

Isotopic fingerprints on lacustrine organic matter from Laguna Potrok Aike (southern Patagonia, Argentina) reflect environmental changes during the last 16,000 years

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Abstract A combination of carbon-to-nitrogen ratios (TOC/TN), Rock Eval-analyses, and stable isotope values of bulk nitrogen ($\delta^{15}\text{N}$) and organic

carbon ($\delta^{13}\text{C}_{\text{org}}$) was used to characterize bulk organic matter (OM) of a piston core from the Patagonian maar lake Laguna Potrok Aike (Argentina) for the purpose of palaeoenvironmental reconstruction. Sedimentary data were compared with geochemical signatures of potential OM sources from Laguna Potrok Aike and its catchment area to identify the sources of sedimentary OM. Correlation patterns between isotopic data and TOC/TN ratios allowed differentiation of five distinct phases with different OM composition. Before 8470 calibrated ^{14}C years before present (cal. yrs BP) and after 7400 cal. yrs BP, isotopic and organo-geochemical fingerprints indicate that the sediments of Laguna Potrok Aike consist predominantly of soil and diatom OM with varying admixtures of cyanobacterial and aquatic macrophyte OM. For a short phase of the early Holocene (ca. 8470–7400 cal. yrs BP), however, extremely high input of soil OM is implied by isotopic fingerprints. Previous seismic and geochronological results indicate a severe lake-level drop of 33 m below present-day shortly before 6590 cal. yrs BP. It is suggested that this lake level drop was accompanied by increased erosion of shore banks and channel incision enhancing soil OM deposition in the lake basin. Thus, isotopic data can be linked to hydrological variations at Laguna Potrok Aike and allow a more precise dating of this extremely low lake level. An isotopic mixing model was used including four different sources (soil, cyanobacteria, diatom and aquatic macrophyte OM) to model OM

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variations and the model results were compared with quantitative microfossil data.

Keywords Stable isotopes · Rock Eval analyses · Organic matter · Soil erosion · Isotope mixing model · South America · Late Quaternary · Lake sediments

Introduction

The uptake of dissolved inorganic carbon (DIC) by submersed aquatic primary producers is accompanied by isotopic fractionation due to physical and biological processes (Farquhar et al. 1989). The preferential ^{12}C uptake by algae and aquatic macrophytes and its removal by sedimentation of particulate organic matter gradually enrich the remaining DIC pool in the heavy isotope (^{13}C), especially when replenishment of CO_2 is limited (e.g., in stratified lakes; Quay et al. 1986). The carbon isotope signature of autochthonous algal biomass reflects variations of the isotopic value of the dissolved inorganic carbon pool ($\delta^{13}\text{C}_{\text{DIC}}$) induced by photoautotrophic DIC consumption (e.g., McKenzie 1985; Hollander and McKenzie 1991). Thus, $\delta^{13}\text{C}_{\text{org}}$ variations of autochthonous sedimentary OM can serve as a proxy of lacustrine paleoproductivity (e.g., Schelske and Holdell 1991; Gu et al. 1996; Brenner et al. 1999). However, the $\delta^{13}\text{C}_{\text{DIC}}$ value is also influenced by the geochemistry and morphometry of a lake (Bade et al. 2004) which may play a role especially over longer (e.g., millennial) timescales.

In many cases, lacustrine sedimentary organic matter consists of a mixture of OM from lake-internal and -external sources. These sources may have clearly distinguishable isotopic signatures, and therefore changes in the sources of OM may likewise be reflected in the stable isotope composition of sedimentary OM (e.g., Meyers 1994, 2003; Lücke and Brauer 2004; Mackie et al. 2005). For instance, it is possible to distinguish isotopically between plants using the C_3 or C_4 metabolic pathways due to their different biological isotope fractionations (e.g., Ehleringer 1991). These isotopic signatures were used to model changes in vegetation (e.g., from bulk soil OM isotopic composition; Delègue et al. 2001). With respect to lake sediments, it has to be considered that HCO_3^- -utilizing aquatic macrophytes (Spence and

