

Interannual variation of the isotopic composition of sedimenting organic carbon and nitrogen in Lake Lugano: A long-term sediment trap study

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Abstract

We examined the evolution of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of sedimenting particulate organic matter (SPOM) in response to changes in primary productivity, nutrient loading, and plankton dynamics in Lake Lugano between 1985 and 1998. A decreasing $\delta^{13}\text{C}$ reflects the decline of phosphorus loading in Lake Lugano, suggesting that the $\delta^{13}\text{C}$ of SPOM is a good indicator of P availability in the lake, with phosphate being the major control on the CO_2 draw-down in the photic zone. However, annual primary production and $\delta^{13}\text{C}$ do not correlate. The expansion of the trophogenic layer in response to lowered plankton biomass concentrations balanced the effect of reduced phosphate concentration on total primary production (per unit area) and, thus, biased the correlation of $\delta^{13}\text{C}$ and primary productivity. Whereas a substantial decrease of total phytoplankton biomass in the late 1980s clearly affected the $\delta^{13}\text{C}$ of SPOM, it did not seem to affect $\delta^{15}\text{N}$. Marked changes in the plankton population composition did not have a major effect on $\delta^{15}\text{N}$. If at all, the effects of primary productivity, nitrate utilization, and changes in the intensity of denitrification are superimposed on a signal dominantly derived from changes in the amount and isotopic composition of dissolved inorganic nitrogen from external sources. A marked positive shift (+3‰) in the $\delta^{15}\text{N}$ observed in 1994/1995 corresponded to the introduction of a denitrification stage in wastewater treatment. This study demonstrates that the $\delta^{13}\text{C}$ of exported organic matter is a useful indicator of the trophic state of lacustrine environments. The $\delta^{15}\text{N}$ of sedimentary organic matter is unlikely to reflect nitrate utilization or denitrification if the input of external N sources dominates the N-isotope dynamics within the lake. However, in those systems, organic matter $\delta^{15}\text{N}$ can provide information on the development of N pollution and subsequent effects of lake restoration measures.

Organic matter particles in lacustrine environments carry valuable geochemical information that can be used to trace distinct biogeochemical processes or to reconstruct past changes in environmental conditions. The accumulation of organic matter and its carbon isotope composition is thought to be an effective tool for reconstructing paleoproductivity and the evolution of trophic state in lakes (Schelske and Hodell 1991; Hollander et al. 1992; Hodell and Schelske 1998; Brenner et al. 1999). In the lower Great Lakes, it has been demonstrated that the carbon isotope composition of sedimentary organic matter most closely approximates historic changes in P loading and primary productivity (Schelske and Hodell 1991, 1995; Hodell and Schelske 1998). The $\delta^{15}\text{N}$ values of organic matter have been used in many aquatic environments to study reaction pathways of nitrogen, such as algal assimilation, respiration, N_2 fixation, nitrification, and denitrification (e.g., Lehmann et al. 2004). In marine

and, to a lesser extent, in lacustrine environments, the measurement of $^{15}\text{N}/^{14}\text{N}$ ratios in sedimentary organic matter has become an effective tool to infer past changes in primary productivity (Calvert et al. 1992; Shemesh et al. 1993), surface-water nitrate utilization (Altabet and François 1994; Sigman et al. 1999; Teranes and Bernasconi 2000), denitrification (Altabet et al. 1995; Ganeshram et al. 1995), or N_2 fixation (Struck et al. 2001). In lakes, processes other than N transformation reactions might be more important. Fluxes of dissolved nitrogen from external sources might represent the predominant control on the N-isotope dynamics in a lake. These can strongly affect the N isotopic composition of the dissolved inorganic nitrogen (DIN) pool and subsequently affect the isotope signal incorporated in the newly synthesized organic matter (Teranes and Bernasconi 2000; Lehmann et al. 2004). Changes in phytoplankton species composition or the contribution from allochthonous or heterotrophic sources can be additional factors in determining the C and N isotopic composition of lacustrine organic matter (Minigawa and Wada 1984; Peterson and Fry 1987; Meyers and Ishiwatari 1993; Lehmann et al. 2004).

Isotopic data for sedimenting organic matter from Lake Lugano have been presented in a previous study (Bernasconi et al. 1997), and several other sediment trap studies have addressed the variability of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values in lacustrine organic matter (e.g., Hodell and Schelske 1998; Owen et al.

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1999; Teranes and Bernasconi 2000). However, these studies all focused on the seasonal variation of isotope ratios in trap material. Covering only one to three sequential seasonal cycles, the data do not allow for the assessment of longer records of interannual variations in the carbon and nitrogen isotope dynamics of a lake. Consequently, they do not constrain the long-term controls on the primary isotope signal of lacustrine organic matter. Measuring $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values in organic matter from sediment cores and integrating the results with historical information on nutrient loading and eutrophication of lacustrine environments has proven to be a promising approach to better understand historic changes in the C and N isotopic composition of a lake's particulate organic matter pool (Hodell and Schelske 1998; Ostrom et al. 1998; Teranes and Bernasconi 2000). However, possible isotopic alteration during early sedimentary diagenesis and uncertain age models can bias the interpretation of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values in sedimentary organic matter and, therefore, represent a significant impediment to reconstruct paleoenvironmental conditions.

This is the second of two companion manuscripts (see Lehmann et al. 2004) addressing the biogeochemical cycling of C and N in eutrophic Lake Lugano. In this study, we investigate the carbon and nitrogen isotope dynamics in Lake Lugano (Switzerland) by examining a greatly expanded data set on isotopic variations in sedimenting organic matter collected between 1985 and 1998. In contrast to sediment cores, flux-weighted $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of sedimenting organic matter should provide primary isotope signals that are minimally altered by secondary sedimentary processes or possible early diagenetic isotope alteration. The goal of this study is to evaluate the potential of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of organic matter to record changes in nutrient loading, primary productivity, and plankton dynamics. In particular, we test the use of $\delta^{15}\text{N}$ values of organic matter as indicators of nitrate utilization and denitrification, and examine their response to lake restoration measures. Because of its well-documented history of eutrophication, as well as changes in hydrochemistry and plankton populations (LSA 1980–2003; Barbieri and Mosello 1992; Polli and Simona 1992; Barbieri and Simona 2001), Lake Lugano is an ideal environment in which to conduct this calibration experiment.

