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The origin and recycling of sedimented biogenic debris in a subalphine eutrophic lake (Lake Bled, Slovenia)

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Abstract. The areal distribution of organic C contents, $\delta^{13}C$ values, total N and P and biogenic Si contents in surficial sediments were used to study the distribution, origin and diagenetic transformations of sedimented biogenic debris in the eutrophic subalpine Lake Bled (Slovenia), which for most of the year has an anoxic hypolimnion. The influence of an allochthonous input, restricted to the western basin, was clearly traced by higher organic C and total N and P contents, higher $\delta^{13}C$ values, and higher sedimentation rate in comparison to the eastern basin. The low $\delta^{13}C$ values of sedimentary organic matter in the major part of the lake, lower than the $\delta^{13}C$ values of different types of organic matter, suggest that this sedimentary organic matter is most probably the product of a microbial community and not a residue of primary production.

The temporal variation of benthic diffusive fluxes of NH_4, Si and PO_4, derived from modelling the pore water profiles, was related to sedimentation of phytoplanktonic blooms, while the PO_4 fluxes were also dependent on changing redox conditions at the sediment-water interface in the period of the winter-spring overturn. The removal of PO_4 in pore waters is probably due to the adsorption of phosphate and precipitation of apatite and vivianite. The budget of C, N and P at the sediment-water interface revealed a high recycling efficiency (>70%), also confirmed by the rather uniform (or only slightly decreasing) vertical profiles of organic C, total N and P in sediment cores and C/N and C/P ratios. The percentage of biogenic Si recycling is low (<10%), suggesting its removal in sediments.

Introduction

The characterization of the origin and fate of organic matter in lacustrine sediments is important from a variety of points of view. Lacustrine sediments provide a paleolimnological and paleoclimatic record of past conditions in the lake (Schelske 1988, 1991). However, the deposited organic matter is modified by early diagenetic reactions. During sedimentation and deposition the organic matter is microbially transformed, mostly resulting in protein and carbohydrate degradation. Only the less susceptible components remain unaltered and they can provide evidence for past biogeochemical conditions (Meyers 1984, 1990). Diagenetic reactions influence the recycling and fluxes of nutrients and other biogenic elements between sediment pore waters and the overlying water, and thus have an important role in the general biogeochemical cycling of these elements (Schindler et al. 1986). The diagenetic breakdown of sedimentary organic matter controls the redox conditions in sediments (Golterman et al. 1977) and subsequently influences the speciation and behaviour of these elements at the sediment-water interface. It is generally believed that the sequential order of electron acceptors involved in these reactions are $O_2 > NO_3^- > Mn(IV) > Fe(III) > SO_4^{2-} > CO_3^{2-}$ (Froelich et al. 1979). Fermentation reactions are also important in anoxic lake sediments (Kelly & Chynoweth 1981).

A knowledge of the fate of the biogenic elements C, N, P and Si after heir deposition on the bottom is necessary to construct their elemental budgets and to contribute to a better understanding of eutrophication processes in water basins. This is important in those alpine lakes influenced by natural as well as anthropogenically accelerated eutrophication processes and frequently containing an anoxic hypolimnion.

In this paper we present the results of investigations of the nature and fate of sedimentary biogenic debris in subalpine eutrophic Lake Bled (Slovenia) in terms of organic C, total N, total and organic P and Si contents and respective benthic diffusive fluxes. Special attention was paid to the elucidation of the source and diagenesis of recent and Holocene sedimentary organic matter in the lake by measurement of $\delta^{13}C$ values and biogenic elemental ratios. Pore water measurements and the calculation of benthic diffusive fluxes was the second aim of this study, and the construction of budgets for elemental recycling at the sediment-water interface the third.

Environmental setting

Lake Bled (Fig. 1) is situated in the NW part of Slovenia and occupies an area of 1.4 km^2. The maximal depths in the western and eastern basins are 30.2 and 24.5 m, respectively. The total volume of the lake is 26×10^6 m^3. Two small streams, i.e. the Mišca and Solznik, discharge into the lake, while the water outflow proceeds through the Jezernica into the river Sava. The lake is strongly eutrophic with algal blooms mostly of the species *Oscillatoria rubescens* (Vrhovšek et al. 1984). The water column in the lake is stratified most of the year, except during the early spring overturn. The bottom water temperature is nearly constant, ranging between 4 °C in winter and 8 °C in the late summer. The bottom layer below a depth of 15 m is anoxic (Fig. 2) during most of the year, containing high concentrations of N and P nutrients, sulphide (Molnar et al. 1978) and methane. Two amelioration projects were undertaken in the past: in 1965 a fresh water inflow was diverted from the river Radovna,

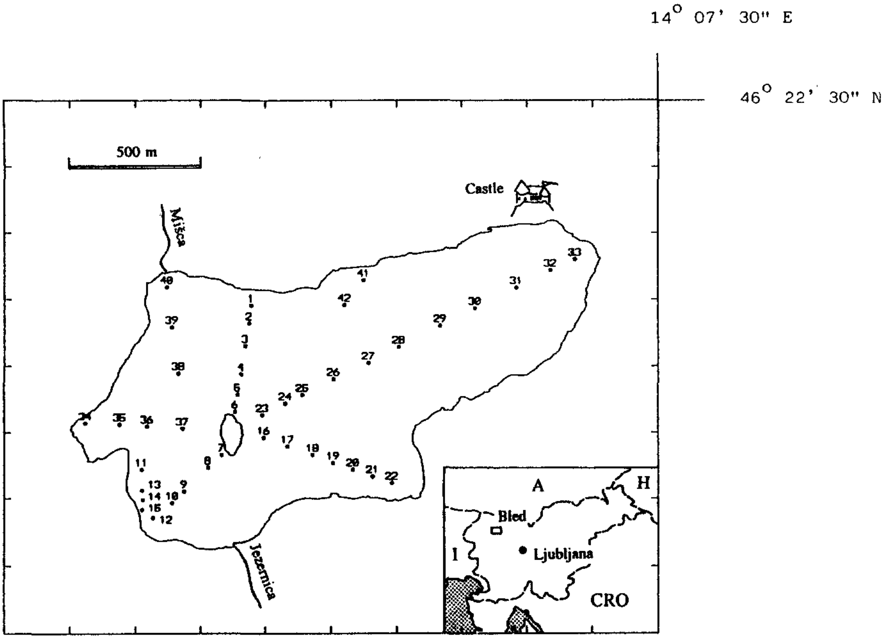


Fig. 1. Sampling locations in Lake Bled (Slovenia).

introducing about 4 × 10^6 m^3 monthly in the spring and summertime; and in 1979, siphonic pumping of anoxic water from the eastern basin. The renewal rate of the lake water is about 3.6 years (Vrhovšek et al. 1984).