Maberly 1985; Sand-Jensen 1987) can contribute OM with similar $\delta^{13}\text{C}$ signatures as C_4 plants (Keeley and Sandquist 1992; Meyers 2003; Mayr et al. 2005). Nitrogen isotopes in combination with carbon isotopes of organic matter can equally typify OM sources of bulk lacustrine sediments (e.g., Talbot and Johannessen 1992; Mayr et al. 2005) and have been successfully applied to differentiate between OM of marine versus terrestrial origin in studies of marine sediments (e.g., Peters et al. 1978; Schubert and Calvert 2001). More frequently, however, ratios of total organic carbon to total nitrogen (TOC/TN) have been used to distinguish whether bulk sedimentary OM originated predominantly from microalgae or from vascular land plants (e.g., Meyers 1994; Hassan et al. 1997; Kaushal and Binford 1999; Mackie et al. 2005). TOC/TN ratios lower than ten are generally regarded as being of algal origin, while higher ratios can be interpreted as mixtures between algae and vascular plant OM (Elser et al. 2000; Meyers 2003) although lake-internal processes such as N-limitation can also produce elevated C/N ratios in aquatic organic matter (e.g., Hecky et al. 1993; Talbot and Lærdal 2000).

Rock Eval analysis is another method for geochemical characterization of bulk sedimentary organic matter. Originally developed for evaluation of hydrocarbon source rocks, the method is increasingly used in paleolimnological studies (e.g., Talbot and Livingstone 1989; Wilkes et al. 1999; Ariztegui et al. 2001; Meyers and Teranes 2001). Rock Eval analysis represents the amount of hydrocarbons (in $\text{mg HC g}^{-1}\text{ TOC}$) given as the hydrogen index (HI) and the amount of oxygen (in $\text{mg CO}_2 \text{ g}^{-1}\text{ TOC}$) given as oxygen index (OI) generated from total OM. It is based on the detection of evolving hydrocarbons and carbon dioxide during temperature-controlled pyrolysis of whole-sediment samples in an inert atmosphere (Espitalié et al. 1977, 1985; Tissot and Welte 1978). Measured HI and OI values allow categorization of sedimentary kerogens into three different organo-geochemical facies related to different OM sources and different degrees of organic matter oxidation (Tissot and Welte 1978; Meyers and Teranes 2001).

Here, we present stable isotope ($\delta^{13}\text{C}_{\text{org}}$, $\delta^{15}\text{N}$) data of an 18.9-m-long sediment core from the centre of the maar lake Laguna Potrok Aike located in south-eastern Patagonia, Argentina (Fig. 1). The aim