Study site

Site characteristics—Lake Lugano is a deep, subalpine lake located at 271 m above sea level on the Swiss–Italian border (46°00'N, 3°30'E; Fig. 1). The lake has a surface area of 48.9 km² and a catchment area of 615 km². Lake Lugano can be divided into three subbasins: the northern and southern basins and a smaller basin located in front of the outlet, the Tresa River. This study concentrates on the southern basin of Lake Lugano. The southern basin is 95 m deep at the deepest location, has an area of 20.3 km², and has a volume of 1.14 km³. Its mean water residence time is comparatively short (1.4 yr). The major inflows to the southern basin are from the northern basin (catchment area 270 km²) and the Veduggio River (catchment area 92 km²). The nutrient loading to the lake derives from anthropogenic (household/sew-

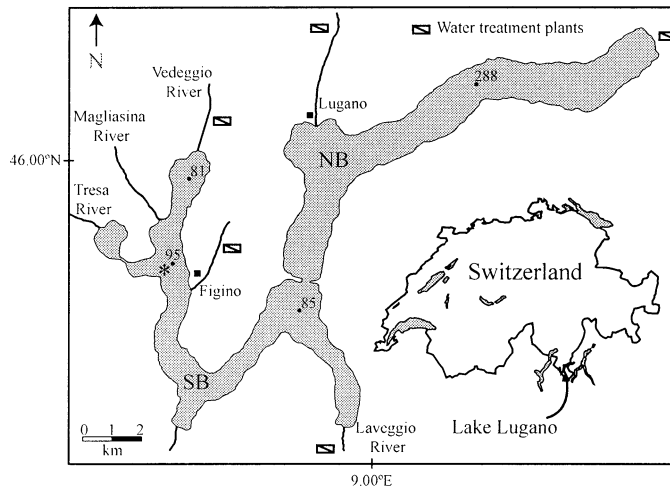


Fig. 1. Map of the Lake Lugano study area. The asterisk indicates the site of sediment trap deployment in the southern basin (Figino locality). Water depths (m) are given by numbers.

age, 85%), industrial (10%), and agricultural (5%) sources (Barbieri and Simona 2001). Primary productivity and water column characteristics display distinct seasonal patterns (Bernasconi et al. 1997; Lazzaretti-Ulmer and Hanselmann 1999; Lehmann et al. 2004). After the yearly winter holomixis—the complete overturn and, thus, chemical and thermal homogenization of the lake in January/February—stratification of the water column starts to develop with increasing surface-water temperatures. During spring and summer, euphotic zone productivity increases and plankton blooms consume surface-water nutrients. Augmented organic matter fluxes and microbial respiration result in enhanced consumption of oxygen in the hypolimnion and lead to anoxic conditions promoting nitrate reduction in near-bottom waters (Lehmann et al. 2004). With a new holomixis, surface-water nutrients are replenished and oxygen is supplied to bottom waters.

History of nutrient loading and trophic evolution in Lake Lugano—During the last 120 years, Lake Lugano has undergone severe changes in primary productivity, eutrophication, and oxygenation conditions in response to changes in nutrient loading from industrialization and agriculture (Niessen 1987; Barbieri and Mosello 1992; Barbieri and Simona 2001). The onset of varve sedimentation in the 1930s as a consequence of seasonal anaerobic conditions at the sediment–water interface can be interpreted as an early indication of eutrophication in the southern basin (Niessen 1987). Hydrochemical studies performed in the last 60 years, including routine measurements conducted by the Commission for the Protection of Swiss–Italian Waters (Laboratorio Studi Ambientali) since 1980 (LSA 1980–2003), revealed the continuous increase in trophic level of Lake Lugano until the late 1970s (Barbieri and Mosello 1992). Progressively increasing P and N loads resulted in hypertrophic conditions, with whole-lake phosphorus concentrations approaching 150 $\mu\text{g L}^{-1}$ at the end of the 1970s (Barbieri and Simona 2001). Lake restoration measures, including the legislated removal of P in domestic and industrial detergents (1986) and the

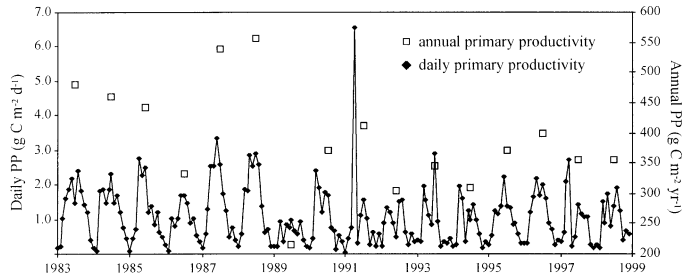


Fig. 2. Time series of primary productivity (PP) for the period 1983–1998.

gradual activation of several multistage (mechanical, chemical, biological) water treatment plants since 1976, led to a significant reduction of P loads. Since 1995, the effectiveness of the main treatment plants has been increased by the introduction of a fourth stage of wastewater treatment (post-precipitation of phosphorus, denitrification, and filtration). Since the early 1980s, the annual external P load to Lake Lugano has been reduced from ~250 to 63 kg 10³ yr⁻¹ (1997) and P concentrations in the southern basin decreased from 130 to 32 μg L⁻¹ from 1984 to 1999. Total nitrogen concentration continued to increase until 1989 and, since then, remained relatively constant at ~1.4 mg L⁻¹ (Barbieri and Simona 2001). Primary productivity and chlorophyll concentrations in the photic zone of the southern basin have decreased by more than 25% since peak-time eutrophication (Fig. 2; Tables 1, 2; Barbieri and Simona 2001). Regular surveys of plankton populations in Lake Lugano since 1981 revealed that lake restoration measures led to profound changes in the food chain structure at the very end of the 1980s, with a significant drop (ca. -50%) in phytoplankton biomass corresponding to a strong increase (ca. +50%) in zooplankton biomass (LSA 1980–2003; Polli and Simona 1992; Barbieri and Simona 2001). The exact triggering mechanisms leading to these abrupt changes in the plankton population of Lake Lugano remain uncertain.

Table 2. Mean values for plankton biomass, primary production, thickness of the trophogenic zone ($Z_{1\%}$, depth at which 99% of the light is absorbed), and sediment trap $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ (weighted by flux) in the southern basin (Figino). Except for stable isotope values, all data are taken from Barbieri and Simona (2001) and LSA (2003).

Phytoplankton biomass (dry weight, g m ⁻²)	
1981–1988	14.7±2.4
1989–1996	7.4±1.3
Zooplankton biomass (dry weight, g m ⁻²)	
1981–1988	3.42±0.89
1989–1996	4.6±0.95
Primary production (g C m ⁻² yr ⁻¹)	
1983–1988	469±81
1989–1998	344±56
Thickness of trophogenic zone ($Z_{1\%}$, m)	
1983–1988	6.97±0.38
1989–1998	9.41±0.60
POC $\delta^{13}\text{C}$ (‰)	
1985–1986	-26.9±0.2
1990–1997	-29.0±0.64
PON $\delta^{15}\text{N}$ (‰)	
1985–1986	+7.25±0.21
1990–1997	+7.07±1.36

Methods

Sinking particulate matter was collected by cylindrical sediment traps (diameter 10 cm, height 78 cm) deployed in 1985, 1986, 1990, and 1993–1998 at 20-m water depth at the Figino sampling location in the deepest part (95 m) of the southern basin of Lake Lugano (Fig. 1). The 20-m trap coincides with the base of the thermocline during water column stratification where temperature variations are in the range of 4–7°C during the annual cycle. Except for winter, when 3-week deployment periods were required to obtain enough material, sediment traps were emptied every other week. No preservatives to hinder microbial activity were

Table 1. Annual fluxes of POC and PONs, average $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and C:N ratio weighted by organic matter fluxes, surface-water nutrient concentrations after winter overturn ($[\text{NO}_3^-]_{\text{max}}$, $[\text{PO}_4^{3-}]_{\text{max}}$), annual primary productivity (PP), and mean epilimnetic (0–20 m) concentration of phytoplankton biomass (dry weight). The apparent nitrate fraction that has been used during nitrate assimilation (f_{NO_3}) is an approximation of the degree of nitrate utilization (high % values represent high nitrate utilization). f_{NO_3} is calculated from $[\text{NO}_3^-]_{\text{max}}$ and $[\text{NO}_3^-]_{\text{min}}$, which is the minimum surface-water nitrate concentration during peak-time phytoplankton growth in July and August (see Eq. 1).