This subalpine lake was formed in the Würm glacial period. The lake basement is composed of lacustrine and glacial clay while the surrounding area is mostly composed of Permian clastic rocks and Triassic limestones and dolomite (Molnar et al. 1978). The highest sediment carbonate contents (63–92%) are localized in the central deepest part and in the shallow littoral platform in the SW part (94–97%) of the lake, where calcite (so-called chalk) is precipitated (Dolenec et al. 1984). Most of the carbonate comprises low Mg-calcite (with up to 5 mol % of $MgCO_3$) and is of authigenic origin, but a minor percentage is also composed of detrital dolomite and calcite from the Mesozoic carbonate rocks of the surrounding area. The mean carbonate content is ca. 75%. Among detrital non-carbonate minerals, quartz (4–11%) and feldspars (5–16%) prevail over clay minerals (up to 13%) mostly composed of muscovite/Illite and chlorite. In the deepest anoxic part to the lake sediment, authigenic pyrite (<3%) is also found. Grain size analysis showed a rather uniform distribution: clayey silt, with a mean grain size of 10–20 μm, is composed of 25–40% clay (<2 μm) and up to 15% silt (2–63 μm). A

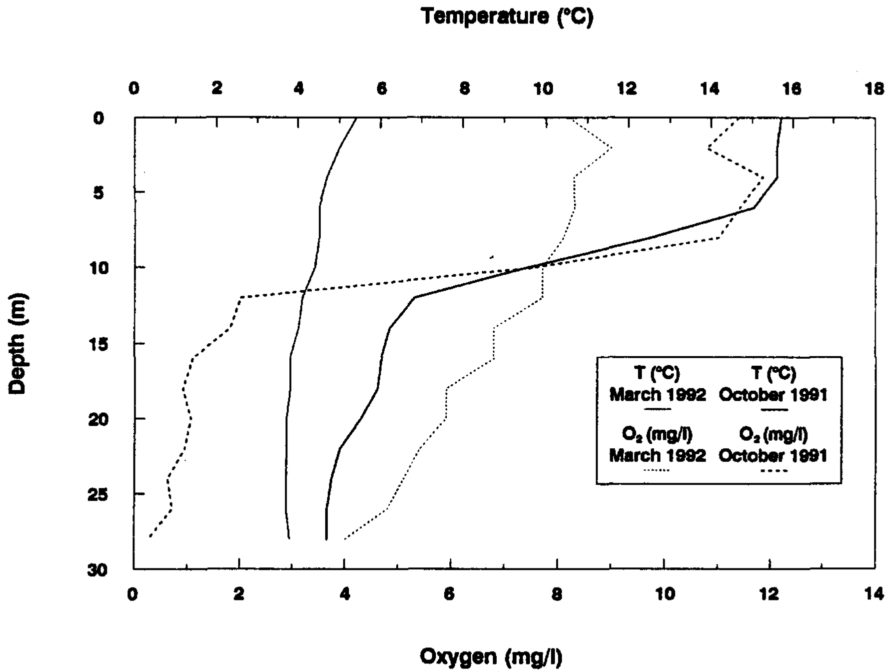


Fig. 2. Vertical profiles of temperature (T) and oxygen (O_2) concentrations in the lake water column in March and September 1992 (Šiško pers. comm.).

sedimentation rate of about 0.5 mm yr^{-1} was estimated in the eastern basin using palynological data (Shultze 1984).

Materials and methods

Sampling

Sediment solid phase samples were collected in September, 1988, 1989 and 1990. Sediment cores to a depth of 55 cm were taken at the 42 locations depicted in Fig. 1 using the gravity core sampler of Meischner & Rumohr (1974) equipped with a plastic liner (4 cm i.d.). Samples for pore water analyses were taken in October 1990, and every two months during 1991 at locations 27 and 37 (Fig. 1) in the eastern and western basins. All cores were sectioned at 2 or 5-cm intervals in a glove box filled with N_2 and the pore waters removed by centrifugation at 9500 g for 10 min. The resulting pore waters were successively filtered through 0.45 μm Millipore HA membrane filters in an inert atmosphere. Peat samples were collected in the surrounding area of the lake. Solid phase samples were freeze dried and homogenized with a mortar and pestle and sieved so that up to 90% of the material passed through a 100 μm mesh sieve.

The fishes *Rutilis rutilis* and *Perca fluviatilis* were caught from shore by hook and line in 1989, while periphyton and the submerged plants *Myriphyllum spicatum, Nymphea sp.* and *Nepher lutetum* were collected by hand along the shoreline in 1989 and 1990. Phytoplankton and zooplankton samples were collected by horizontal tows using nylon nets of 20 and 250 μm mesh size, respectively, in 1989 and 1990. Plants and animals were freeze-dried and ground to a fine powder.

Analyses

Pore water samples were analyzed for phosphate, silicate, and ammonia using the colorimetric procedures described by Grasshoff et al. (1983), pH by glass electrode (NBS buffer scale) and titration alkalinity by the method of Gieskes & Rogers (1973). Dissolved inorganic carbon (DIC) was calculated from pH and alkalinity.

Analysis of organic carbon in sediment samples was performed using the wet oxidation method of Gaudette et al. (1974). The total carbon and nitrogen contents were determined with a Carlo Erba (mod. EA 1108) elemental analyzer at a combustion temperature of 1020 °C. The total phosphorus contents in the samples were analyzed by extraction with 1M HCl after ignition at 550 °C (Aspila et al. 1976). Organic phosphorus was determined by the difference in phosphorus contents of HCl extracts before and after ignition of the samples at 550 °C. Biogenic Si was determined by leaching the samples with 1% Na_2CO_3 for 1 hour at 85 °C (DeMaster 1981).

Samples for determination of the stable isotope composition of organic carbon were first acid treated with 3M HCl and then ignited to CO_2 in a recirculating stream of O_2. The stable isotopic composition of carbon was determined using a Varian MAT 250 mass spectrometer and the results reported as deviations in ‰ from the $^{13}C/^{12}C$ ratio of the Chicago PDB standard ($\delta^{13}C$).

Sedimentary accumulation rates were determined by means of ^{137}Cs and ^{210}Pb analyses (Johnson & Evans 1982). The nuclides were measured by γ-ray spectrometry using an HP Ge well-type detector and a Canberra 90 multichannel analysis system.

Porosity ($\emptyset$) was determined by measuring the weight loss of sediments dried overnight at 110 °C and calculating

$$\emptyset = (M_w/1.0)/(M_s/2.5) + (M_w/1.0),$$

where M_w is the weight of water lost on drying, M_s is the weight of dry sediment, and 1.0 and 2.5 are the densities of water and sediment.

Statistical evaluation of data were performed using the Statgraphics (Stsc. Inc., USA) statistical program.

Results and discussion

Sources of sedimentary organic matter

The results for the $\delta^{13}C$ values of different types of organic matter in Lake Bled and its surroundings are presented in Fig. 3. The mean $\delta^{13}C$ values of phytoplankton was −27.7‰ and that of net zooplankton −30.1‰. These low values are common in stratified lakes (Oana & Deevey 1960; Rau 1978, 1980; Fry 1986) due to the CO_2 produced by respiration in the bottom layer and characterized by low $\delta^{13}C$ values (a mean benthic respired values of −30‰; Oana & Deevey 1960). This lowers the $\delta^{13}C$ isotopic composition of the lake DIC (Lee et al. 1987) relative to the air equilibrated value of about 0‰. Measurements of DIC (Dolenec et al. 1984) at the sediment-water interface revealed $\delta^{13}C$ values in the range between −7.6 to −13.4‰. The highest values were detached during the early spring overturn in the presence of a homogeneous water column. Also, a gradual decrease of $\delta^{13}C$ – DIC from the surface to the bottom, from −5.7 to −13.4‰, was normally seen. The rather low lake water $\delta^{13}C$ values are also affected by the inputs of DIC probably derived from the oxidation of organic matter in the inflowing streams, i.e. Mišca and Solznik. These DIC values range between −8.6 and −10.5‰ (Dolenec et al. 1984).

The $\delta^{13}C$ values of periphyton on the other hand were, rather high, averaging −11.4‰. Analyses of $\delta^{13}C$ values of submerged plants revealed high values (−11.8 to 15.8‰) for *Myriophyllum spicatum* but lower for *Nymphea sp.* and *Nuphar lutetum* (−24.6 to −29.1‰). The $\delta^{13}C$ values of some fishes from the lake, *Rutilis rutilis* and *Perca fluviatilis*, ranged between −29.7 and −32.4‰. Their $\delta^{13}C$ values fell close to the most negative end-members (i.e. zooplankton and phytoplankton) and the fishes must receive a large fraction of their C through food chain beginning with phytoplankton (Carlos et al. 1986).