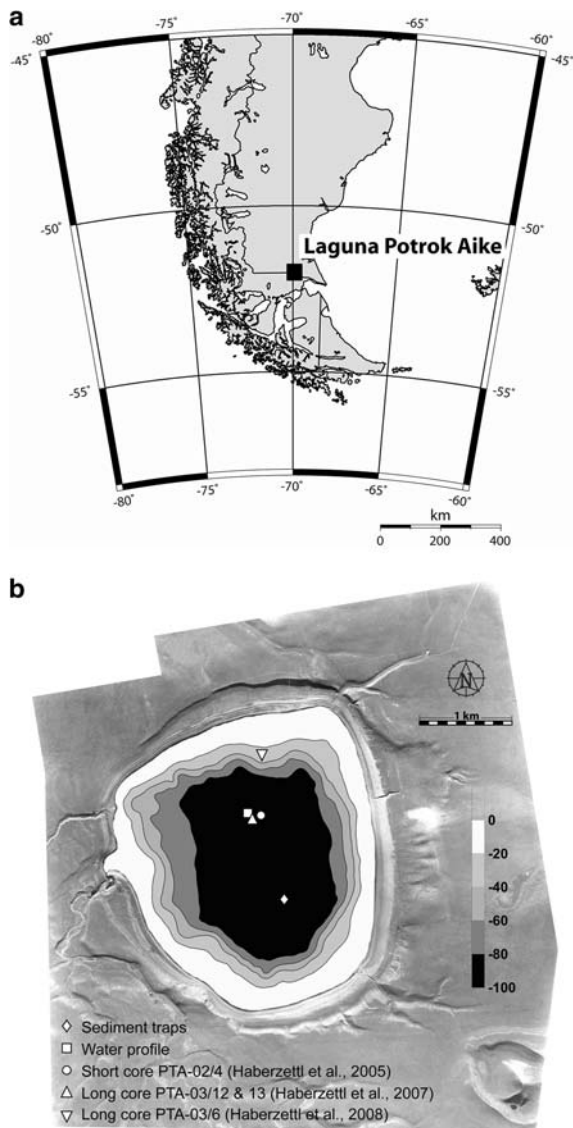


Fig. 1 Position of Laguna Potrok Aike in southern South America (a) and aerial photo with bathymetry of Laguna Potrok Aike and positions of sediment cores, sediment traps and water profile (after Zolitschka et al. 2006) (b)

of this study is to elucidate the causes of isotopic and organo-geochemical variations in OM composition and to discuss their palaeoenvironmental significance. Interpretation of the sedimentary isotope record is based on organo-geochemical and isotopic signatures of potential OM sources and Rock Eval analyses. Results of the profundal core are compared with those of a shallow-water sediment core (Fig. 1) to evaluate intra-basin variability. Finally, the results

are related to quantitative results of microfossil analyses and seismic lake-level reconstructions from the Laguna Potrok Aike record to shed further light on the composition of bulk OM and the environmental causes for changes in the depositional history of OM.

Site description

Laguna Potrok Aike (PTA; 51°58' S, 70°23' W) is a 100 m deep crater lake (Fig. 1) in the Patagonian steppe with a maximum lake diameter of 3.5 km and a volume of 0.41 km³ (Zolitschka et al. 2006). The climate in the region is very windy (mean annual wind speed: 7.4 m s⁻¹) and semi-arid (<300 mm of annual precipitation). The lake has neither a permanent surface inflow nor outflow and is mainly fed by groundwater. Episodic/ephemeral surface runoff reaches the lake through deeply incised canyons. Vegetation in the catchment area is formed of dry Magellanic steppe characterized by different species of Poaceae, herbs and a few shrubs (Oliva et al. 2001). Within the lake basin shallow water areas below the base of wind induced waves are densely covered with aquatic macrophytes (e.g., *Potamogeton pectinatus*, *Myriophyllum cf. quitense*) down to ca. 15 m water depth.

The lake is fully exposed to the strong westerly winds that prevail in these latitudes (Prohaska 1976). For this reason, Laguna Potrok Aike is polymictic and the water column is mixed throughout almost the entire year (Zolitschka et al. 2006). Phosphorus concentration in the lake is very high (1300–3600 µg l⁻¹ total P). Despite the high phosphorus concentration, preliminary investigations indicate that mesotrophic (to eutrophic) conditions prevail in Laguna Potrok Aike as suggested by preliminary plankton studies (Wille et al. 2007; Maidana, unpublished data) and Secchi depths of 6.0 m and 6.9 m in March 2003 and March 2005, respectively. Possible reasons for the lower-than-expected trophic state of the lake are its increased salinity (2.2–2.5 g l⁻¹), the high water turbulence, and limited nitrogen supply for algal growth. The ionic composition of the lake water and other limnological data are summarized in Zolitschka et al. (2006).

Material and methods

Core recovery and processing

Short sediment gravity cores (up to 1 m) were recovered in 2002 (PTA02/4; Haberzettl et al. 2005) and several longer piston cores in 2003 (PTA03/12, PTA03/13, PTA03/6). The coring sites were located in the 100-m-deep central basin (PTA02/4, PTA03/12, PTA03/13) and on a submerged lake-level terrace in 30-m water depth close to the northern shore (PTA03/6, see Fig. 1 for detailed positions). A 1892-cm-long composite profile from the lake centre was established from two parallel long cores (PTA03/12, PTA03/13) and a short core (PTA02/4), the latter containing the sediment-water interface (Haberzettl

et al. 2007). This profile covers the last 16,100 years. The age control for that record is given by 18 accelerator mass spectrometer radiocarbon (AMS ^{14}C) ages and three tephras with known ages (Fig. 2).

