 1880 and P-concentrations in the lake increased steadily, reaching a maximum value of almost 0.6 mg P L^{-1} in 1974. Government restrictions on P influx into natural waters, initiated in 1974, decreased phosphate concentrations to present levels of $<0.1\text{ mg P L}^{-1}$ (Fig. 2A). Conversely, N-influx was not regulated along with phosphate, and DIN concentrations have steadily increased over the last 40 yrs (Fig. 2B).

Progressive nutrient loading in Baldeggersee has profoundly influenced primary productivity and hypolimnic oxygen conditions. Niessen and Sturm (1987) reconstructed the

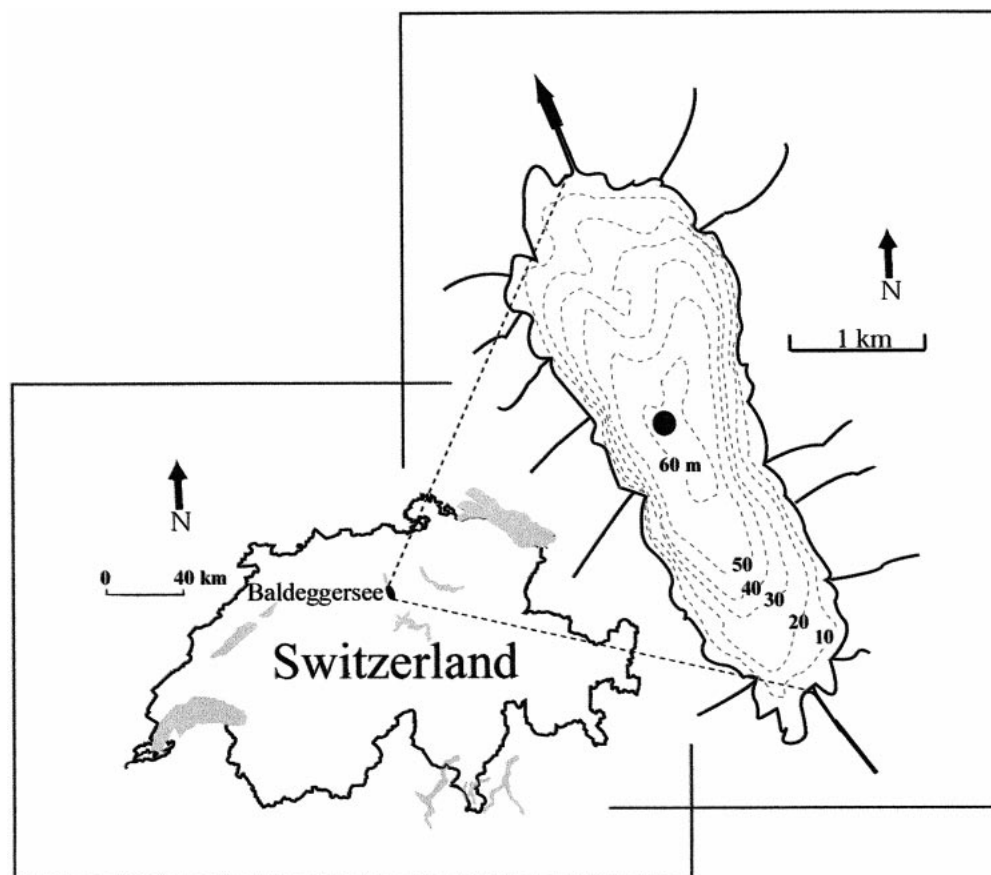


Fig. 1. Map of the Baldeggersee study area presenting the location of Baldeggersee ($47^{\circ}12'N$, $8^{\circ}16'E$) and (inset) the Baldeggersee bathymetric map with water depth, stream inflow and outflow and core recovery location (circle).

history of anoxia in Baldeggersee for the last century using sediment varve numbers as indicators for the onset of anoxia at different water depths. Since 1885, perennially anoxic conditions existed below 60 m (i.e., in the deepest part of the lake). By 1940 anoxia developed in water depths greater than 40 m. Meromictic conditions from 1970 to 1982 created permanent anoxia in the hypolimnion and prevented nitrification. During this time, a large fraction of DIN was present as ammonia (even in the mixolimnion; Fig. 2B) and nitrate concentrations dropped to $<0.3 \text{ mg N L}^{-1}$. An internal lake restoration program, consisting of a bubble plume of pure 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).

Monthly surface water nitrate concentrations have been measured routinely since 1981, and occasionally between 1976 and 1981. Figure 3 displays surface water nitrate concentrations throughout the seasonal cycle from representative years and the long-term monthly average. Surface water nitrate concentrations are lowest just before the end of the stratified period, typically in late October or November. Be-

tween 1976 and 1983, surface water nitrate was often completely utilized by phytoplankton uptake during spring-summer and late summer-autumn photosynthesis (e.g., 1976; Fig. 3). But after 1983, phytoplankton again had abundant N supplies throughout the entire spring-autumn productivity cycle (e.g., 1987; Fig. 3), with the exception of the years between 1990–1992, when unusually large spring and autumn cyanobacteria blooms (Buergi and Stadelmann 2000) incorporated almost all available N by autumn.

Materials and methods

Sediment material was collected daily from a Technicap (Markasub® Basel, Switzerland) sediment trap device deployed in the deepest part of Baldeggersee (60 m water depth, approximately 6 m above the lake bottom) from March 1995 until October 1996 (Fig. 1). The sediment trap consists of a 190 cm tall funnel, which collects sediments over a $5,000 \text{ cm}^2$ surface area into one of 24 individual collection containers. The collection containers electronically rotate every 24 h and were collected approximately every 3 weeks.

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 (Lotter et al. 1997a). Varves were identified

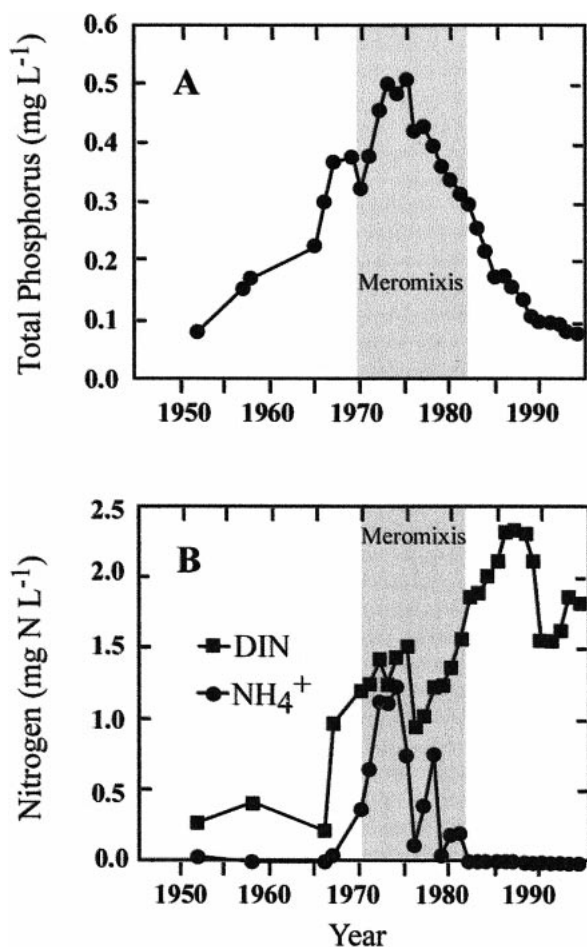


Fig. 2. Time series of nutrient loading in Baldeggersee for the period of 1952–1994. (A) Total phosphorus and (B) dissolved inorganic nitrogen ($\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$) and ammonia. The values were obtained from depth-averaged profiles taken during spring at the deepest point of the lake. Data from the Limnological Research Center, EAWAG-Kastanienbaum as presented in Wehrli et al. (1997).

and counted using petrographic thin-sections of the core. The established varve chronology was confirmed with independent ^{137}Cs and ^{210}Pb dating of annual layers (Lotter et al. 1997b). Sampling of the freeze core sediment was carried out in a cold room at temperature between -20 and -15°C . Seasonal samples were obtained by scratching off each alternating light and dark layer with a thin, sharp blade.