Year	POC (g C m ⁻² yr ⁻¹)	PON (g N m ⁻² yr ⁻¹)	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	C:N	$[\text{NO}_3^-]_{\text{max}}$ (mg L ⁻¹)	f_{NO_3} (%)	$[\text{PO}_4^{3-}]_{\text{max}}$ (μg L ⁻¹)	PP (g C m ⁻² yr ⁻¹)	Phyto- plankton biomass (mg L ⁻¹)
1985	107.4	12.8	-26.9	7.1	9.8	1.05	92	119	443	3.59
1986	91.02	10.5	-26.9	7.4	10.1	1.10	96	122	331	2.42
1990	116.4	12.7	-27.9	7.9	10.6	1.28	68	73	370	1.80
1993	95.9	10.0	-29.1	6.2	11.2	1.25	57	50	346	1.82
1994	102.6	8.8	-27.8	4.7	13.5	1.33	70	63	309	1.45
1995	110.8	10.0	-28.1	8.0	12.8	1.26	65	69	371	1.54
1996	90.3	11.5	-29.9	8.2	9.1	1.23	81	42	399	1.82
1997	87.6	11.2	-29.0	7.4	9.1	1.30	71	32	356	1.70

added during deployment because work by Bloesch and Burns (1980) showed that exposure times of two weeks or less is adequate to avoid significant degradation of organic matter. We are aware that microbial degradation might alter the isotopic composition of the material collected in the trap. For example Lehmann et al. (2002) have shown that alteration of the $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ of fresh algal material occurs within 20 d of degradation (incubation experiments at room temperature). Although an alteration of the absolute isotope composition of the individual traps cannot be excluded, because of the consistency of the exposure time of all traps and the small temperature range at the depth of deployment, we consider that if an alteration of the isotopic composition has occurred, it is probably consistent for all samples because no temperature-driven increase of bacterial activity should occur. In addition, the variability observed in fresh organic material collected by filtering in the water column in 1999 (Lehmann et al. 2004) is in the same range as that observed in the youngest sediment trap series. We therefore conclude that degradation of the original isotopic composition of the organic matter during trap deployment is not a significant problem. Immediately after sample collection on precombusted Whatman GF/F glass fiber filters, particulate matter was freeze-dried or oven-dried (60°C, 4 d) and weighed in order to calculate bulk sediment accumulation rates.

For particulate organic carbon (POC) quantification, sediment trap material was decarbonated with sulfuric acid (1 N), rinsed with deionized water, dried, and analyzed with a Carlo-Erba elemental analyzer (NA 1500). The particulate organic nitrogen (PON) content of bulk sediment was determined by digestion of sample material in an oxidizing solution containing NaOH (0.35 mol L⁻¹), K₂S₂O₈ (0.2 mol L⁻¹), and H₃BO₃ (0.5 mol L⁻¹), filtration through a Whatman GF/C filter, and subsequent [NO₃⁻] measurement in the filtrate by ultraviolet spectrophotometry at 210 nm (APHA 1989). Estimated analytical precision was ±4% for C and ±2% for N analysis. Fluxes of organic carbon and nitrogen (g m⁻² d⁻¹) were calculated by multiplying weight percent of each component, with respect to the total dry weight, by the bulk sediment accumulation.

For stable nitrogen and carbon isotopic measurements, 2–12 mg of homogenized sample was loaded into tin capsules and analyzed in a Carlo-Erba elemental analyzer (NCS 2500) interfaced with a Fisons Optima spectrometer for isotope ratio mass spectrometry (IR-MS). Sample material was combusted in the presence of O₂ in an oxidation column at 1,030°C. Combustion gases were passed through a reduction column (650°C), and produced N₂ and CO₂ gases were purified and transferred to the IR-MS via an open split for on-line isotope measurements. Nitrogen isotope ratios were determined on an aliquot of untreated bulk sample. For carbon isotope analysis, bulk trap material was acidified with dilute HCl (1 mol L⁻¹) and washed with deionized water to remove inorganic carbon. Stable nitrogen and carbon isotope compositions are expressed in the conventional δ -notation, defined as per mil (‰) deviation versus atmospheric N₂ (AIR) and V-PDB carbonate standard, respectively. Analytical reproducibility based on repeat analyses of laboratory stan-

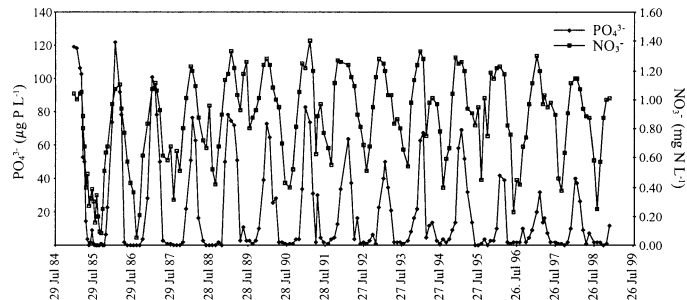


Fig. 3. Time series of surface-water (5 m) nutrient concentrations ([NO₃⁻] and [PO₄³⁻]) for the period 1985–1998. Note that summer minimum nitrate concentrations were significantly lower in 1985 and 1986 as compared to those measured in subsequent years, indicating more efficient nitrate utilization (i.e., high *f* in Table 1) in 1985 and 1986.

dards and international nitrogen (IAEA-N1, IAEA-N2) and carbon (NBS 22) standards was ±0.2‰ for both N and C.

Primary productivity and hydrochemical data, as well as data on phytoplankton dynamics, were compiled as part of a long-term lake monitoring program conducted by the Laboratorio Studi Ambientali (LSA 1980–2003). For measurements of [NO₃⁻] and [PO₄³⁻], aliquots of prefiltered water samples were microfiltered through 0.45-µm-membrane filters and analyzed colorimetrically with an automatic analyzer (TRAACS 2000, Bran and Luebbe). Primary productivity was measured by ¹⁴C assimilation and the Steemann-Nielsen (1952) method, modified by Gächter and Marès (1979). Monthly values of primary productivity were obtained according to Gächter (1972) and Polli and Simona (1992) by interpolation from short-interval, depth-integrating (0–20 m) measurements, taking into account diurnal solar radiation variability and metrological changes (determined in Lugano by the Swiss Meteorological Service) and the quantity of productive biomass, which controls solar radiation extinction. Monthly values were used to calculate a weighted annual mean primary productivity. Errors for annual primary productivity are estimated to be <10%. A detailed description of all the sampling and analytical methods is given elsewhere (LSA 1990; Polli and Simona 1992).