The $\delta^{13}C$ composition of terrestrial detritus from the surroundings was not directly measured. However, the $\delta^{13}C$ composition of the peat in the area surrounding the lake revealed values of about −25‰ and these could be considered as representative of terrigenous organic detritus in that area.

Our $\delta^{13}C$ analyses of organic C in surficial sediments in Lake Bled revealed low values (between −32 to −37 ‰) in the eastern basin and somewhat higher (−28.5 to −32‰) in the western basin affected by the allochthonous input. Nearly all sedimentary organic carbon was $\delta^{13}C$ more negative than the plant

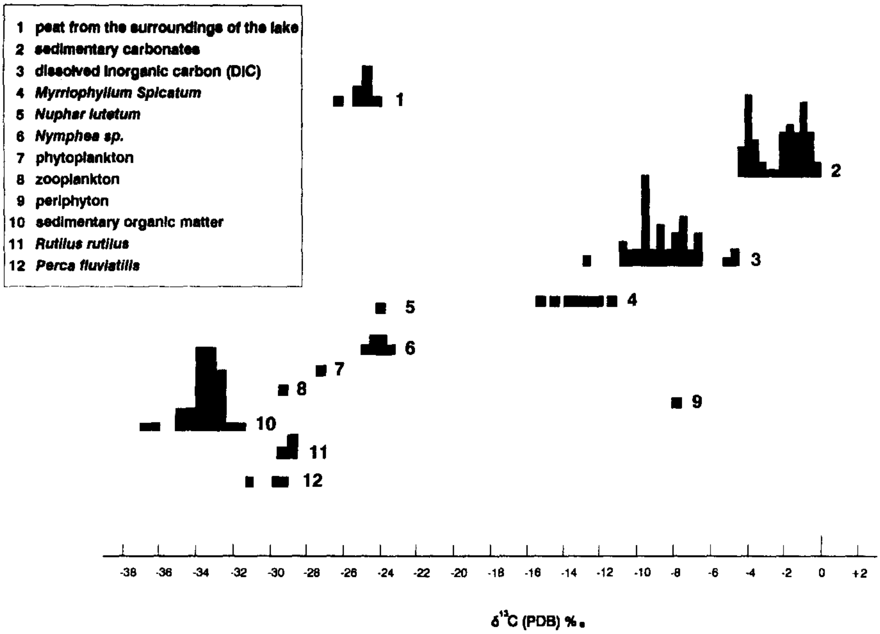


Fig. 3. $\delta^{13}C$ values of peat from surrounding area (1), and sedimentary carbonates (2), dissolved inorganic carbon (DIC, 3) and various types of organic matter – *Myrriophyllum spicatum* (4), *Nuphar lutetum* (5), *Nymphea sp.* (6), phytoplankton (7), net-zooplankton (8), periphyton (9), sedimentary organic matter (10), *Rutilus rutilus* (11), and *Perca fluviatilis* (12) in Lake Bled.

source material. This would imply that surficial sedimentary organic C could reflect the synthesis of organic matter in the hypolimnion and sediments produced by methanotrophic bacteria (Freeman et al. 1990; Hayes 1993). Aerobic methane oxidation is relatively well known (Coleman et al. 1981) but there is also strong evidence for the existence of anaerobic methane oxidation in nature (Reeburgh 1976; Oremland & DesMarais 1983). Recently, a significant $\delta^{13}C$ depletion was observed in specific biomarker lipids of possible methanotrophic origin (Hayes et al. 1987) and cultured aerobic methanotrophs (Summons et al. 1994). It is also well known that the $\delta^{13}C$ values of methane produced by hydrolitic cleavage of acetate, forming CH_4 and CO_2, range between −30 to −40‰ while those from CO_2 range between −60 to −77‰ (Alperin et al. 1988; Landsdown et al. 1992; Blair & Carter 1992). Other possible sources for the $\delta^{13}C$ depleted sedimentary organic matter could be the microaerophylic chemoautotrophs using a low $\delta^{13}C$-DIC, such as NH_4-oxidizing bacteria grown at the oxycline in the water column, and especially heterotrophic bacteria reworking the primary biological material in the anoxic hypolimnion and sediments producing methane (Freeman et al. 1990).

Using a mixing equation in the form:

$$\delta^{13}C = F_m\, \delta^{13}C_m + F_a\, \delta^{13}C_a \text{ and } F_m + F_a = 1$$

it is possible to establish the percentage of autochthonous (product of a microbial community – F_m) and allochthonous (terrestrial – F_a) organic matter in the surficial sedimentary organic matter of the lake. For $\delta^{13}C_m$ we used the lowest $\delta^{13}C$ observed in the lake sediments (−36.6‰). For $\delta^{13}C_a$ we applied the mean $\delta^{13}C$ value of peat (−25‰; Fig. 6) in the lake surroundings (Fig. 1), a value typical of C_3 terrestrial organic matter (Fry & Sherr 1984). The autochthonous fraction of sedimentary organic matter generally showed high percentages (60–100%), except in the northwestern part (29–43%) under the influence of the Mišca and Solznik streams. The rather high calculated F_m of sedimentary organic matter, if correct (and there is some doubt due to the somewhat arbitrarily chosen end-members), is supported by previous analyses of dissolved gases from the lake bottom waters. It was demonstrated that CH_4 is one of the most abundant dissolved gasses (Leskovšek pers. comm.).

Organic carbon, total nitrogen, phosphorus and biogenic silica

The results for organic carbon, its $\delta^{13}C$ values, total nitrogen and phosphorus contents and biogenic Si are presented in condensed form in Table 1. Using the chi square test the normal distribution of organic carbon, its $\delta^{13}C$ values, total nitrogen and phosphorus at the significance level $p = 95\%$ was demonstrated. For organic phosphorus, though not normally distributed according to this test, the Kolmogorov-Smirnov test implied a normal distribution of data (approximate significance level = 0.37882). R factor analysis of all five variables showed that the first three factors comprised 84.4% of the variance. The first factor (comprising 42.2% of the variance) relates to $C_{org.}$, $\delta^{13}C$, $P_{tot.}$ and $N_{tot.}$, the second factor (comprising 23% of the variance) by $C_{org.}$ and $P_{org.}$, and the third by only $C_{tot.}$. The factor rotation (Varimax) did not have an important influence on the factor values despite their being shifted: the second factor was influenced by $C_{tot.}$ and $N_{tot.}$ and the third by $C_{org.}$ and $P_{org.}$. We concluded, therefore, that the first factor was influenced by variables indicating allochthonous (organic and inorganic) input, the third factor represented the production and sedimentation of autochthonous organic matter and hence the eutrophication processes, while the second was principally influenced by the $C_{org.}/P_{org.}$, $C_{org.}/N_{tot.}$ ratios and thus by the processes occurring during the early diagenesis of sedimentary organic matter. A significant correlation ($r = 0.76$; $n = 24$) between $P_{tot.}$ and $\delta^{13}C$, suggested linkage between the parameters influenced by the allochthonous input.

Table 1. Summary of organic carbon, its $\delta^{13}C$ values, total nitrogen, total and organic phosphorus and biogenic Si data in surficial sediment (0–5 cm) in Lake Bled.

	Range	$\overline{X} \pm SD$	*n*
Org. C (%)	0.52 - 5.93	3.08 ± 1.20	30
$\delta^{13}C$ (‰)	−28.32 - −36.62	−33.33 ± 2.38	26
Tot. N (%)	0.22 - 0.99	0.83 ± 0.11	28
Tot. P (ppm)	166 - 984	508 ± 178	27
Org. P (ppm)	44 - 583	230 ± 100	27
Biogenic Si (%)	13.9 - 34.8	23.7 ± 7.9	19

Principal component analysis of organic carbon and the relative proportion of clay and sand (first component) and the sand/clay ratio (second component) of surficial sediment in the Lake Bled showed that these two components account for nearly 100% of the data variance. Therefore, the differences between the samples were correlated to the ratio between clay and sand fractions, and the silt fraction. The latter represented more than 50% of the bulk sediment. Regression analysis showed a significant inverse relationship ($r = 0.64$; $n = 20$) between $C_{org.}$ contents and grain size in the silt fraction.