All sediment trap and core samples were weighed, freeze-dried and then weighed again to obtain dry weights and porosity for accumulation rate determination. Material from each sample was thoroughly homogenized for chemical analysis.

Total carbon and nitrogen for the BA-93 core samples and for the sediment trap material were measured using a Carlo-Erba CNHS[®] analyser with autosampler. Percent organic carbon was calculated by subtraction of carbonate carbon (data from Teranes et al. 1999a,b) from total carbon. Accumulation rate of organic carbon and nitrogen were calculated by

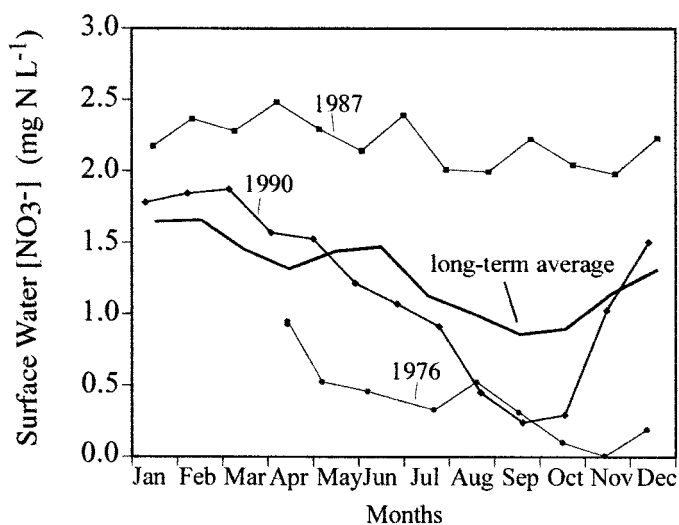


Fig. 3. Monthly surface water (0–12.5 m) nitrate concentrations measurements from representative years: Nitrate limiting (1976), abundant nitrate (1987), and 1990, when unusually large productivity blooms depleted nitrate in the surface waters by September. Also plotted is the long term average of all the years with monthly measurements: 1976–1978 and 1981–1996. Data from the Limnological Research Center, EAWAG-Kastanienbaum.

multiplying weight percent of each component, relative to the total dry weight, by the bulk sediment accumulation.

Approximately 6–12 mg of homogenized bulk core and sediment trap material for N isotopic analysis were 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. N isotope values are reported in the conventional delta notation with respect to atmospheric N. Analytical reproducibility is ± 0.2 for $\delta^{15}\text{N}$, determined on repeat analyses of international nitrogen isotope standards (IAEA-N1 and IAEA-N2).

Results

Sediment traps—On average, over 0.3 g m^{-2} of org C and 0.04 g m^{-2} of total N were collected per day, although accumulation varied considerably over the study period (Fig. 4A). Relatively high org C and N accumulations ($1 \text{ g-C m}^{-2} \text{ d}^{-1}$ and $0.1 \text{ g-N m}^{-2} \text{ d}^{-1}$) occurred during algal blooms, lasting days to weeks throughout spring, summer, and into early autumn. Essentially no organic matter accumulated during the winter months. Exceptionally high influxes of organic matter, which occurred on 11 June and 23 July 1996, represent storm inputs of resuspended sediment and allochthonous material. Atomic C/N ratios of the sediment trap material varied between 6 and 10 (Fig. 4B) indicating that the primary source of organic matter in the sediment traps is phytoplankton detritus (Meyers and Ishiwatari 1993). Atomic C/N ratios above 10 indicate a larger (but still minor) component of terrestrial organic matter, i.e., on 11 June and 23 July 1996 and in winter when no autochthonous material was produced (Fig. 4B).

Comparison of nitrogen isotope analysis of the sediment trap material and monthly surface water (0–12.5 m) nitrate

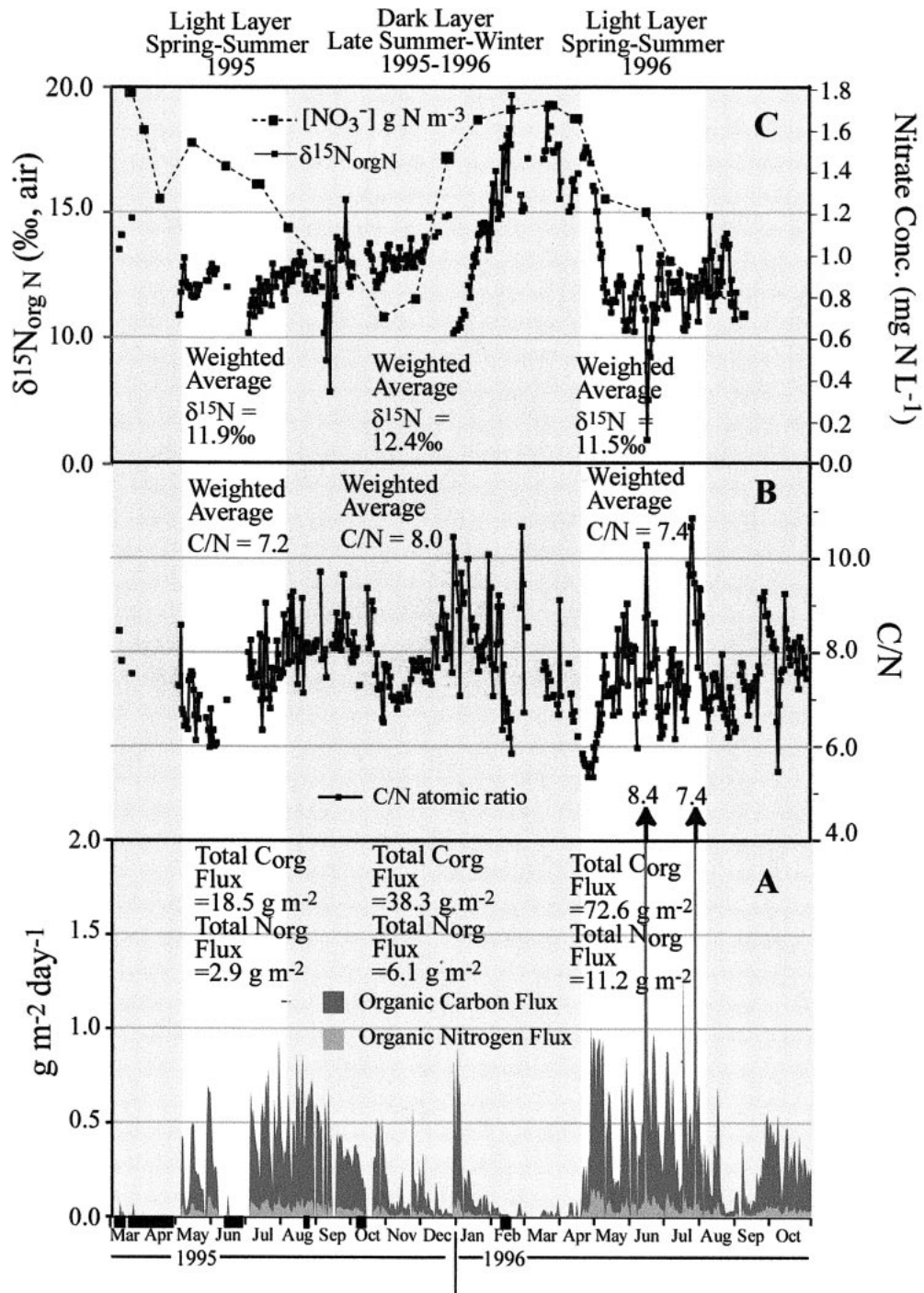


Fig. 4. Sediment trap Org C and N accumulation and N-isotopic data from March 1995–October 1996. (A) Daily Org C and Total N accumulations, black bars represent periods when no sediment was collected due to problems with the sediment traps. Little to no primary organic matter is produced during the winter months (January–March) (B) Measured C/N atomic ratios of sedimenting organic matter. (C) Measured $\delta^{15}\text{N}$ values of sedimenting organic matter and monthly surface water nitrate concentrations. $[\text{NO}_3^-]$ data from the Limnological Research Center, EAWAG-Kastanienbaum.