The second long sediment profile (PTA03/6), recovered from a submerged lake-level terrace, has a composite length of 900 cm (Haberzettl et al. 2008). This profile contains an erosional unconformity. The lower part dates to ca. 56,000 yrs BP (Haberzettl et al. 2008 and unpublished OSL data) and is overlain by a rapidly deposited sediment layer (379–312 cm sediment depth) representing the re-start of sedimentation after a Holocene lake-level low stand that formed the terrace and hence the unconformity (Haberzettl et al. 2008). The uppermost 311 cm are undisturbed and represent the last

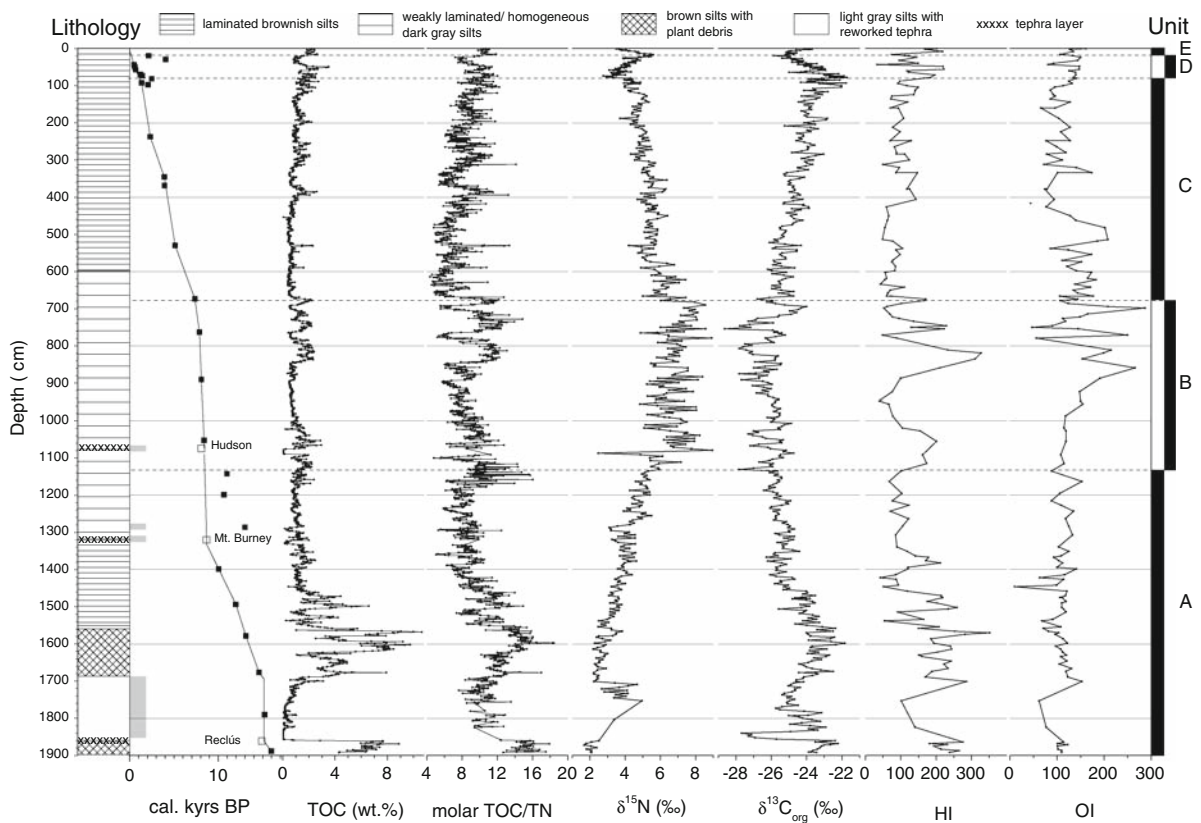


Fig. 2 Lithology, age-depth relation, TOC, molar TOC/TN ratios, $\delta^{15}\text{N}$, $\delta^{13}\text{C}_{\text{org}}$, HI and OI values of the sediment record from the centre of Laguna Potrok Aike (composite profile of PTA02/4, PTA03/12, PTA03/13). TOC/TN ratios and TOC values are from Haberzettl et al. (2007). Apart from calibrated ^{14}C dates (solid squares), the record contains three macroscopically visible tephra layers (open squares) from the eruptions of