The areal distribution of $C_{org.}$ showed an irregular pattern. The $C_{org.}$ content in the southern and northern parts of the lake was <3%, in the eastern basin between 3–4.2%, in the western basin between 2.5–3.8% and was the highest (up to 6%) along the northwestern shore. The $\delta^{13}C$ values were higher in the western basin. The areal distribution of biogenic Si exhibited the highest content in the eastern basin of clearly phytoplanktonic origin, and the lowest in the southwestern part influenced by the water outflow. The rather low $C_{org.}/N_{tot.}$ ratios in surficial sediments, except those influenced by the allochthonous input (Fig. 5), suggest the important presence of organic matter produced by microbial community (Coffin et al. 1989). Regression analysis of $\delta^{13}C$ and $C_{org.}$ (Fig. 4) as well as of $\delta^{13}C$ and $P_{tot.}$, for western sampling points alone showed a significant correlations, indicating the influence of the allochthonous input from the Mišca stream. The differences between the two basins are also clearly seen from the plots between $\delta^{13}C$ and $C_{org.}/N_{tot.}$ and $C_{org.}/P_{org.}$ ratios, showing linear relationships for the western, but scattered data for the eastern basin (Fig. 5).

Sedimentary record of organic matter deposition in Lake Bled

Vertical profiles of $C_{org.}$ and $N_{tot.}$ show approximately constant values (Fig. 6), indicating constant *in situ* degradation of bulk organic matter in the past 100–

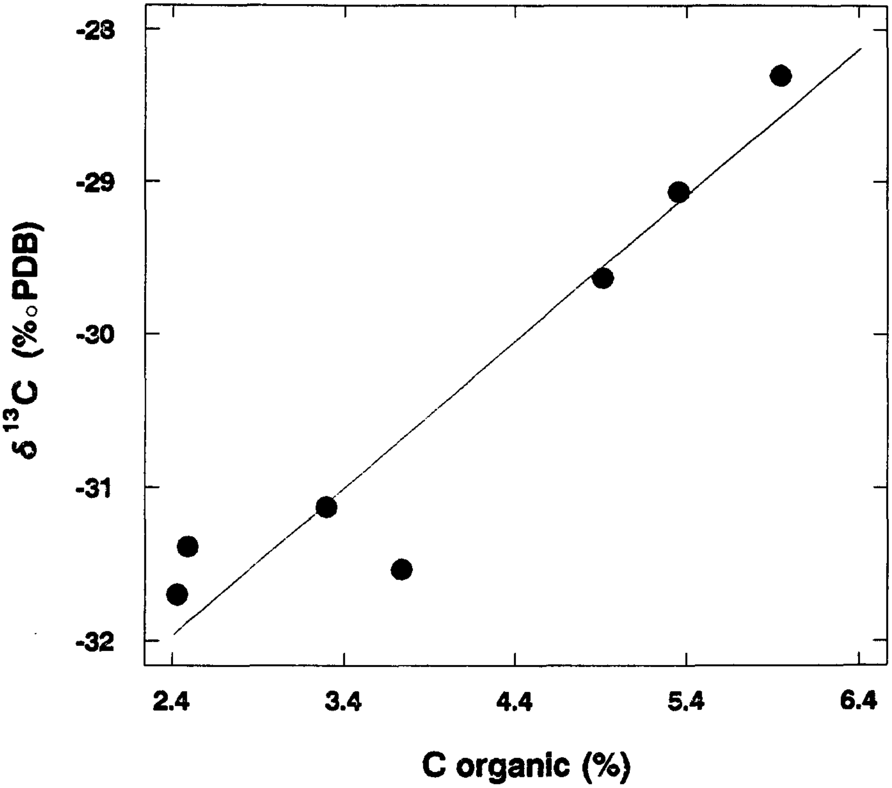


Fig. 4. Relationship between organic C content and its $\delta^{13}C$ values in surficial (0–5 cm) sediments of the western basin.

200 years. The recent accumulation rates of 1.2 mm yr^{-1} in the eastern and 2.4 mm yr^{-1} in the western basin were determined using ^{210}Pb and ^{137}Cs activity measurements (Fig. 7) since the chronologies based on either nuclide appeared similar. The higher accumulation rate observed in the western depression is due to the inflow of the Mišca stream (Fig. 1). The vertical profile of $P_{tot.}$ (Fig. 6), on the other hand, exhibits a slight depth decrease, due to the increased eutrophication processes in the last approximately 50 years.

Pore water modelling and fluxes at the sediment-water interface

Depth profiles show a general increase of pore water concentrations of DIC, NH_4, PO_4 and Si with steep near-surface gradients (Fig. 8). A general equation (Berner 1980) used for the mass balance of a dissolved nutrient in pore water is:

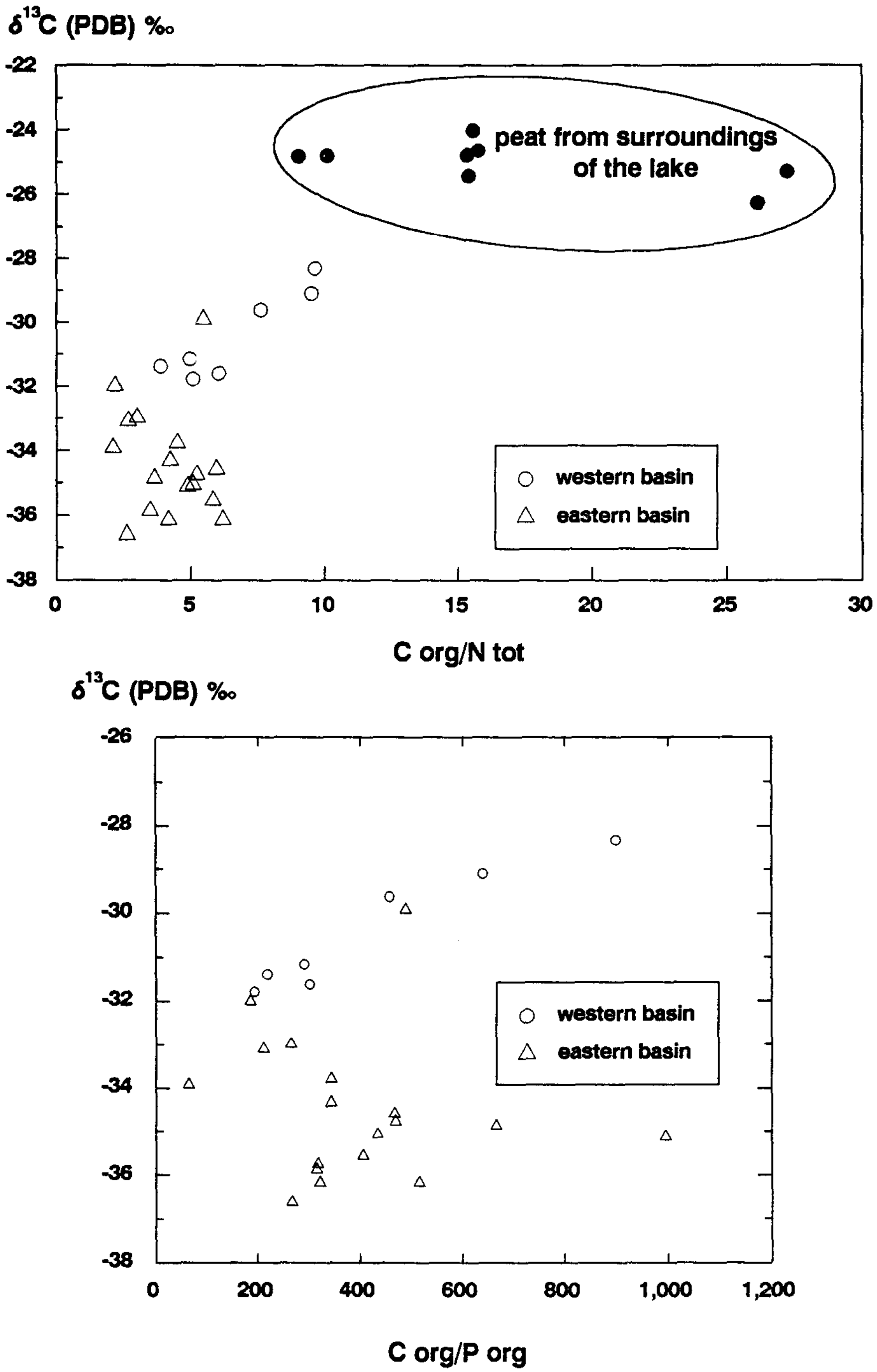
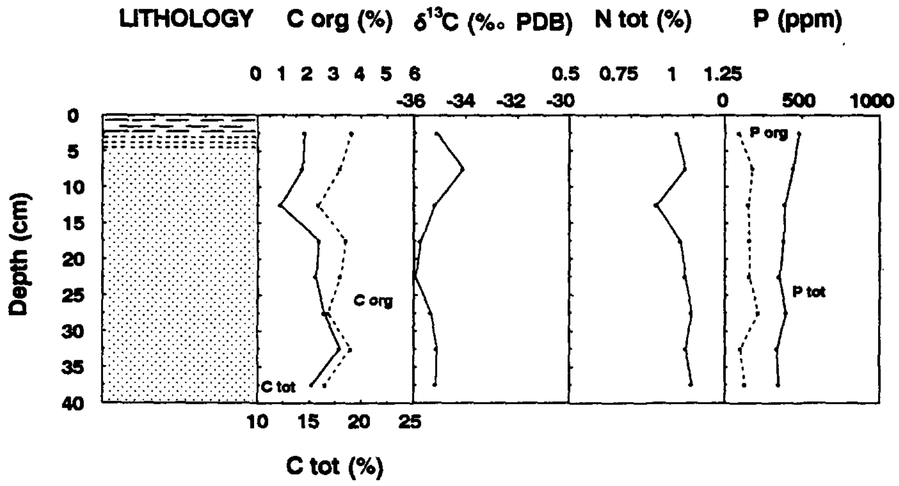


Fig. 5. Relationship between δ^{13}C values and $C_{org.}/N_{tot.}$ (atomic) ratios, and δ^{13}C values and $C_{org.}/P_{org.}$ (atomic) ratios in surficial sediments.

EASTERN BASIN



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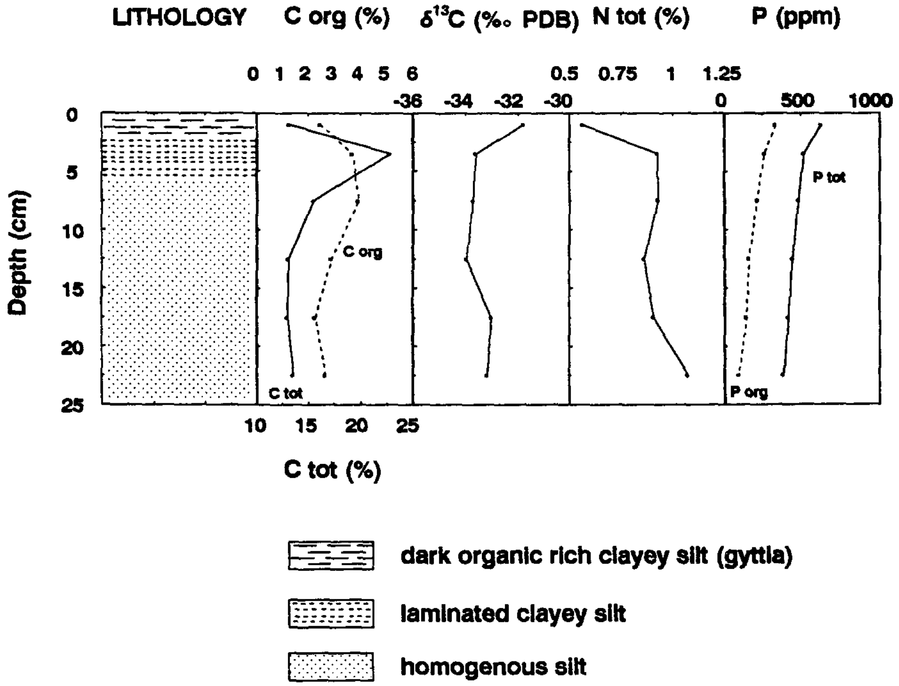

Fig. 6. Vertical distribution of organic C and its $\delta^{13}C$ values, total N and P, and organic P contents at sampling locations 27 (eastern basin) and 37 (western basin).