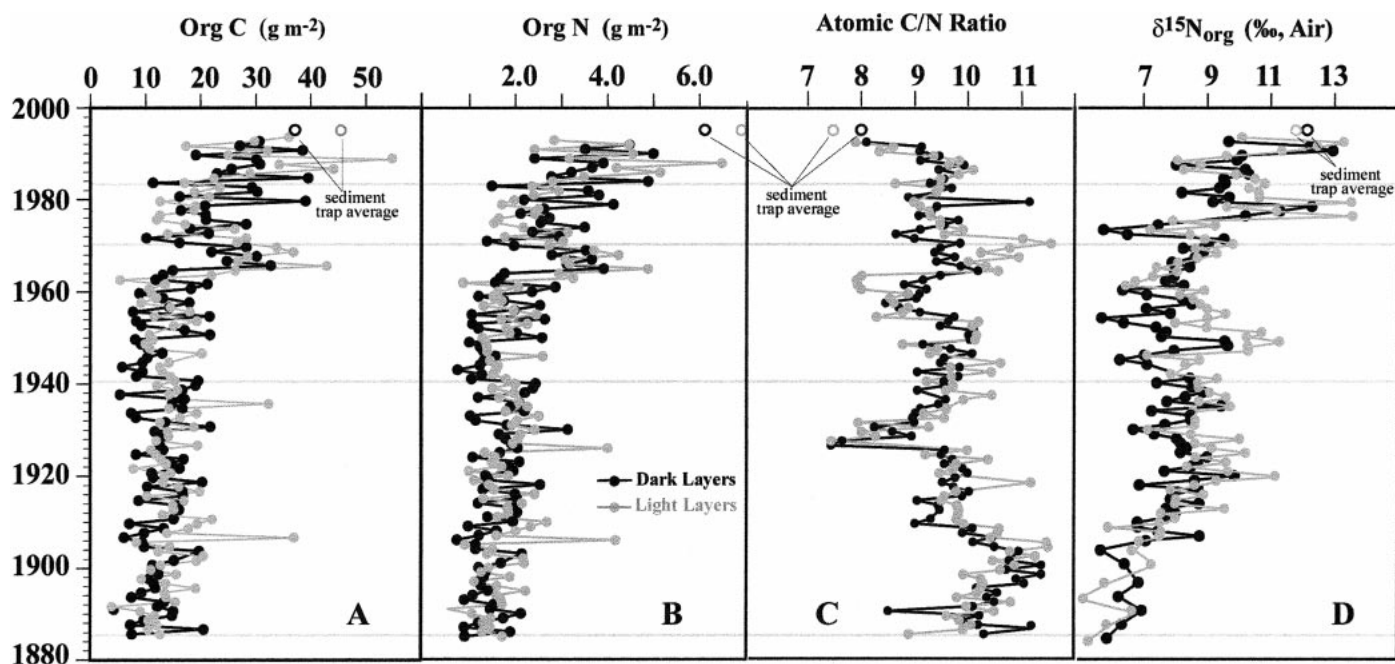


Fig. 5. (A) Stratigraphic plots of Org C accumulation, (B) Total N accumulation, (C) C/N atomic ratios and, (D) $\delta^{15}\text{N}_{\text{org}}$ from the Baldeggersee laminated sequence. Results from the light and dark laminae are plotted separately. Open circles on the graph represent average sediment trap values for theoretical light and dark layers, weighted by mass.

concentrations in Fig. 4C documents the relationship between nitrate utilization and sediment $\delta^{15}\text{N}$ values taken at similar temporal resolution. Nitrate concentrations decreased from 1.4 mg N L^{-1} at the onset of stratification in April/May to 0.7 mg N L^{-1} when the lake turned over in late autumn, whereas $\delta^{15}\text{N}$ values were relatively low in the spring (between 10–12‰), then steadily increased over the stratified period to reach values of 13–14‰ by autumn.

Discrete large phytoplankton blooms, which occurred when surface water nitrate concentrations were high, resulted in low $\delta^{15}\text{N}$ values (Figs. 4A,C). This was observed in early spring 1996, when $\delta^{15}\text{N}$ -values from organic matter decreased dramatically (4–5‰), and again in late December 1995 through early January 1996 when a sudden peak in autochthonous organic matter production occurred after nitrate concentrations in the surface waters were replenished by lake turn-over. Only very small amounts of organic matter were collected in the sediment traps in the winter (January–March 1996; Fig. 4A). Their heavy nitrogen isotopic compositions (15–19‰) suggest either a detritus or heterotrophic source.

Theoretical accumulation rates for individual sediment core laminations can be estimated by totaling the daily fluxes by season. Sediment produced from May to the end of July would eventually constitute the light layer in the core (unshaded regions in Fig. 4). Sediment production from August through April of the following year would eventually constitute the dark layer (the shaded boxed regions in Fig. 4; see Teranes et al. 1999a).

Total seasonal fluxes of organic matter that would eventually correspond to an individual layer in the sediment core are: 18.5 g C m^{-2} and 2.9 g N m^{-2} for May–July 1995; 38.3 g C m^{-2} and 6.1 g N m^{-2} for August 1995–April 1996; and

72.6 g C m^{-2} and 11.2 g N m^{-2} for May–July 1996 (Fig. 4A). Average atomic C/N ratios, weighted by amount, are 7.2 for May–July 1995; 8.0 for August 1995–March 1996; and 7.4 for April–July 1996 (Fig. 4B). Weighted average $\delta^{15}\text{N}$ values are 11.9‰ for May–June 1995, 12.4‰ for August 1995–March 1996 and 11.5‰ for April–July 1996 (Fig. 4C). Note that the average isotopic composition of the dark layer is not substantially greater than the average $\delta^{15}\text{N}$ of the light layer values, indicating that the amount of isotopically enriched detrital or heterotrophic organic matter accumulated in the winter will not significantly influence the isotopic composition of dark layer core sediment.

Sediment core—Down-core organic C and N accumulations, atomic C/N ratios, and $\delta^{15}\text{N}$ values reveal several changes in the production of organic matter in Baldeggersee (Fig. 5). Organic matter accumulation in the sediment core was relatively constant from the 1880s until the 1960s at $12\text{--}15 \text{ g C m}^{-2}$ and $1.5\text{--}2.0 \text{ g N m}^{-2}$ per lamination (Figs. 5A,B). A sharp increase occurred in the early 1960s to values of 30 g C m^{-2} and 3 g N m^{-2} per lamination. Organic C and N accumulation rates remained constant or even dropped slightly after the 1960s. Despite the lake quality improvement program initiated in the 1980s, organic matter accumulation in the sediments has increased slightly over the last decade. This recent increase is due to the fact that organic matter in the more recent sediment has experienced less diagenetic degradation and that primary productivity in the lake has not waned in the last decades despite the exponential drop in phosphate concentrations. The difference in organic C and N accumulation between the light and dark layer is minimal.

Core-top accumulation rates are 25–28% lower per layer

in org C and 41–43% in total N than total seasonal sediment trap accumulations (Figs. 5A,B). This preferential diagenetic loss of N is also manifested in the down-core increase in C/N atomic ratios from values near 8 at the top of the core, to 10 at the base (Fig. 5C). However, core-top $\delta^{15}\text{N}$ values (~ 10 – 13‰), reflect the weighted mean isotopic values of the sediment trap material (11.5–12.4‰) quite well (Fig. 5D) indicating that, despite the diagenetic loss of N, and the possibilities for selective loss of lighter or heavier isotopes, the average isotopic composition of the sediment is preserved. Light layer N-isotopic ratios are 0.5‰ higher on average than dark layer values.