Results

Primary production and sediment fluxes—The evolution of primary productivity in the southern basin of Lake Lugano is depicted in Fig. 2. Fluctuations clearly follow seasonal trends: variations in primary productivity and phytoplankton growth are coupled with summer lows and winter highs in nutrient concentration (Fig. 3). Phosphate concentrations decreased below the detection limit in all years and were biolimiting during summer. Nitrate concentrations decreased to values close to 10 mg N L⁻¹ in the summers of 1985 and 1986 but thereafter never decreased below 20 mg N L⁻¹. The annual primary productivity experienced significant variability, with values ranging between 216 and 556 g C m⁻² yr⁻¹ (Fig. 2). In response to the reduction of phosphate availability, the mean primary productivity in the southern basin dropped from 469 ± 81 g C m⁻² yr⁻¹ (1983–

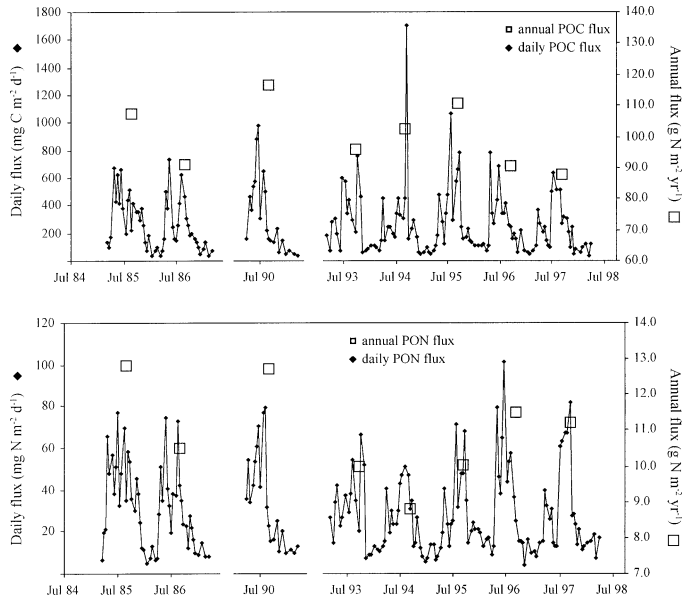


Fig. 4. Fluxes of particulate organic carbon and nitrogen determined in 1985–86, 1990, and 1993–98. 1994-data are taken from Bernasconi et al. (1997). A short-term depositional event occurred in September 1994 and can be attributed to large riverine inputs of terrestrial material (Bernasconi et al. 1997).

1988) to $344 \pm 56 \text{ g C m}^{-2} \text{ yr}^{-1}$ (1989–1998). This change in productivity in 1989 is also reflected in the drop of phytoplankton biomass concentration in the photic zone (Table 2). Organic matter fluxes displayed similar seasonal variations with the highest fluxes during spring and summer (Fig. 4). Discrete phytoplankton blooms resulted in maximum POC and PON fluxes of up to $1 \text{ g C m}^{-2} \text{ d}^{-1}$ and $0.1 \text{ g N m}^{-2} \text{ d}^{-1}$. An extremely high flux of POC was observed in September 1994. This short-term event can be attributed to the input of large amounts of terrestrial organic matter (C:N ratio of 57.5) during a storm (Bernasconi et al. 1997). Little organic matter accumulated in the 20-m trap during the winter months. Between 1985 and 1997, total annual export fluxes of POC and PON from the photic zone ranged between 88 and $116 \text{ g C m}^{-2} \text{ yr}^{-1}$ and between 8.8 and $12.8 \text{ g N m}^{-2} \text{ yr}^{-1}$, respectively (Fig. 4; Table 1). Accordingly, at most $25\% \pm 5\%$ of the carbon fixed during photosynthesis leaves the photic zone. Annual POC fluxes did not decrease significantly between 1985 and 1997. The C:N ratios of organic matter ranged between 5 and 15 and did not display considerable seasonal trends. Weighted annual means for the period 1985–1997 are shown in Table 1.

Carbon and nitrogen isotope biogeochemistry—The evolution of the carbon and nitrogen isotope composition of sinking particulate organic matter is shown in Fig. 5. Consistent with the water column study by Lehmann et al. (2004), both carbon and nitrogen isotope ratios of trap material displayed strong seasonal fluctuations. High $\delta^{13}\text{C}$ (-30‰ to -19‰) and low $\delta^{15}\text{N}$ ($+1\text{‰}$ to $+10\text{‰}$) values were observed during spring and summer, and low $\delta^{13}\text{C}$ (-41‰ to -30‰) and high $\delta^{15}\text{N}$ ($+10\text{‰}$ to $+19\text{‰}$) values were observed during winter. The changes in isotope ratios

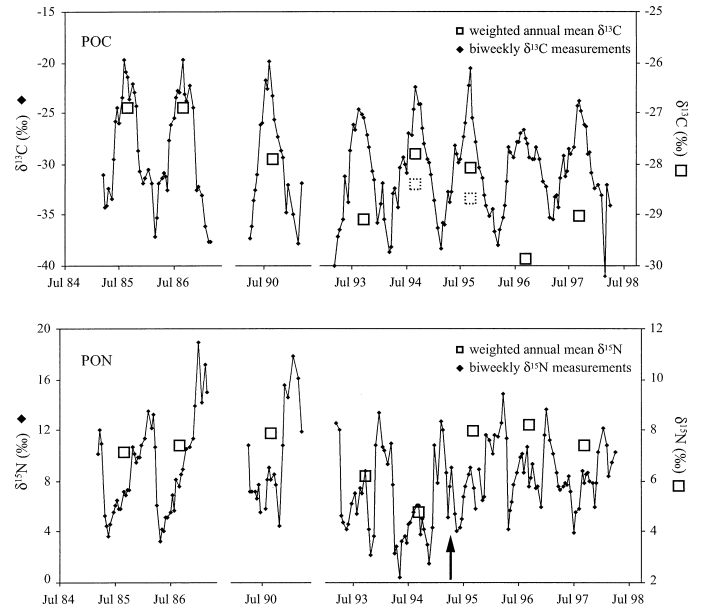


Fig. 5. Carbon and nitrogen isotope composition of sediment-trap organic matter collected biweekly in 1985–1986, 1990, and 1993–1998 from a water depth of 20 m. Squares depict the average annual stable isotope composition weighted by organic matter flux (see also Table 1). The reproducibility for single C- and N-isotope measurements (biweekly samples) is 0.2‰ . The standard error of the weighted annual mean is much smaller because it integrates up to 23 discrete isotope measurements ($\sigma < 0.1\text{‰}$ for both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$). Note different scales. 1994-data are taken from Bernasconi et al. (1997). Dashed-line symbols in the upper panel represent annual weighted $\delta^{13}\text{C}$ values in 1994 and 1995 corrected for the contribution of land-derived organic carbon. The arrow in the lower panel indicates the timing of the introduction of a denitrification stage of waste-water treatment in the water purification plants around the lake. See text for discussion.

are closely related to the seasonal changes in particulate organic matter fluxes.