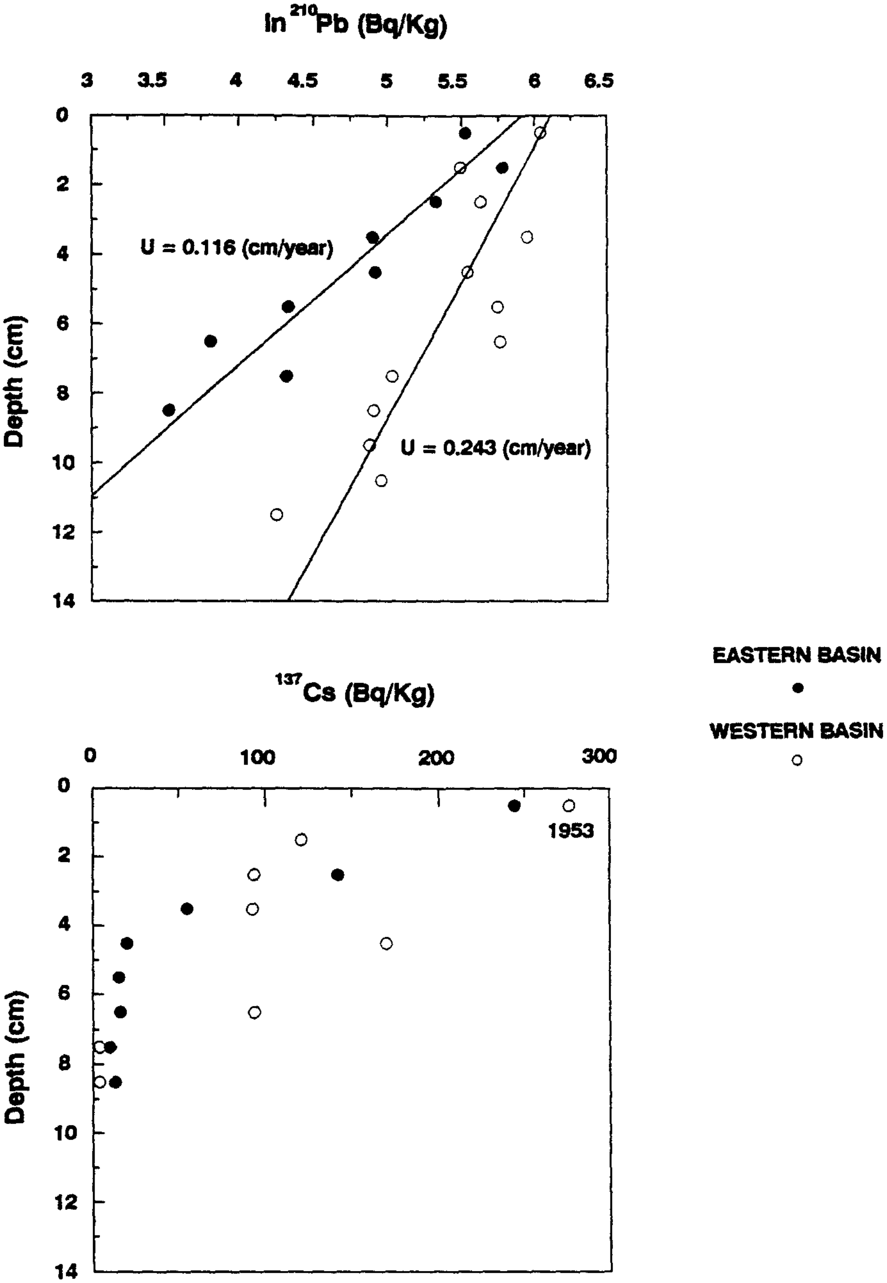

Fig. 7. Vertical distribution of ^{137}Cs, and ^{210}Pb activity with linear regression for determining the accumulation rate in surficial sediment at sampling locations 27 and 37.

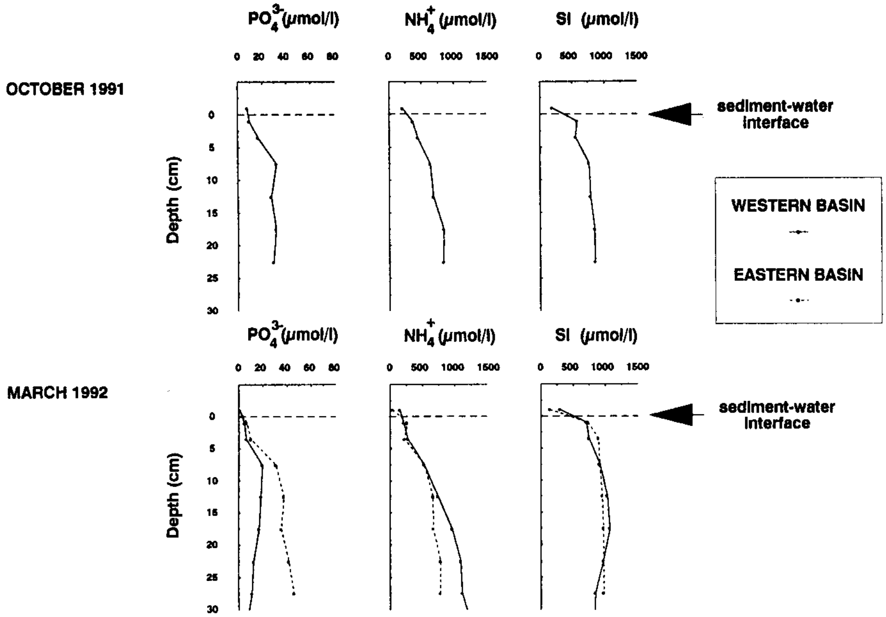

Fig. 8. Concentration profiles of pore water PO_4, NH_4 and Si concentrations at sampling locations 27 (eastern basin) and 37 (western basin) in October 1991 and March 1992.

$$\emptyset \frac{\partial C}{\partial t} = \frac{\partial}{\partial z}\left(\emptyset D_s \frac{\partial C}{\partial z}\right) + R = 0 \qquad (1)$$

where C = concentration in pore water, $\emptyset$ = porosity, t = time, z = depth in sediment, D_s = molecular diffusion coefficient corrected for tortuosity, and R = reaction rate per unit volume of bulk sediment.

For NH_4, the solution of equation (1) is

$$C = C_{(z=0)} + K(1 - \exp(-K_g/U)z)$$

(Van Cappellen & Berner 1988), where U = sedimentation rate (cm/yr), K = concentration of NH_4 at the maximal depth in the core $C_{max.}$ (mole/l), $K = (JGU^2)/(DK_g + (1 + K_{ads})U^2)$, K_g = first order rate constant for organic N release (yr^{-1}), K_{ads} = coefficient of NH_4 adsorption (Rosenfeld 1979), J = ratio of dry bulk density to porosity (g cm^{-3}), D = whole sediment molecular diffusion coefficient of NH_4 (cm^2 yr^{-1}), R = NH_4 production rate from metabolizable organic N (mole cm^{-3} yr^{-1}), $\emptyset$ = porosity 0.9. Because the reaction rate constant of first order removal by precipitation (k) is much less than $U^2/4D^2$ (yr^{-1}), the flux at the sediment water-interface ($F_{z=0}$) is

$$F_{(z=0)} = (-\emptyset DR/DK_g + U(1 + K_{ads})) + \emptyset U(K_{ads} + 1)C_{(z=0)}.$$

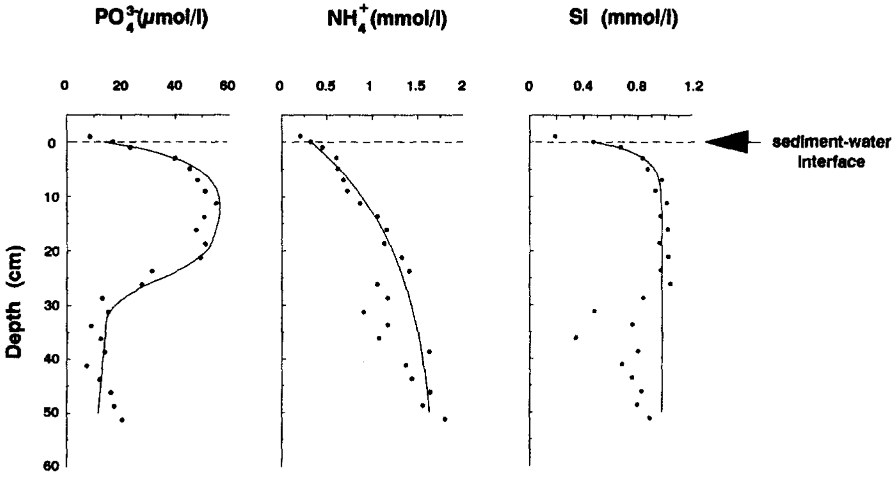

Fig. 9. Concentration profiles of pore water PO_4, NH_4 and Si concentrations at sampling location 37 (western basin) in March 1992 with best fit curves for determining concentration gradients at sediment-water interface (see the text).

The coefficients $C_{(z=0)}$, K and b are determined by fitting the measurements of NH_4 in the upper 50 cm of sediment (Fig. 9) using a nonlinear regression method.

The solution of equation (1) for Si is defined by

$$C = C_{max.} - (C_{max.} - C_{(z=0)}) \exp(-bz)$$

(Lerman 1979), where $b = \sqrt{(K/D)}$ (cm^{-1}), k = reaction rate constant of Si dissolution (yr^{-1}), D = whole sediment molecular diffusion coefficient of Si (cm^2 yr^{-1}), $\emptyset$ = porosity 0.9. Because the sedimentation rate is much lower than $\sqrt{K/D}$, the supply of Si by sedimentation can be neglected and the inequality $U \ll 4kD$ is maintained. The coefficient $C_{(z=0)}$ and b are obtained by fitting the concentrations of Si in pore waters in the upper 50 cm of sediment (Fig. 9).