There is an overall increase in $\delta^{15}\text{N}$ values from the beginning of record ($\delta^{15}\text{N} = 6$ – 7‰) to the top of the core ($\delta^{15}\text{N} = 10$ – 13‰). $\delta^{15}\text{N}$ values from sediment trap material and from the upper part of the Baldeggersee core sequence are significantly higher than other reports of nitrogen isotopes in lake sediments (e.g., Meyers 1997 reports an average $\delta^{15}\text{N}$ range of 1–5‰ for lacustrine sediments). In addition, several abrupt positive N-isotope excursions occur in the upper core record. A 6‰ positive $\delta^{15}\text{N}$ shift occurred between 1972–1976, coincident with the time of maximum P-loading, meromixis in the water column, strongest N-limitation on phytoplankton, and maximum extent of the anoxic hypolimnion. Another abrupt nitrogen isotope increase (4‰) occurred in the most recent years of the record and $\delta^{15}\text{N}$ values of the light layers again reached values $>13\text{‰}$.

Discussion

Effect of nitrate utilization on sediment trap $\delta^{15}\text{N}$ values—Nitrogen isotopic fractionation associated with N incorporation by phytoplankton is an important process in the biogeochemical cycling of N. A large range of isotope fractionations and enrichment factors during assimilation of nitrate (-24 to 0‰) and ammonium (-27 to 0‰) have been compiled from field and laboratory experiments (Fogel and Cifuentes 1993), and are strongly dependent on both local conditions and concentration of dissolved nitrogen. The isotope enrichment factor, ϵ_{p-s} , is defined as:

$$\epsilon_{p-s} = 1,000(\alpha_{p-s} - 1) \quad (1)$$

where α is the isotopic fractionation factor between the product (p) and the substrate (s). Estimates of the ϵ_{p-s} associated with nitrate incorporation based on field observations at micromolar concentrations of nitrate range from -5 to -4‰ (Wada 1980; Altabet and McCarthy 1985). A more recent estimate for ϵ_{p-s} is -5.2‰ , based on laboratory studies of nitrogen incorporation by a marine diatom (Waser et al. 1998).

If N-incorporation uses a significant amount of a lake's nitrate reservoir, the residual nitrate will become steadily enriched in ^{15}N which, in turn, will lead to a subsequent increase in $\delta^{15}\text{N}$ of the newly produced organic matter. This can occur on seasonal time scales if surface waters are significantly depleted in nitrate, and over longer time scales if ^{14}N is removed from the system by organic matter accumulation in the sediments or by export through outflow.

We explored the relationship between $\delta^{15}\text{N}$ values and nitrate concentrations using Rayleigh fractionation kinetics to

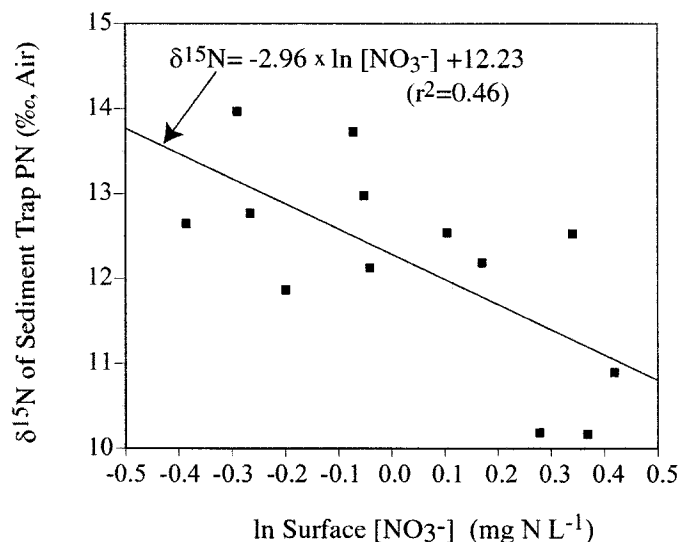


Fig. 6. Analysis of sediment trap $\delta^{15}\text{N}$ data versus surface water $\ln[\text{NO}_3^-]$ measurements on monthly sampling days. Data for January–March, 1996 are excluded from this analysis because no primary organic matter is produced these months.

document the response of nitrogen isotopes in lake sediment in Baldeggersee as proxies for past changes in productivity. A Rayleigh fractionation model describes the evolution of the isotopic composition of the substrate and of the instantaneous product during reaction progress and has been used to explain N-isotopic evolution of marine sedimentary organic matter (Altabet and François 1994). The Rayleigh equation for systems with a constant fractionation factor is:

$$\delta = \delta_0 + \epsilon_{p-s} \ln(f) \quad (2)$$

where δ_0 is the initial composition of the substrate and f is the remaining fraction of the substrate. Applying Eq. 2 to the nitrogen system gives:

$$\delta^{15}\text{NO}_3^- = \delta^{15}\text{NO}_3^-_o + \epsilon_{p-s} \ln(f) \quad (3)$$

and for the produced organic matter

$$\delta^{15}\text{N}_{\text{om}} = \delta^{15}\text{NO}_3^- + \epsilon_{p-s} \quad (4)$$

where f is the remaining fraction of NO_3^- , and ϵ_{p-s} is the biological fractionation factor associated with NO_3^- utilization in ‰ units.

Equations 3 and 4 require a linear relationship between $\delta^{15}\text{N}$ and $\ln[\text{NO}_3^-]$ with a slope defined by the fractionation factor, ϵ_{p-s} . A fundamental requirement for a reaction to be described by a Rayleigh model is that the amount of reactant is finite. This will not be the case in a lacustrine system where nitrate is continuously replenished as productivity progresses during the season (albeit at a lower rate than it is consumed). As the pool of nitrate cannot be considered finite, the fractionation factor obtained by such a simple model will represent only an apparent fractionation factor.

A linear fit is achieved with our sediment trap $\delta^{15}\text{N}$ and $\ln[\text{NO}_3^-]$ data ($r^2 = 0.46$, $P < 0.05$; Fig. 6). High nitrogen isotopic values (15–19‰) from the insignificant amounts of N in the winter (from detritus or heterotrophic sources, rather than a phytoplankton organic matter source) were excluded

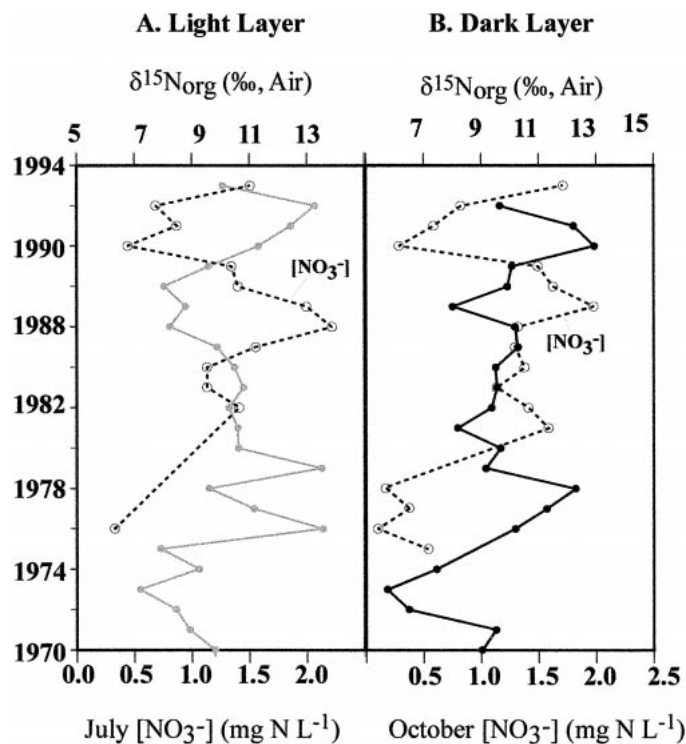


Fig. 7. Illustration of the inverse relationship between $\delta^{15}\text{N}$ of individual laminations and surface water $[\text{NO}_3^-]$ (A) $\delta^{15}\text{N}$ values of the light layer and surface water $[\text{NO}_3^-]$ in July, the last month of organic matter production that eventually accumulates in the light layer. (B) $\delta^{15}\text{N}$ from the dark layer and surface water $[\text{NO}_3^-]$ in October, the last month of organic matter production that eventually accumulates in the dark layer.

from the regression analysis. The derived value for ϵ , -2.96‰ , in Fig. 6 is within reported values for fractionation factors in association with NO_3^- utilization for marine phytoplankton (Altabet and Francois 1994) and lacustrine phytoplankton (Kendall 1998). Substantial scatter in this relationship can be partially attributed to seasonal differences in species composition or growth conditions, which could contribute to nonconstant fractionation factors between the substrate and product, an irregular supply of nitrate from the catchment, or to water column mixing.