Spring and summer production clearly dominates the annual weight-averaged $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values calculated from organic matter fluxes and corresponding C- and N-isotope ratios. Extreme C- and N-isotope ratios for low-flux winter samples do not play an important role in the weighted average. Weighted annual $\delta^{13}\text{C}$ values decreased from -26.9‰ in 1985 and 1986 to values ranging between -27.9‰ and -29.1‰ between 1990 and 1997 (Fig. 5; Tables 1, 2). Annual $\delta^{15}\text{N}$ values increased slightly between 1985 and 1990 before dropping to significantly lower values in 1993 and 1994 (Fig. 5). The most pronounced shift in the N isotopic composition occurred in 1995, when the $\delta^{15}\text{N}$ value increased dramatically by more than 3‰ . Thereafter, it remained high at approximately $+7.8\text{‰}$.

Discussion

Seasonal-scale changes in primary productivity clearly controlled the seasonal variation in the export flux of organic matter, with maxima in summer and minima in winter (Fig. 4). Possible controls on the seasonal variation of the C and

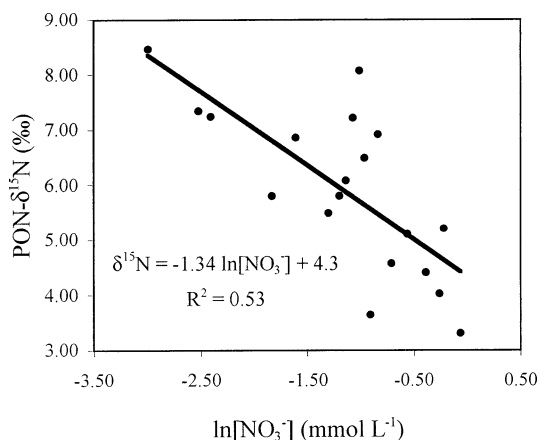


Fig. 6. Sediment trap PON $\delta^{15}\text{N}$ collected between 25 April and 26 September 1985 and between 25 April and 11 September 1986 versus $\ln[\text{NO}_3^-]_{\text{sm}}$. The data document the inverse relationship between surface-water nitrate concentration and the $\delta^{15}\text{N}$ of sedimenting organic matter according to 'Rayleigh' fractionation kinetics. The slope of the linear regression line (-1.34‰) provides an estimate of the apparent N-isotope fractionation associated with nitrate assimilation by phytoplankton. During subsequent sampling years, a similar correlation between $\delta^{15}\text{N}$ and $[\text{NO}_3^-]$ during the productive season does not exist (data not shown). See text for discussion.

N isotopic composition of organic matter from the photic zone at the same sampling locality are discussed in detail by Lehmann et al. (2004). Changes in the $\delta^{13}\text{C}$ of POC can be directly related to the annual biological cycle. The ^{13}C enrichment in POC during spring and summer can be explained by the reservoir effect associated with the discrimination against $^{13}\text{C}\text{-DIC}$, as well as by decreased C-isotope fractionation and/or enhanced utilization of bicarbonate as alternative carbon source at low surface water $\text{CO}_2(\text{aq})$ levels (Hollander and McKenzie 1991; Hodell and Schelske 1998; Lehmann et al. 2004). The seasonal pattern of PON $\delta^{15}\text{N}$ values mirrors that of $\delta^{13}\text{C}$. During spring and summer, comparatively low $\delta^{15}\text{N}$ values ($+2\text{--}7\text{‰}$) are attributed to fresh autochthonous organic matter production. Under conditions of unlimited supply of nitrate, the uptake of ^{14}N during phytoplankton assimilation results in low $\delta^{15}\text{N}$ of phytodetritus. The bulk PON $\delta^{15}\text{N}$ could be further reduced temporarily if N_2 fixation contributes significantly to the total primary production (Lehmann et al. 2004). In 1985 and 1986, $\delta^{15}\text{N}$ values progressively increased during summer in association with the strongest decrease in nitrate concentrations between March and August observed during the sampling period, indicating that the reservoir effect associated with the preferential utilization of $^{14}\text{NO}_3^-$ (Rayleigh fractionation kinetics) was an important factor on surface-water N-isotope dynamics (Fig. 6). During the more recent years, the seasonal pattern was quite different, and the decrease in nitrate concentration was not directly associated with an increase in $\delta^{15}\text{N}$ of organic matter. This indicates that processes other than the isotope fractionation associated with nitrate utilization become more important with the decrease in P:N ratios in the water column. Because the nitrate concen-

tration in Lake Lugano continued to increase whereas the P concentration decreased because of the improved water treatment in adjacent purification plants and the ban of phosphates from detergents, nitrogen excess over phosphate has increased and the factors controlling $\delta^{15}\text{N}$ of organic matter seem to have changed. Our data suggest that changes in the relative availability of N with respect to P (i.e., changes in the surface-water P:N ratio) might lead to changes in the N isotopic composition of lacustrine organic matter.

Winter $\delta^{15}\text{N}$ values are generally high, probably because of a contribution from either a heterotrophic or allochthonous source (Bernasconi et al. 1997). Hodell and Schelske (1998) and Teranes and Bernasconi (2000) observed similar seasonal patterns in the N isotopic composition of sinking organic material during sediment trap studies in Lake Ontario and Lake Baldegg, respectively, and related them to changes in the source of organic matter (isotopically light phytodetritus vs. isotopically heavy heterotrophic or detrital sources or both). Relatively low C:N ratios (5–10) observed for ^{15}N -enriched winter material in Lake Lugano, however, are inconsistent with a nonphytodeutral source. ^{15}N enrichment in winter PON seems to be a widespread and, as our long-term sediment trap study shows, a consistently reoccurring phenomenon in lacustrine environments that requires further investigation.

The weighted average $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values, as well as total annual organic matter fluxes, should directly reflect the well-documented changes in environmental conditions since 1985. Temporal variations in the accumulation of organic matter and its C isotopic composition were reported to reflect historic changes in phosphorus loading and primary productivity (Schelske and Hodell 1991). Whereas primary productivity and organic matter fluxes seem to be closely coupled on a seasonal timescale, we did not observe a close relationship in the long term when looking at annual means; that is, no significant decrease in weighted organic carbon fluxes was observed with the decrease in primary productivity (Fig. 4; Table 1). Also, on a multiannual timescale, organic matter fluxes do not reflect the abrupt decline in phytoplankton biomass observed in 1989–1999 (Table 2). This indicates that, in a eutrophic lake undergoing restoration, decreasing productivity and phytoplankton biomass in the photic zone does not necessarily result in a reduction of export organic matter fluxes into the hypolimnion. Enhanced epilimnetic organic matter recycling might partly compensate for the effect of high primary productivity on the net export flux of organic matter. In addition, it was observed that, over the last two decades, the thickness of the trophogenic layer increased in response to the decrease in primary productivity per volume (LSA 2003; Table 2). Light represents an important biolimiting factor in the southern basin (Polli and Simona 1992). It remains uncertain to what extent an increase of light penetration, which is likely to balance the effect of reduced phosphate concentrations in the surface layer on the total production, might control the ratios of primary production, biomass, and net organic matter export flux.