The diffusive flux ($F_{(z=0)}$) is obtained from the equation

$$F_{(z=0)} = \emptyset \sqrt{4kD}\,((C_{(z=0)} - C_{max.})/1000.$$

For phosphate, the solution of equation (1) is

$$\begin{aligned} C = {} & (C_{(z=0)} - C_{eq.} + R_0 \exp(-bz)/(Db^2 + U(1 + K_{ads})b - k)) \\ & \exp(\sqrt{U(1 + K_{ads}) - ((U(1 + K_{ads})^2 + 4DK)}\,/2D)z) + \\ & C_{eq.} - (R \exp(-bz)/(Db^2 + U(1 + K_{ads})b - k))), \end{aligned}$$

where, $C_{eq.}$ = saturation concentration of total dissolved phosphate, given by (305.831–74.654 pH + 4.583 ph^2) (1 − (T − 10)x) (Atlas & Pytkowicz

1977), $x = 0.020 - 0.033$, $\emptyset$ = porosity 0.9, D = whole sediment molecular diffusion coefficient of PO_4 ($cm^2\ yr^{-1}$, U = sedimentation rate ($cm\ yr^{-1}$), K_{ads} = adsorption coefficient (Krom & Berner 1980), R = production rate of phosphate from metabolizable organic P per unit volume of bulk sediment mole $cm^{-3}\ yr^{-1}$), b = rate of degradation of organic P in sediment (yr^{-1}), k = reaction rate constant of the first order removal processes – precipitation (yr^{-1}). The diffusive flux ($F_{(z=0)}$) of phosphate at the sediment-water interface is defined by

$$F_{(z=0)} = -\emptyset D(dC/dz)_{(z=0)} + \emptyset U(1 + K_{ads})\, C_{(z=0)}$$

The pore water concentrations of PO_4 (Fig. 9) are lowered at depths below approximately 25 cm probably due to the removal processes: adsorption of phosphate and precipitation of apatite (Čermelj et al. in prep.) and vivianite (Emerson 1976). The temporal variations of Si, NH_4 and PO_4 benthic diffusive fluxes are presented in Fig. 10. The seasonal variations of fluxes were rather small. However, higher NH_4 and Si diffusive fluxes observed in winter are mostly likely a consequence of the winter thermal convection. The introduction of nutrient depleted surface waters into the bottom layer leads to the formation of steep nutrient gradients across the sediment water interface and consequently to higher diffusive fluxes. High summer NH_4 and Si diffusive fluxes are due to the degradation of the deposited spring phytoplanktonic bloom after the winter-spring water column mixing, and the summer bloom of blue-green algae *Oscillatoria rubescens* in deeper lake water layers (Vrhovšek et al. 1984). Variations of PO_4 diffusive fluxes probably reflect the redox conditions at the sediment-water interface since the lowest fluxes are observed at the winter-spring overturn when the oxygenated water penetrates down to the sediment-water interface. The mean ($n = 7$) calculated diffusive fluxes in both basins at the sediment-water interface were 0.81 ± 0.30 mmol $m^{-2}\ d^{-1}$ for Si, 2.82 ± 1.22 mmol $m^{-2}\ d^{-1}$ for NH_4 and 0.092 ± 0.027 mmol $m^{-2}\ d^{-1}$ for PO_4.

Alkalinity and DIC fluxes at the sediment water interface in the western basin were determined from pore water alkalinity (Fig. 11) and DIC profiles from March 1993 using a simplified version of the diagenetic equation (1) in the form:

$$\Delta C = \alpha \left(\frac{D_i k_i/U^2 + (1 + K_i}{D_c k_c/U^2 + (1 + K_c)} \right) \Delta i \qquad (2)$$

(Berner 1977; Kuivila & Murray 1984), where ΔC = change in concentration of alkalinity or DIC in a depth interval, α = stoichiometric coefficient between the production of species i and alkalinity or DIC, D_i, D_c = *in situ* diffusion coefficients corrected for porosity (0.9) and temperature (4.5 °C) (Lerman

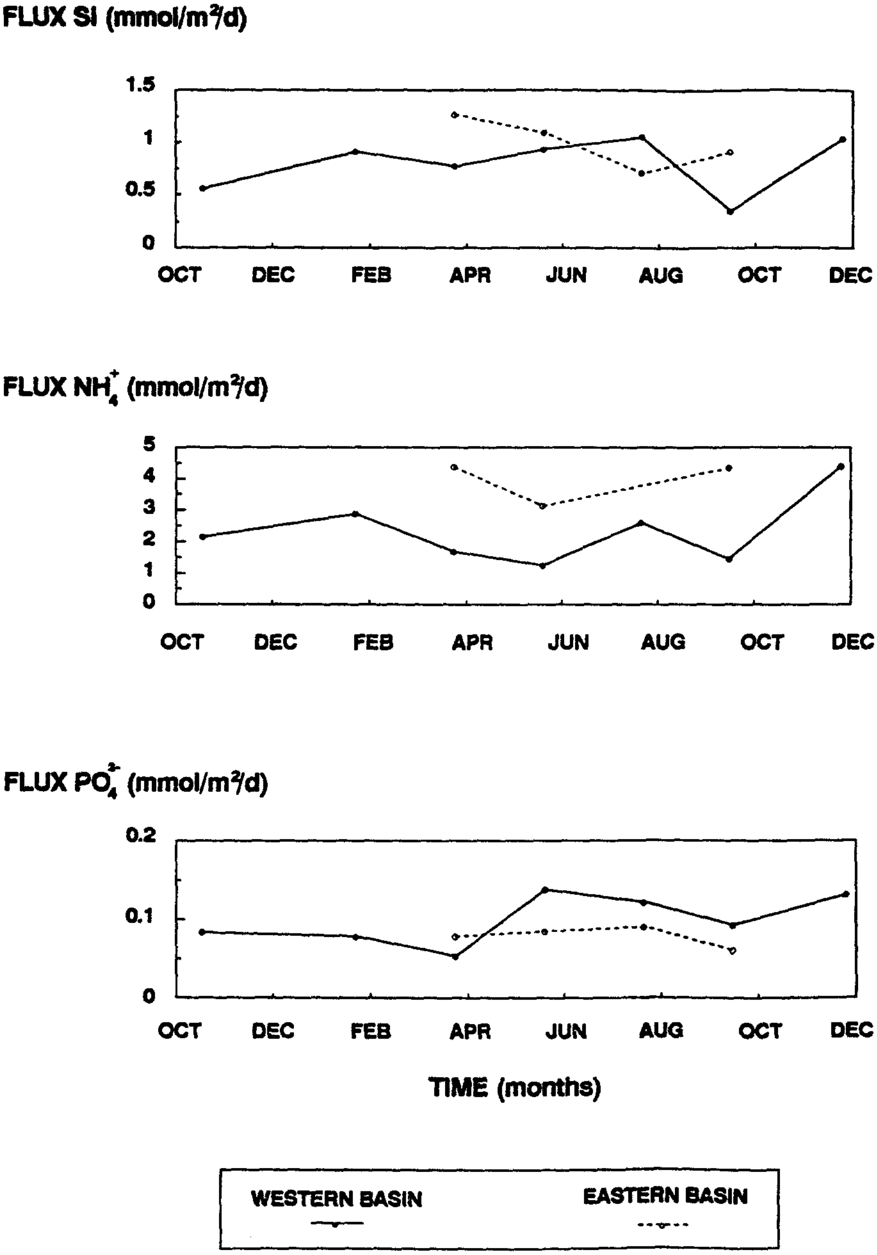

Fig. 10. Temporal variation of NH_4, Si and PO_4 diffusive fluxes at the sediment-water interface at sampling colations 37 (western basin, solid line) and 27 (eastern basin, dashed line) in the period from October 1991 to December 1992.