This sediment trap data quantitatively documents the inverse relationship between surface water $[\text{NO}_3^-]$ and the $\delta^{15}\text{N}$ of sedimenting organic matter in lacustrine environments. Although these variations observed in the instantaneous product of the reactions (in this case the sediment trap material) will be much larger than the variations that will be observed in the integral product (in this case the core sediment). These results are consistent with previous limited observations of the response of nitrogen isotopes in lacustrine organic matter to nitrate utilization and N-limited productivity. Gu et al. (1996) have reported a weak positive correlation between $\delta^{15}\text{N}$ in lacustrine plankton and phosphate levels, growth rate, and primary productivity in studies of Florida Lakes. Hollander (1989) found that $\delta^{15}\text{N}$ values in Greifensee, Switzerland, were generally higher during the May–August productivity period ($\delta^{15}\text{N} = 12\text{--}14\text{‰}$) when nitrate concentrations were lower, compared with values of

$\delta^{15}\text{N}$ values of 10–11‰ during the mixed period in the lake when nitrate concentrations were higher.

However, contrary to these results in a study of Lake Lugano, Bernasconi et al. (1997) did not find higher $\delta^{15}\text{N}$ values in their late-summer sediment traps, despite a 75% reduction in nitrate concentrations in the epilimnion during the growth season. The lack of correlation between $\delta^{15}\text{N}$ and nitrate concentrations suggests other factors may be more important in controlling the nitrogen isotopic composition of organic matter in this lake.

Reconstructing nitrate utilization and nitrate-limited productivity in Baldeggersee sediment core record—Large nitrogen isotopic excursions (e.g., 6‰ increase within 4 yrs) are recorded during the period from 1970–1993 in the sediment core. A plausible mechanism for such large positive N-isotopic shifts is substantially increased productivity such that the DIN pool in the surface water is depleted and $\delta^{15}\text{N}$ values of DIN gradually increase. To test this mechanism, we compared $[\text{NO}_3^-]$ data to $\delta^{15}\text{N}$ values for each laminae for all years when nitrate data was available during 1970–1993 (Fig. 7). In order for phytoplankton growth to have enriched DIN in ^{15}N by the spring and early summer, and subsequently be recorded as a positive $\delta^{15}\text{N}$ shift in org-N accumulated in the light layer, nitrate concentrations must have been depleted by July (see Fig. 3), typically the last month of sediment deposition to the light sediment layer. To

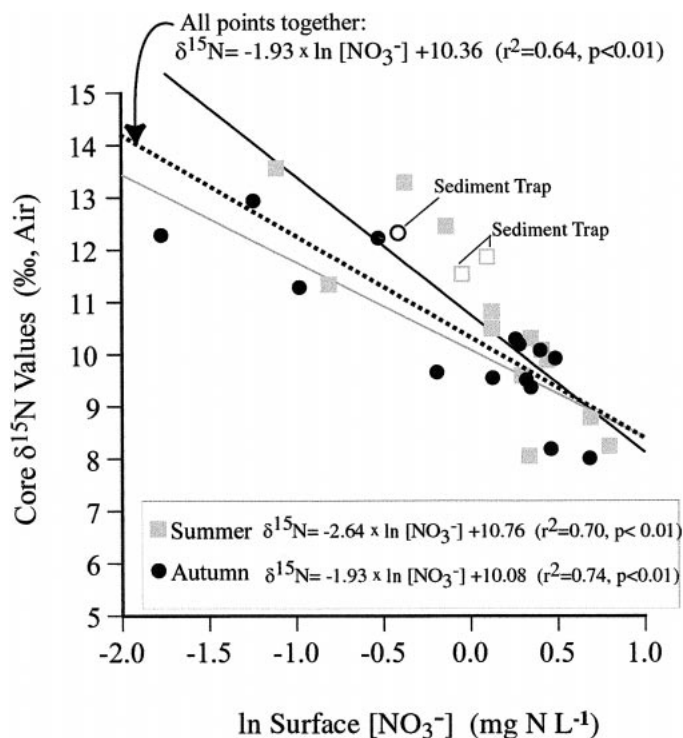


Fig. 8. Analyses of $\delta^{15}\text{N}$ data from individual sediment core laminae versus surface water $\ln[\text{NO}_3^-]$ measurements in either July, for comparison with the light layer values, or October, for comparison with the dark layer values. Different regression lines show the effects of plotting the seasons separately. The open symbols plot the theoretical sediment layer $\delta^{15}\text{N}$ values, based on the weighted average sediment trap values, and measured surface water $\ln[\text{NO}_3^-]$ in July and October 1995–1996.

impact the nitrogen isotopic composition of the dark layers, nitrate concentrations would have been exhausted by October (*see* Fig. 3), the last month for significant organic matter production in the dark layer. If the nitrate is completely consumed during a productivity cycle, the final composition of the sediment layer will correspond to the initial isotopic composition of the nitrate reservoir.

Figure 7 illustrates an inverse relationship between available nitrate concentrations and $\delta^{15}\text{N}$ values. Sediment layers with extremely positive $\delta^{15}\text{N}$ values (11–13‰) consistently occurred in years when nitrate concentrations were $<0.7 \text{ mg N L}^{-1}$. If nitrate concentrations in the stratified surface waters were depleted by July, light layer $\delta^{15}\text{N}$ values for those years were extremely positive. This occurred in 1976, 1979, and 1990–1992. In each of these years, increased nitrate utilization can be linked to a particularly large spring phytoplankton blooms as noted by Buergi and Stadelmann (2000). Dark layer $\delta^{15}\text{N}$ values were extremely positive in years when nitrate concentrations in the surface waters were depleted by October. This occurred in 1977–1978 and again in 1990–1991. In each of these years, increased nitrate utilization in the autumn can be linked to large phytoplankton blooms (Buergi and Stadelmann 2000). It is noteworthy that even after the initiation of the lake recovery program in 1982, and a corresponding sixfold decrease in P concentrations, spring and autumn phytoplankton blooms are intense

enough to temporary cause N-limitation in the surface water (*i.e.*, 1990–1992; Fig. 7).

In addition to explaining the extremely positive $\delta^{15}\text{N}$ values, our data show a significant linear relationship between $\ln[\text{NO}_3^-]$ and $\delta^{15}\text{N}$ values ($r^2 = 0.64$, $P < 0.01$; Fig. 8). Theoretical values for 1995 and 1996 sediment layers, calculated from sediment trap totals (weighted by mass) are also plotted on Fig. 8, along with the corresponding July and October surface water nitrate concentrations for those years. This result is in accordance with daily sediment trap data and Eqs. 3 and 4. The r^2 value is increased by plotting the relationship between $\ln[\text{NO}_3^-]$ and $\delta^{15}\text{N}$ values separately for light layers ($r^2 = 0.70$, $P < 0.01$) and dark layers ($r^2 = 0.74$, $P < 0.01$; Fig. 8). The slope, ϵ , varies between -2.64‰ and -1.68‰ for the light and dark layer, respectively. This difference in seasonal fractionation factors associated with phytoplankton uptake could be a result of seasonal variations in species composition, growth conditions or relative inputs of new nitrate.