In some cases, as observed in 1994 (a heavy rainfall event), the POC flux is also influenced by changes in input of terrestrial organic matter. PON is not as strongly influ-

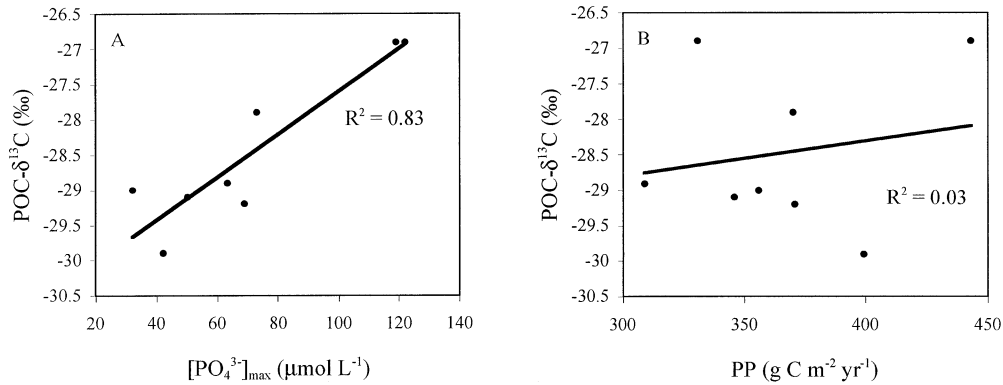


Fig. 7. Weighted annual mean $\delta^{13}\text{C}$ of sediment trap organic matter A) versus surface-water phosphate concentrations after winter overturn ($[\text{PO}_4^{3-}]_{\text{max}}$) and B) versus annual primary productivity.

enced by allochthonous inputs because terrestrial organic matter has high C:N ratios and, thus, PON appears to be a better indicator of primary productivity than the accumulation of POC.

Variable inputs of terrestrial organic matter might also explain why, in parts, $\delta^{13}\text{C}$ values of bulk POC do not directly correlate with total annual primary productivity. For example, the isotope excursion toward less negative values observed in 1994/1995 can be attributed to a significant contribution from land-derived vascular plants, as indicated by comparatively high C:N ratios (Table 1). The short-term deposition of large amounts of (mostly land-derived) POC with a $\delta^{13}\text{C}$ of ca. -24.2‰ (i.e., enriched in ^{13}C relative to the annual mean) in September 1994 had a dominating influence on the weighted annual mean $\delta^{13}\text{C}$ values because this event accounted for a significant portion ($\sim 25\%$) of the total annual bulk POC flux. The C:N ratio of 57.5 and the large difference with mostly autochthonous POC fluxes determined for the same month during the other sampling years ($1,756 \text{ mg C m}^{-2}$ in September 1994 versus more typical values of $<300 \text{ mg C m}^{-2}$) indicate that $>80\%$ of the POC in this sample was land-derived vascular plant material with a C:N ratio of ~ 70 and a $\delta^{13}\text{C}$ of ca. -24‰ . We corrected for this short-term event by subtracting $1,450 \text{ mg C m}^{-2}$ with a $\delta^{13}\text{C}$ of -24‰ from the total annual C flux. A comparatively high weighted annual mean C:N ratio for 1995 (12.8) suggests that, also in 1995, the $\delta^{13}\text{C}$ value is biased by a significant contribution from nonautochthonous material. However, because there was no single depositional event bringing in large amounts of land-derived carbon (which, as shown above, would be easy to account for when determining the annual $\delta^{13}\text{C}$), a correction for terrestrial admixture is rather difficult. Yet, if we assume that autochthonous organic matter has, on average, a C:N of 10 (see Table 1) we can calculate the contribution of land-derived organic matter to the total POC flux in 1995 on the basis of the observed C:N ratio. In turn, we can correct the weighted annual $\delta^{13}\text{C}$ for the admixture of terrestrial organic carbon (again, assuming a $\delta^{13}\text{C}$ of -24‰ for land plant detritus). Both the corrected average annual $\delta^{13}\text{C}$ values for 1994 and 1995 are lower by -1.1‰ and, thus, better match the general trend toward more negative values with time (Fig. 5).

The $\delta^{13}\text{C}$ values of POC correlate with the surface-water phosphate concentrations after water column holomixis (Fig. 7A). Supply of available PO_4^{3-} is a major control on the total algal biomass and, thus, on the CO_2 draw-down by phytoplankton in the photic zone. The greater the aqueous $[\text{CO}_2]$ ($[\text{CO}_2(\text{aq})]$) depletion, the higher the $\delta^{13}\text{C}$ values of autochthonous organic matter (Hollander and McKenzie 1991; Hodell and Schelske 1998; Lehmann et al. 2004). We propose that the observed trend in weight-averaged annual $\delta^{13}\text{C}$ values reflects the historic decrease in P loading. The correlation between total annual primary productivity and the POC $\delta^{13}\text{C}$ is poor (Fig. 7B). The $\delta^{13}\text{C}$ –primary productivity relationship is probably biased by the change in thickness of the trophogenic zone over the last two decades. Reduced primary productivity per volume in response to lower phosphate availability in the same volume leads to lower POC $\delta^{13}\text{C}$ (lower degree of CO_2 draw-down). At the same time, less biomass per volume and the associated increase in light penetration result in the thickening of the trophogenic zone, maintaining a relatively high level of total primary productivity (per area). We conclude that, in Lake Lugano (and most likely in other aquatic environments that are P-limited), the carbon isotope ratios of sedimentary organic matter are reliable indicators of the longer-term evolution of trophic state (P concentration) but not necessarily of the total primary productivity and the export flux of organic matter. However, it needs to be stressed that variable inputs of terrestrial organic matter strongly complicate the use of POC $\delta^{13}\text{C}$ values as a proxy for internal biogeochemical lake processes.

Barbieri and Simona (2001) reported a profound change in the pelagic biocenosis as a consequence of lake recovery measures and the associated limitation of nutrients for primary producers in Lake Lugano. They documented that, after 1988, the algal biomass in the southern basin (Figino locality) decreased abruptly from 14.7 ± 2.4 to $7.4 \pm 1.3 \text{ g dry weight m}^{-2}$ (Table 2). The relative abundance of cyanobacteria decreased by 70% and that of diatoms decreased by 50%, whereas green algae and cryptophytes became more abundant ($+20\%$; Barbieri and Simona 2001). At the same time, the zooplankton biomass, largely the contribution of herbivores, displayed a marked increase ($\sim 35\%$ at the

Figino locality), with post-1988 values between 4 and 5 g dry weight m^{-2} (Barbieri and Simona 2001; Table 2). Changes in trophic structure can influence the C and N isotopic composition of the bulk organic matter (Minigawa and Wada 1984; Peterson and Fry 1987; Yoshii et al. 1999). Animals are generally enriched in ^{13}C and ^{15}N by ca. +1‰ and ca. +3‰, respectively, relative to their diet (Michener and Schell 1994). However, the weighted $\delta^{13}C$ and $\delta^{15}N$ values of bulk organic matter did not experience a shift toward higher values, suggesting that the significant reorganization of the whole food chain at the end of the 1980s (i.e., enhanced phytoplankton grazing leading to a higher zooplankton to phytoplankton ratio) had no striking effect on the C- or N-isotope signal in sediment trap material (see Fig. 5; Table 2). We have shown previously that a shift in algal population can lead to changes in the N isotopic composition of bulk organic matter because the isotope effect associated with nitrate uptake varies with phylogenetic group (Lehmann et al. 2004). The decline in the relative abundance of diatoms in Lake Lugano, which have been shown to assimilate nitrate with a relatively small N-isotope effect ($\epsilon = 1\%$; Lehmann et al. 2004), might have resulted in higher bulk N-isotope fractionation and, in turn, to lower PON $\delta^{15}N$ values in the 1990 sediment trap sample. Yet, this was not observed.