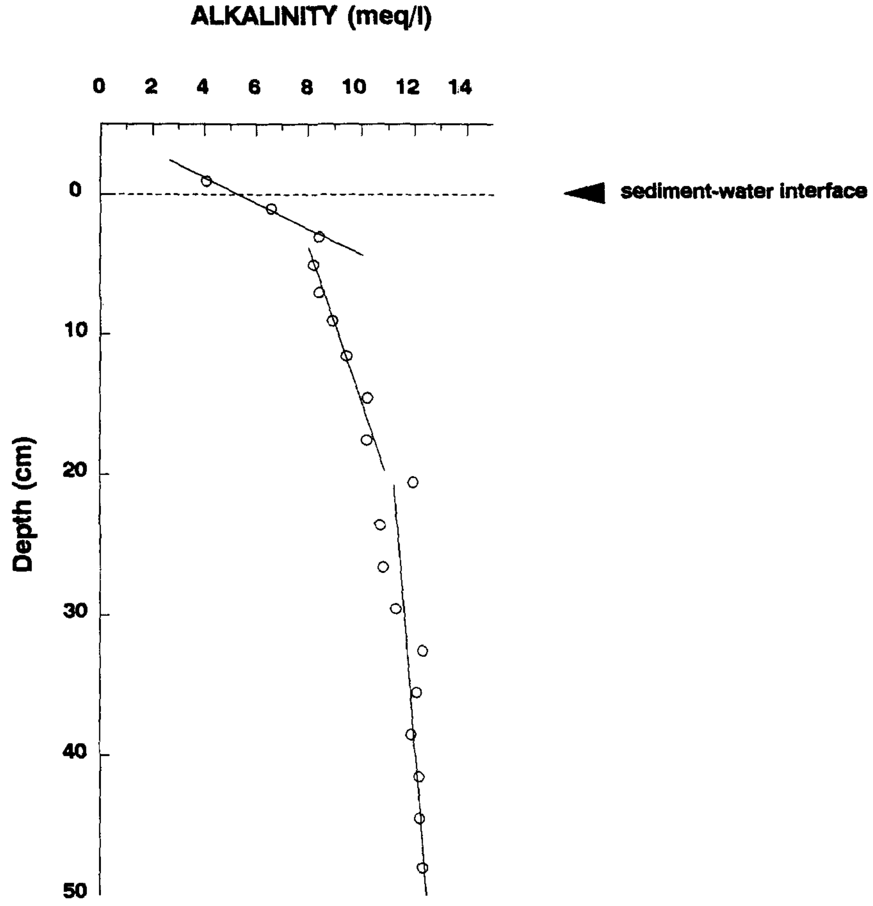

Fig. 11. Concentration profile of pore water alkalinity at sampling location 37 (western basin) in March 1992 with linear regressions for determining concentration gradient at the sediment-water interface (see the text).

1979, k_i, k_c = first order rate constants for organic matter decomposition, U = sedimentation rate, K_i and K_c = adsorption coefficients, Δi = change in concentration of species i contributing to change of alkalinity or DIC in the same depth interval. Advection and adsorption of DIC are insignificant and thus ignored.

The high correlation found between alkalinity and NH_4 pore water concentrations ($r^2 = 0.94$) indicated the major influence of NH_4 production on alkalinity, according to the equation $NH_3 + H_2O + CO_2 \rightarrow NH_4^+ + HCO_3^-$. This suggests that reduction of sulphate, Fe and Mn, and carbonate dissolution probably have only a minor influence. Linear regression analysis between

DIC and NH4 pore water concentrations ($r^2 = 0.93$) gives the following equation:

$$\frac{\Delta}{\Delta z} = 4.39C_{NH_4} + 4.54. \tag{3}$$

Considering the ratio between D_{NH_4}/D_{DIC} of 1.143 and equations (2) and (3), we obtain the following equation for estimation of the DIC diffusive flux at the sediment-water interface in the western basin:

$$F_{(z=0)} = 4.568 \frac{\Delta NH_4^+}{\Delta z} = 4.56 \text{ mmol m}^{-2} \text{ d}^{-1}.$$

Budgets for C, N, P and Si

Budgets for C, N, P and Si in the sediments of Lake Bled show the efficiency of reactions in recycling deposited biogenic material. The burial flux can be estimated from measurements of the content of these biogenic elements in surficial sediments and from the average accumulation rates calculated from sedimentation rates (Fig. 7), dry sediment density (2.5 g cm^{-3}) and surficial porosity (0.9). The resulting budget (Table 2) shows that a rather high percentage of organic C (>70%) is recycled in surficial lake sediments in the western basin when considering CO_2 and CH_4 (unfortunately not measured) as decomposition products and a mean methanogenic CO_2:CH_4 ratio of 1 (Kelly et al. 1982). The flux of dissolved organic carbon may be important (Kuivila & Murray 1984) but was not measured in this study. This efficient and constant recycling is supported by the rather uniform vertical profiles of organic C contents in sediment cores (Fig. 6) and assuming a constant supply rate. The recycled percentages of N and P in both basins are also high, amounting to >80% and >75%, respectively, and thus explaining the rather uniform depth distribution of total N and P in sediment cores. The Fe minerals are probably dissolved (Boström et al. 1982, 1988) in the anoxic lake sediments and hypolimnion and thus contribute to release of PO_4 to the overlying water. Low N accumulation may suggest low rates of nitrogen fixation (Horne & Galat 1985), also supported by a high N/P ratios (Howarth et al. 1988) in lake water (N/P > 20, atomic; Vrhovšek et al. 1984).

The recycling percentage of Si is low, amounting to <10%, suggesting a sink of Si in new phases and adsorption by clays (Johnson & Eisenreich 1979; Schelske 1985).

Conclusions

1) A distribution study of organic carbon content, $\delta^{13}C$ of organic carbon and total nitrogen and phosphorus content in surficial sediments of the

Table 2. Summary of burial and benthic fluxes of C, N, P and biogenic Si in both basins of Lake Bled (mole m^{-2} yr^{-1}).

		C	N	P	Si
Western basin	Benthic fluxes	3.32	0.89	0.036	0.30
	Burial	1.25	0.24	0.012	5.18
Eastern basin	Benthic fluxes		1.44	0.028	0.36
	Burial	0.85	0.15	0.005	3.85

eutrophic Lake Bled showed higher values in the northwestern part of the lake due to the inflow of the Mišca stream, and the lowest in the southwestern part near the lake outflow. The impact of this allochthonous (terrestrial) input is also confirmed by the good correlation of organic carbon and total phosphorus with $\delta^{13}C$ values in the western basin, and by the higher ^{210}Pb and ^{137}Cs sedimentation rates in the western vs the eastern basin.

2) The low $\delta^{13}C$ values of sedimentary organic carbon in the major part of the lake, lower than the $\delta^{13}C$ values of different types of organic matter, suggest that this sedimentary organic carbon is most probably the product of a microbial community and not a residue of primary production.

3) Benthic diffusive fluxes of NH_4, Si and PO_4 at the sediment-water interface, derived from modelling the pore water profiles, showed rather weak temporal variations related to spring and summer phytoplanktonic blooms. The lowest PO_4 diffusive fluxes were observed during the winter-spring overturn when oxygenated water penetrates into the hypolimnion, changing the redox conditions at the sediment-water interface. The removal of PO_4 in pore waters is probably due to the adsorption of PO_4 and precipitation of apatite, as suggested by modelling and mineralogical analyses, and vivianite.

4) The budget of C, N and P at the sediment-water interface in both basins showed that recycling efficiency of biogenic material, assuming a constant supply rate, was high (>70%). This efficient recycling is consistent with the rather uniform vertical profiles of organic C, total N and P content in sediment cores in the last 200 in the eastern and 100 years in the western basin. Also, rather uniform organic C, total N and P contents and $\delta^{13}C_{org.}$ values suggest that the biogeochemical conditions in the lake

were approximately constant for the last 100–200 years. The recycling of Si is low (<10%), suggesting its removal in sediments.

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