Although ammonium incorporation is not currently an important process in Baldeggersee, it probably was prevalent during periods of anoxia and meromixis in the lake, especially from 1973–1975, when NH_4^+ was the predominant form of N. The fractionation factor associated with N incorporation of ammonia in field experiments ($\epsilon = -10\text{‰}$; Cifuentes et al. 1988) is typically greater than for the frac-

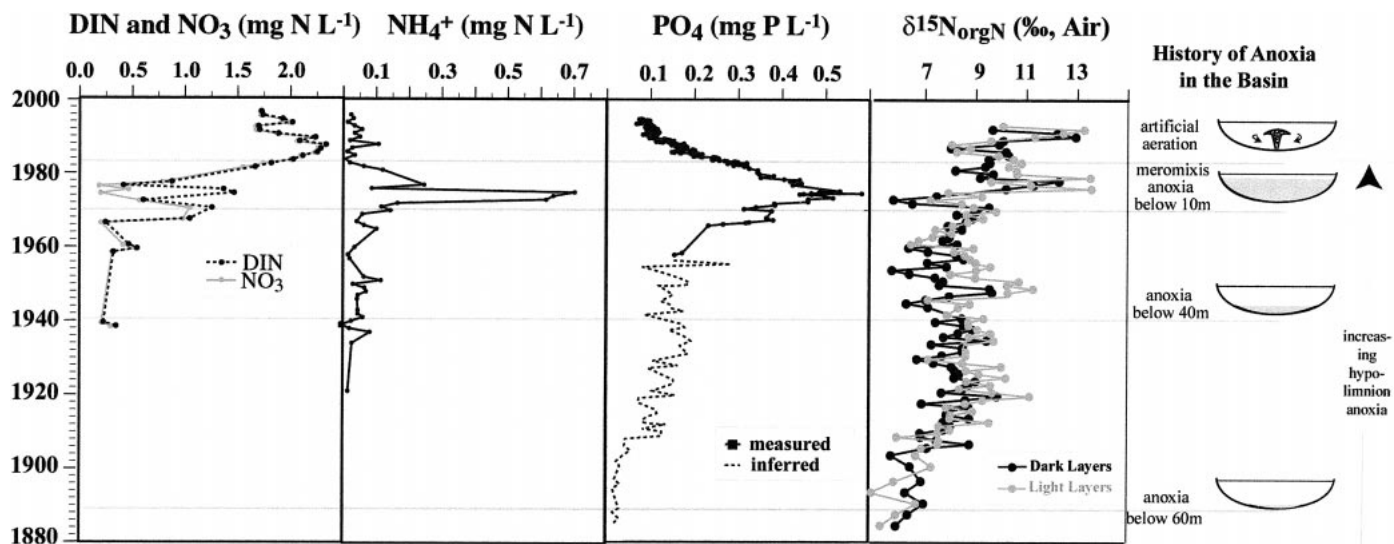


Fig. 9. Stratigraphic plots of nutrient loading in the lake, the development of hypolimnion anoxia, and corresponding $\delta^{15}\text{N}$ values. (A) Surface water nitrate and DIN concentrations during the spring for the period of 1938–1993. Data from the Limnological Research Center, EAWAG-Kastanienbaum. (B) Surface water ammonium concentrations of the productivity period (May–October). Data from the Limnological Research Center, EAWAG-Kastanienbaum. (C) Measured and inferred average phosphorous concentration in the Baldeggersee water column for the period 1880–1993. Inferred phosphorous concentration data from Lotter (1998). (D) $\delta^{15}\text{N}$ sediment core data. Basin anoxia reconstructions from Niessen and Sturm (1987) and Wehrli et al. (1997).

tiation factor for nitrate assimilation. Also, because ammonia in lakes is mainly derived from organic matter decomposition, it should have lower $\delta^{15}\text{N}$ values than nitrate. Therefore, it can be expected that organisms using ammonia as a nitrogen source will have lower $\delta^{15}\text{N}$ than those using nitrate as a N source. The highest measured concentrations of ammonium in the water column were recorded between 1972–1975 coincident with a decrease in nitrogen isotopic values to 6‰ (Fig. 9). This decrease in $\delta^{15}\text{N}$ reflects phytoplankton incorporation of NH_4^+ for their nitrogen source.

Long-term trends in the nitrogen isotope values—Figure 9 summarizes the history of nutrient loading in the lake, the development of hypolimnion anoxia, and the overall increase in $\delta^{15}\text{N}$ of the sediment core layers. In general, the up-core increase in $\delta^{15}\text{N}$ corresponds to increased external phosphate and nitrate loading in the lake. Specifically, an increase in $\delta^{15}\text{N}$, from 6 to 8‰, occurred between 1900 and 1920, corresponding to the first step in eutrophication ($>0.1 \text{ mg P L}^{-1}$). Another increase in $\delta^{15}\text{N}$, from 8 to 10‰, occurs after 1960 in correspondence to the exponential increase in phosphate and nitrate concentrations in the lake. Although it is not unreasonable to suppose that the increase in sedimentary nitrogen isotope values in the early and middle parts of the century could be partially due to increased relative levels of nitrate uptake, the good correlation between augmented nutrient loading and progressive increase of $\delta^{15}\text{N}$ values in sedimentary organic matter suggest that agricultural runoff and sewage inputs of nitrogen (with characteristically high $\delta^{15}\text{N}$) were a more significant control on organic matter $\delta^{15}\text{N}$, through progressive isotopic enrichment of the DIN pool available for phytoplankton utilization.

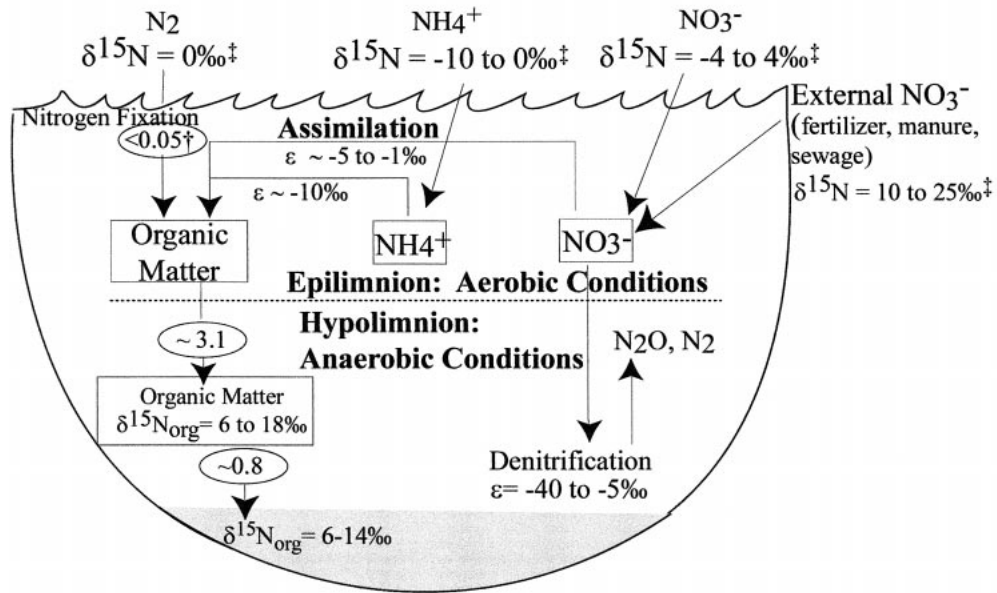
The total nitrogen content of the Baldeggersee has increased at a rate of approximately 10 tons yr^{-1} between 1965

and 1996, and a significant amount the total nitrogen content is NO_3^- derived from animal manure from proximal pig and cow farms (an estimated flux of $8.2 \text{ mmol N m}^{-2} \text{ d}^{-1}$; Mengis et al. 1997). Nitrate derived from manure, agriculture, and sewage has $\delta^{15}\text{N}$ values of 10–25‰, on average, which are very enriched in ^{15}N relative to nitrate derived from natural soils ($\delta^{15}\text{N} = 2\text{--}5\text{‰}$) and/or from atmospheric sources ($\delta^{15}\text{N} = 0 \pm 3\text{‰}$; Kendall 1998).

Increasing denitrification rates, with the expansion of anoxia in the hypolimnion and increasing nitrate concentrations, is another potential process that would progressively enrich the DIN pool in ^{15}N , causing an increase in the N-isotope composition of organic matter. Denitrification of dissolved NO_3^- by microorganisms in oxygen-depleted water selectively releases $^{14}\text{N}_2$, leaving the remaining nitrate enriched in ^{15}N (Cline and Kaplan 1975). Measured enrichment factors associated with denitrification range from -40‰ to -5‰ (Kendall 1998). Thus, denitrification of nitrate with an original $\delta^{15}\text{N}$ value of -4 to 4‰ can yield residual nitrate with $\delta^{15}\text{N}$ values of 10–30‰, or within the range of compositions expected from nitrate from a manure source (e.g., 10–25‰).