Several studies of particulate fluxes in the ocean (e.g., Altabet and François 1994, 2001) but only two studies in a lacustrine environment (François et al. 1996; Teranes and Bernasconi 2000) indicate that an increase in relative nitrate utilization causes an increase in suspended or sinking PON $\delta^{15}N$ values. As a result of preferential uptake of $^{14}NO_3$ during progressive nitrate depletion, the residual nitrate and, in turn, newly produced organic matter becomes steadily enriched in ^{15}N . This phenomenon can similarly occur on seasonal and on multiannual timescales. After 1986, annual variations in the N isotopic composition of PON are clearly not consistent with this pattern because a decrease in P:N ratio of the inputs has led to a smaller decrease of nitrogen concentrations at the end of the productive season. During the long-term lake monitoring project, phosphate has always been the limiting nutrient. As such, it controls the nitrate depletion in surface waters (given a constant N:P ratio for phytoplankton biomass). The degree of nitrate utilization f_{NO_3} , with

$$f_{NO_3} = \{1 - ([NO_3^-]_{min}/[NO_3^-]_{max})\} \times 100 \quad (1)$$

where $[NO_3^-]_{min}$ is the minimum surface-water nitrate concentration during peak-time phytoplankton growth in July and August, varied quite significantly with time (Table 1; Fig. 3), but it did not correlate with the average $\delta^{15}N$ values weighted by N flux (Fig. 8). For example, in 1985 and 1986, when whole-lake PO_4^{3-} concentrations were highest and, in turn, nitrate consumption was most complete (>90%), $\delta^{15}N$ values for PON were not higher than in 1990 or 1995 when the apparent nitrate depletion was <70% (Table 1). This implies that, in Lake Lugano, $\delta^{15}N$ values for sinking PON are not indicators of historic changes in the degree of surface-water nitrate utilization associated with phytoplankton growth. Lehmann et al. (2004) suggested that, on a seasonal timescale, variations in the $\delta^{15}N$ value of the nitrogen source and contributions of the N-fixing cyanobacteria hinder the

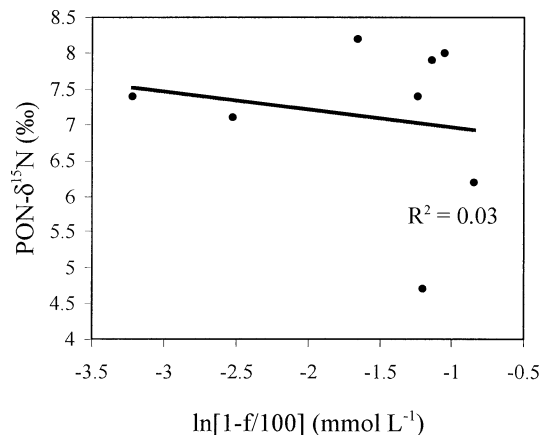


Fig. 8. Weighted annual mean $\delta^{15}N$ of sediment trap organic matter versus the natural logarithm of $[1 - f/100]$, which represents the remaining fraction of surface-water nitrate during summer high productivity ('Rayleigh plot'). See also Equation 1. The poor correlation indicates that nitrate utilization is not the dominant factor controlling inter-annual PON $\delta^{15}N$ variations.

use of organic matter $\delta^{15}N$ values as indicators of the degree of nitrate utilization in Lake Lugano. They could show that a discrete bloom of potentially N_2 -fixing cyanobacteria was associated with extremely low $\delta^{15}N$ values for suspended organic matter. Between 1985 and 1997, however, potential N_2 -fixers never accounted for >5% (generally <2%) of the total living biomass (LSA 1980–2003, L.S.A unpublished data), and whether they really fixed nitrogen, although nitrate was non-limiting, remains uncertain. Therefore, changes in the contribution from N_2 fixation could not have affected the weight-averaged $\delta^{15}N_{PON}$ values.

Changes in the N isotopic composition of the dissolved inorganic nitrogen pool might have modulated the interannual variations in the $\delta^{15}N$ values of PON. In other lake studies, water column denitrification and external nitrogen loading were suggested to be important controls on lacustrine N-isotope budgets. Hodell and Schelske (1998) interpreted a linear increase in the $\delta^{15}N$ of organic matter in a sediment core from Lake Ontario as a possible signature of enhanced denitrification. Teranes and Bernasconi (2000) have attributed a 6‰ increase, observed in Lake Baldegg sediments, to the progressively increasing influence of external N sources with characteristically high $\delta^{15}N$ values. Ostrom et al. (1998) explained very low nitrate $\delta^{15}N$ values in Lake Superior by large inputs of nitrogen from wet precipitation directly to the lake. Mass balance calculations revealed that, in the southern basin of Lake Lugano, the amount of nitrogen being eliminated via denitrification displayed marked temporal variations. On the whole, it appears to have increased between 1983 and 1997 (Table 3). Although quantitatively important, the changes in the intensity or extent of denitrification in the lake could not be related to variations in the weight-averaged PON $\delta^{15}N$. We cannot rule out the possibility that the effect of variable denitrification on the weighted mean $\delta^{15}N$ is simply masked by other processes. However, our observation is consistent with suggestions made previously (Lehmann et al. 2003, in press) that, in the southern basin of Lake Lugano, the major frac-

Table 3. Nitrogen budget for the southern basin of Lake Lugano. The total N input includes riverine N input (10 rivers), rainwater N, and N from the northern basin. In- and outputs are calculated from flow/precipitation rates and corresponding N concentrations determined by the LSA Lugano (LSA 1980–2003). N elimination is calculated from mass balance considerations ($N_{\text{elim}} = N_{\text{in}} - \Delta N - N_{\text{out}}$). It includes N burial and denitrification. Observed nitrogen fluxes (see Table 1) suggest that total burial rates do not vary by more than $\pm 40 \text{ kg } 10^3 \text{ N yr}^{-1}$. Hence, variations in total N elimination can be assumed to be mainly due to denitrification.

	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997
Total reservoir N (kg 10^3)	1,214	1,202	1,252	1,378	1,590	1,658	1,646	1,638	1,642	1,598	1,634	1,622	1,628
Δ reservoir N (kg 10^3 yr^{-1})	-12	50	126	212	68	12	-8	4	-44	36	-12	6	-122
Total N input (kg 10^3 yr^{-1})	970	1,289	1,393	1,470	1,570	1,242	1,385	1,662	1,518	1,638	1,313	1,274	1,320
Vedeggio River (kg 10^3 yr^{-1})	292	472	518	536	611	464	493	562	536	662	381	231	375
N output (kg 10^3 yr^{-1})	659	834	1,027	1,112	1,180	751	907	1,207	948	1,263	906	950	823
N elimination (kg 10^3 yr^{-1})	323	405	240	146	322	503	486	450	614	339	417	318	619

tion of nitrate is eliminated in partly isolated reservoirs, where nitrate is almost completely consumed (i.e., in the deep anoxic hypolimnion or in the sediment). Then, if the overall isotope effect associated with denitrification were negligible, the whole-lake $\delta^{15}\text{N}_{\text{NO}_3^-}$ value would not be affected by changes in denitrification, and external N loading would be the prime control on the N isotopic composition of the DIN and, thus, the PON pool. The trend towards less ^{15}N -enriched values before 1995 might be from the progressively increasing influence of a light nitrogen source. Although the N contribution from urban sewage or industrial activities has remained constant or has decreased, a general trend toward elevated external nitrogen inputs was observed between 1985 and 1994 (Table 3). Atmospheric deposition of ammonium and nitrate appears to be of significant importance in determining the N levels in rivers of the catchment of south alpine lakes (Mosello et al. 2001). Accordingly, the augmented N input into Lake Lugano can be related to the well-documented increasing trend of atmospheric nitrogen deposition in the catchment area and the concomitant oversaturation of soils (Mosello et al. 2001). $\delta^{15}\text{N}$ values for nitrate from rainwater, collected at a sampling station in Lugano, ranged between $\pm 0\text{‰}$ and -6‰ (Lehmann et al. 2004). In general, nitrogen from both atmospheric precipitation and soils are characterized by low $\delta^{15}\text{N}$ values (see compilation in Kendall 1998). Therefore, enhanced contribution from either source can readily explain the decrease in the $\delta^{15}\text{N}$ value for the bulk organic matter being synthesized in Lake Lugano.

In 1995, the weighted mean $\delta^{15}\text{N}$ value for PON increased dramatically and has remained high since. This increase can be related directly to the introduction of the fourth stage of wastewater treatment in the water treatment plants around the lake. This latest stage of treatment included microbial denitrification. Although this lake restoration measure led to an $\sim 50\%$ reduction ($\sim 300 \text{ kg } 10^3 \text{ yr}^{-1}$) of N loading via the Vedeggio River, the N input from the Vedeggio River remained the quantitatively most important N source to the lake (Table 3). In 1999, we measured $\delta^{15}\text{N}$ values as high as $+15\text{‰}$ for nitrate collected from the Vedeggio River (Lehmann et al. 2004). We conclude that the input of nitrate with characteristically high $\delta^{15}\text{N}$ values resulted in a profound change in the N isotopic composition of the surface-water DIN pool and, in turn, to the shift in the $\delta^{15}\text{N}$ value for algal organic matter (Fig. 5). The correspondence of the $\delta^{15}\text{N}$ val-

ues to the recent history of nutrient loading indicate that, in Lake Lugano, the catchment runoff and sewage inputs of nitrogen are more important controls on the $\delta^{15}\text{N}$ value of organic matter than N-cycling processes (N assimilation, denitrification) within the lake.

This long-term sediment trap study demonstrates the seasonal and interannual variability in particulate organic matter fluxes and the stable isotope composition of POC and PON in the southern basin of Lake Lugano. Over one seasonal cycle, times of peak organic matter fluxes coincide with periods of maximum primary productivity. Seasonal variations in the carbon and nitrogen isotope composition of trap material correspond to organic matter fluxes and primary productivity, with high $\delta^{13}\text{C}$ values and low $\delta^{15}\text{N}$ values associated with high primary production. Total annual organic matter fluxes do not directly reflect the interannual variation in primary production, indicating that epilimnion-internal recycling, loading of external organic matter, or both are important processes controlling the export of organic matter into the hypolimnion and, eventually, into the sediment. Annual flux-weighted $\delta^{13}\text{C}$ correlated with phosphate concentrations but did not correlate with annual primary productivity. A general trend toward a less ^{13}C -enriched organic matter pool is consistent with a several-fold reduction of the phosphate concentration in the basin as a consequence of lake restoration measures. Our data, therefore, provide evidence that the $\delta^{13}\text{C}$ value of organic matter is a reliable reflector of the recent trophic evolution of Lake Lugano toward less eutrophic conditions. The nonlinear relationship between primary productivity and the $\delta^{13}\text{C}$ of exported organic matter can be explained by changes in the thickness of the trophogenic zone. The expansion of the trophogenic zone led to the maintenance of comparatively high total primary productivity levels at lower P availability and reduced CO_2 draw-down per volume (resulting in low POC $\delta^{13}\text{C}$). A profound change in the pelagic biocenosis with an abrupt decline in the phytoplankton:zooplankton ratio and a shift in algal species composition appears not to have affected the bulk C- and N-isotope signal. Moreover, the well-documented temporal evolution of both surface-water nitrate utilization and elimination of N by denitrification did not correspond to the observed variation in flux-averaged $\delta^{15}\text{N}$ of sediment trap organic matter. Increasing external input of ^{15}N -depleted nitrogen to the lake, in response to enhanced N

precipitation and soil saturation in the catchment, most likely explains the decrease in organic matter $\delta^{15}\text{N}$ values observed between 1985 and 1994. A subsequent marked shift in the annual $\delta^{15}\text{N}_{\text{PON}}$ value by more than +3‰ could be related directly to the introduction of a denitrification stage in the main wastewater treatment plants. In order to confirm the strong effect of external sources on the N-isotope dynamics in Lake Lugano, future work will include the measurements of $\delta^{15}\text{N}$ values of source nitrate over several years.

Our findings confirm the use of $\delta^{13}\text{C}$ values and $\delta^{15}\text{N}$ values in autochthonous organic matter as indicators of past changes in environmental conditions. However, although a good proxy for P loading, the POC $\delta^{13}\text{C}$ of sinking organic matter (and, hence, of lacustrine sedimentary organic matter) might not be a reliable indicator of total primary production. The relationship between the trophic state of a lake and the N isotopic composition of organic matter is highly complex. On a multiyear timescale, the N isotopic composition of organic matter in Lake Lugano reflects the history of N pollution in the catchment and the effect of lake restoration measures rather than changes in the N-cycling dynamics within the lake. This implies that, particularly in eutrophic lakes, the effect of external N sources on the $\delta^{15}\text{N}$ of the nitrate pool can be so strong that $\delta^{15}\text{N}$ values of sinking organic matter are of limited use as a proxy indicator for nitrate utilization or denitrification. Moreover, care has to be taken when using both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of bulk organic matter to elucidate the dynamics of food web structures.

When sedimented, the total seasonal flux of organic matter corresponds to an individual varve in the sediment archive of Lake Lugano, which integrates the seasonal variations of the C and N isotopic composition of organic matter. Results from this study could be used to calibrate the factors controlling the isotopic composition of sedimentary organic matter in Lake Lugano or similar lacustrine environments. Yet, possible effects of early diagenesis on the isotope signal must be considered before interpreting the isotopic variations in the sediment record.

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