However, it seems that water column denitrification has never been a dominant influence on Baldeggersee sediment $\delta^{15}\text{N}$ values. Artificial aeration of the bottom water since 1982 has effectively reduced bottom water anoxia and thus, water column denitrification does not occur in the present lake. Even so, present day nitrogen isotopic values in the sediment core data are higher than most all previous periods, suggesting that, even in the years prior to 1982 when the water column was severely anoxic water column denitrification was not the primary influence on sediment $\delta^{15}\text{N}$ values. Instead, the up-core 6‰ increase in $\delta^{15}\text{N}$ values must dominantly reflect progressive ^{15}N -enrichment of the Bal-

A. Nitrogen Cycling in Baldeggersee: Pre 1982



B. Nitrogen Cycling in Baldeggersee: Post 1982

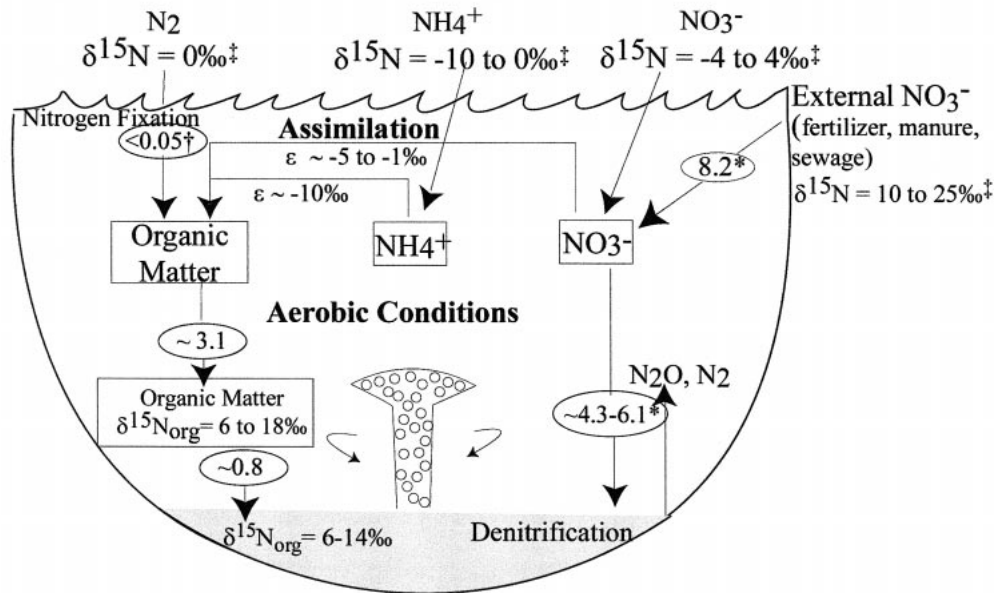


Fig. 10. Important processes of nitrogen transformations affecting the $\delta^{15}\text{N}$ values in Baldeggersee both (A) before the lake restoration, and (B) after initiation of artificial aeration. All fluxes and process rates are in $\text{mmol N m}^{-2} \text{d}^{-1}$. Rates of total N accumulation and sedimentation are from this study. Process rates, such as ammonification, denitrification, nitrogen fixation, and addition of nitrate from atmospheric and anthropogenic sources (*) are from Mengis et al. (1997). Isotope enrichment factors ϵ , are from Fogel and Cifuentes (1993) and are listed here for the product (p)—the substrate (s). The estimate of the flux of N due to nitrogen fixation (†) is from Buergi and Stadelmann (1999). Isotope values (‡) for atmospheric sources of nitrogen are from Kendall (1998).

deggersee DIN pool due to increasing external N-loading from agricultural runoff in the watershed over the last 100 years.

Denitrification within the anoxic sediments, on the other hand, is presently an important process in the biogeochemical cycling of nitrogen in Baldeggersee, accounting for 72–88% of the observed NO_3^- removal ($\sim 4.3\text{--}6.1 \text{ mmol m}^{-2} \text{ d}^{-1}$; Mengis et al. 1997). In contrast to water column denitrification, sedimentary denitrification exhibits a low to zero fractionation factor, and thus would not influence water column nitrate isotopic values (Brandes and Devol 1997).

Our interpretations of the nitrogen isotope data from sediment cores presented here must also address the potential influences of early diagenesis. Selective diagenesis of isotopically heavy or light organic matter fractionations could potentially modify the nitrogen isotope composition of sinking and sedimented organic matter and destroy the utility of the nitrate isotope record of nitrate utilization. It is encouraging to note that the diagenetic effects on the bulk $\delta^{13}\text{C}$ signal in organic matter have been shown to be small (Schelske and Hodell 1991, 1995; Meyers 1994; Hodell and Schelske 1998). Meyers (1997) concluded that the absence of large diagenetic carbon isotopic shifts in many lacustrine isotope records suggests that microbes utilize a large enough fraction of the initial organic matter and incorporate this carbon into their biomass such that the potentially significant effect is minimal. Our $\delta^{15}\text{N}$ data shows that this might also be true for lacustrine nitrogen isotope records. The core-top sediment $\delta^{15}\text{N}$ values match well the $\delta^{15}\text{N}$ values for sinking particles collected in the sediment trap at 60 m, demonstrating that diagenetic alteration of their isotopic signal cannot be significant during sedimentation. In addition, large isotopic variations observed in the core, and their clear correlation with observed nitrate levels and plankton blooms, indicate that the nitrogen isotopic composition of organic matter is preserved without significant isotopic alteration within the sediments.

Conclusions

Organic matter production and N-isotope composition from daily sediment trap and sediment core material from Baldeggersee demonstrate significant variability on seasonal, interannual, and century-long time-scales. We conclude that the most important processes controlling the N-isotopic composition of lacustrine organic matter in Baldeggersee are seasonal and interannual nitrate utilization, and the isotopic composition of external sources of nitrate to the lake. These processes and their associated rates in Baldeggersee both before and after the lake restoration and artificial aeration project are summarized in Figs. 10A,B.

Sediment trap data reveal that seasonal changes in the nitrogen isotopic composition over the productivity cycle, May–October, reflect nutrient utilization in the surface water, even when N is not the limiting nutrient. The amplitude of this effect, dependent on the fractionation factor associated with phytoplankton uptake, is -2.96‰ in Baldeggersee. Importantly, the weighted averages of N-isotopic composition of sediment traps material are nearly the same as core top

values of $\delta^{15}\text{N}$, which is evidence that the sediment can reliably reflect the isotopic composition of the surface-generated $\delta^{15}\text{N}$ signal.

Comparison of the $\delta^{15}\text{N}$ data with historical records of nutrient availability illustrate that $\delta^{15}\text{N}$ variations in the sedimentary record on seasonal and interannual time scales reflect and record variations in relative NO_3^- utilization and depletion. Controls on the abrupt large interannual variations in $\delta^{15}\text{N}$ values in the Baldeggersee sequence reflect the dynamic nature of nutrient limitation in the surface water. N-limiting conditions, occurring intermittently between 1970 and 1993, resulted from a combination of abundant P and large phytoplankton blooms. There is a highly significant linear relationship between nitrate utilization and the nitrogen isotopic composition of organic matter. Light laminae $\delta^{15}\text{N}$ values linearly correspond to July nitrate concentrations (slope $\epsilon = -2.64\text{‰}$) and dark laminae $\delta^{15}\text{N}$ values linearly correspond to October nitrate concentrations (slope $\epsilon = -1.93\text{‰}$). The difference in seasonal fractionation factors associated with phytoplankton uptake could be a result of seasonal variations in species composition, growth conditions, or relative inputs of new nitrate.

Longer-term controls on the N-isotope record in Baldeggersee are complicated by additional dependence of $\delta^{15}\text{N}$ on external nitrate sources, and possibly, processes such as denitrification. On the time scales of decades to centuries, nitrate utilization, even in association with major changes in productivity, is only a minor factor determining nitrate concentrations in the water column. Increasing external inputs of nitrate, with high $\delta^{15}\text{N}$ values, most likely explains the long-term increase of sedimentary $\delta^{15}\text{N}$ over the 108-yr sediment record from Baldeggersee. A better understanding of nitrogen isotope cycling in lakes will be gained from future studies on N isotope of sedimentary organic matter that include measurements of the $\delta^{15}\text{N}$ of source nitrate.

Our findings provide the first conclusive evidence that N-isotopes in lacustrine organic matter record surface nutrient utilization. This result is important for quantifying the control of nitrate utilization on the nitrogen isotopic composition of organic matter that has already been successfully applied to numerous paleoceanographic studies. Our results also indicate the great potential of $\delta^{15}\text{N}$ values to reconstruct algal community structure and nutrient (e.g., N and P) supply in eutrophic lakes, which have experienced anthropogenic N and P-loading, and in natural lakes systems as nutrient sources vary. Finally, our data show the highly dynamic response of the system to lake restoration measures, demonstrating that nitrate can become the limiting nutrient in eutrophic lakes even after control measures have decreased P loads from the catchment.

References

- ALTABET, M. A., AND R. FRANÇOIS. 1993. The use of nitrogen isotopic ratio for reconstruction of past changes in surface ocean nutrient utilization. p. 281–306. *In* R. Zahn, T. R. Pederson, M. Kaminshi, and L. Labeyrie [eds.], NATO ASI Series, Series I: Global Environmental Change V. 17. Carbon cycling in the glacial ocean; constraints on the ocean's role in global change; quantitative approaches in paleoceanography. Springer-Verlag.
- , AND ———. 1994. Sedimentary nitrogen isotopic ratio as

- a recorder for surface ocean nitrate utilization. *Global Biogeochem. Cycles* **8**: 103–116.
- , AND J. J. MCCARTHY. 1985. Temporal and spatial variations in the natural abundance of ^{15}N in PON from a warm core ring. *Deep-Sea Res.* **32**: 755–772.
- 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.
- BRANDES, J. A., A. H. DEVOL. 1997. Isotopic fractionation of oxygen and nitrogen in coastal marine sediments. *Geochim. Cosmochim. Acta* **61**: 1793–1801.
- BUERGI, H. R., AND P. STADELMANN. 2000. Change of phytoplankton diversity during long-term restoration of Lake Baldegg (Switzerland). *Verh. Int. Verein. Limnol.* (in press).
- CALVERT, S. E., B. NIELSEN, AND M. R. FONTUGNE. 1992. Evidence from nitrogen isotope ratios for enhanced productivity during formation of eastern Mediterranean sapropels. *Nature* **359**: 223–225.
- CIFUENTES, L. A., J. H. SHARP, AND M. L. FOGEL. 1988. Stable carbon and nitrogen isotope biogeochemistry in the Delaware estuary. *Limnol. Oceanogr.* **33**: 1102–1115.
- CLINE, J. D., AND I. R. KAPLAN. 1975. Isotopic fractionation of dissolved nitrate during denitrification in the eastern tropical North Pacific Ocean. *Mar. Chem.* **38**: 453–477.
- DENIRO, M. J., AND S. EPSTEIN. 1981. Influence of diet on the distribution of nitrogen isotopes in animals. *Geochim. Cosmochim. Acta* **45**: 341–351.
- FOGEL, M. L., AND L. A. CIFUENTES. 1993. Isotope fractionation during primary production. p. 73–94. *In* S. A. Macko and M. H. Engel [eds.], *Organic geochemistry*. Plenum Press.
- FRANÇOIS, R., M. A. ALTABET, AND L. H. BURCKLE. 1992. Glacial to interglacial changes in surface nitrate utilization in the Indian sector of the Southern Ocean as recorded by sediment $\delta^{15}\text{N}$. *Paleoceanogr.* **7**: 589–606.
- GÄCHTER, R., AND B. WEHRLI. 1998. Ten years of artificial mixing and oxygenation: No effect of the internal phosphorus loading of two eutrophic lakes. *Environ. Sci. Tech.* **32**: 1865–1869.
- GU, B. C. L., SHELSCHE, AND M. BRENNER. 1996. Relationship between sediment and plankton isotope ratios and primary productivity in Florida Lakes. *Can. J. Fish. Aquat. Sci.* **53**: 875–883.
- HODELL, D. A., AND C. L. SHELSCHE. 1998. Production, sedimentation and isotopic composition of organic matter in Lake Ontario. *Limnol. Oceanogr.* **43**: 200–214.
- HOLLANDER, D. J. 1989. Carbon and nitrogen isotope cycling and organic geochemistry of eutrophic Lake Greifen: Implications for preservation and accumulation of ancient organic carbon-rich sediments. Ph. D. dissertation. ETH-Zürich.
- , AND J. A. MCKENZIE. 1991. CO_2 control on carbon isotope fractionation during aquatic photosynthesis: A paleo- pCO_2 barometer. *Geology* **19**: 929–932.
- , ———, AND H. L. HAVEN. 1992. A 200 year sedimentary record of progressive eutrophication in Lake Greifen (Switzerland): Implications for the origin of organic-carbon-rich sediments. *Geology* **20**: 825–828.
- KENDALL, C. 1998. Tracing nitrogen sources and cycling in catchments, p. 519–576. *In* C. Kendall and J. J. McDonnell [eds.], *Isotope tracers in catchment hydrology*. Elsevier.
- LOTTER, A. F. 1998. The recent eutrophication of Baldeggersee (Switzerland) as assessed by fossil diatom assemblages. *The Holocene* **8**: 395–405.
- , I. RENBERG, H. HANSSON, R. STÖCKLI, AND M. STURM. 1997a. A remote controlled freeze corer for sampling unconsolidated surface sediments. *Aquat. Sci.* **59**: 295–303.
- , M. STURM, J. L. TERANES, AND B. WEHRLI. 1997b. Varve formation since 1885 and high-resolution varve analyses in hypereutrophic Baldeggersee (Switzerland). *Aquat. Sci.* **59**: 304–326.
- MENGIS, M., R. GÄCHTER, B. WEHRLI, AND S. M. BERNASCONI. 1997. Nitrogen elimination in two deep eutrophic lakes. *Limnol. Oceanogr.* **42**: 1530–1543.
- MEYERS, P. A. 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chem. Geol.* **144**: 289–302.
- . 1997. Organic geochemical proxies of paleoceanographic, paleolimnologic and paleoclimatic processes. *Org. Geochem.* **27**: 213–250.
- , AND R. ISHIWATARI. 1993. Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenesis in lake sediments. *Org. Geochem.* **20**: 867–900.
- MINAGAWA, M., AND E. WADA. 1984. The stepwise enrichment of ^{15}N along food chains: Further evidence and the relation between $\delta^{15}\text{N}$ and animal age. *Geochim. Cosmochim. Acta* **48**: 1135–1140.
- NIESSEN F., AND M. STURM. 1987. Die Sedimente des Baldeggersees (Schweiz)—Ablagerungsraum und Eutrophierungsentwicklung während der letzten 100 Jahre. *Arch. Hydrobiol.* **108**: 365–383.
- PETERSON, B. J., AND B. FRY. 1987. Stable isotopes in ecosystem studies. *Ann. Rev. Ecol. System* **18**: 293–320.
- SHELSCHE, C. L., AND D. A. HODELL. 1991. Recent Changes in productivity and climate of Lake Ontario detected by isotope analysis of sediments. *Limnol. Oceanogr.* **36**: 961–975.
- , AND ———. 1995. Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie. *Limnol. Oceanogr.* **40**: 918–929.
- TERANES, J. L., J. A. MCKENZIE, 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**: 1891–1899.
- , ———, 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.
- WADA, E. 1980. Nitrogen isotope fractionation and its significance in biogeochemical processes occurring in marine environments. p. 375–398. *In* E. D. Goldberg, Y. Horibe, and K. Saruhashi [eds.], *Isotope marine chemistry*. Uchida Rokakudo.
- WASER, N. A. D., P. J. HARRISON, B. NIELSEN, S. E. CALVERT, AND D. H. TURPIN. 1998. Nitrogen isotope fractionation during the uptake and assimilation of nitrate, nitrite ammonium and urea by a marine diatom. *Limnol. Oceanogr.* **43**: 215–224.
- 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**: 285–295.

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