volcanoes Reclús (14,900 yr cal BP), Mt. Burney (8680 cal. yrs BP) and Hudson (8100 cal. yrs BP), serving as additional time markers. Gray bars next to the lithology represent event layers in part associated with these tephras which were excluded from the age-depth model (Haberzettl et al. 2007). Units A, B, C, D and E were derived from zonation of $\delta^{15}\text{N}$ values and correlation patterns (see text)

6790 years. The age model for this undisturbed upper section is based on three ^{14}C AMS dates (Haberzettl et al. 2008).

Stable isotope analyses

For stable isotope analyses of organic carbon ($\delta^{13}\text{C}_{\text{org}}$) and nitrogen ($\delta^{15}\text{N}$) of the central core, every fourth cm was investigated, with the exception of the already published uppermost 96 cm from which every cm was analysed (PTA 02/4, Haberzettl et al. 2005). PTA 03/6 was subsampled with coarser analytical resolution (8-cm intervals). Freeze-dried samples were sieved and the fine fraction ($<200\ \mu\text{m}$) was used for isotopic analyses to avoid contamination with organic macro-remains. Samples for organic carbon isotope analyses were pre-treated with hydrochloric acid to remove carbonates as described in Mayr et al. (2005). Isotope ratios were determined with an IsoPrimeTM (GV Instruments, UK) continuous-flow isotope ratio mass spectrometer coupled to an elemental analyser (EuroEA3000, Eurovector, Italy). Isotope ratios are given in δ -notation [$\delta = (R_s/R_{st} - 1) \times 1000$, with R_s and R_{st} as isotope ratios of the sample and the standards VPDB for carbon and AIR for nitrogen, respectively]. Analytical precision (one standard deviation) was 0.08‰ and 0.14‰ for organic carbon and nitrogen stable isotope ratios, respectively.

Rock Eval analyses

For selected samples, hydrogen and oxygen indices were analyzed with Rock Eval pyrolysis. Hydrogen (HI) and oxygen (OI) indices were analyzed with a Rock-Eval II instrument according to standardized methods (Espitalié et al. 1977, 1985). The amount of hydrocarbon evolved during programmed pyrolysis between 300 and 550°C is given in relation to the mass of the sediment (S_2) and in relation to TOC (HI). The OI gives the amount of evolved CO_2 generated between 300 and 390°C relative to TOC.

Elemental analyses

Elemental contents were determined with a standard CNS analyser (EuroEA, Eurovector, Italy). Total organic carbon (TOC, weight-%) and the molar ratios

of total organic carbon to total nitrogen (TOC/TN, molar) of the sediment cores are from elemental analyses published in Haberzettl et al. (2007, 2008). TOC/TN ratios for TOC $<0.3\%$ were rejected, because the presence of inorganic nitrogen can bias these ratios (Meyers 2003).

Additional data sets

Additionally, isotope values and TOC/TN signatures of potential allochthonous and autochthonous OM sources from Laguna Potrok Aike and its catchment area were analysed. Collected modern samples comprise soils, aquatic macrophytes, cyanobacteria, aquatic mosses and terrestrial vascular plants. All samples were homogenized thoroughly by sieving (soils) or milling. The isotopic and geochemical data of the samples from Laguna Potrok Aike are complemented by data from Laguna Azul (Mayr et al. 2005), a crater lake approximately 60 km ESE of Laguna Potrok Aike. Sediments of the smaller and more wind-sheltered Laguna Azul (maximum diameter 560 m, volume 0.01 km³) are predominantly of algal origin (Mayr et al. 2005) and thus data of a pelagic sediment core (AZU 03/5) from that lake were taken as representative for diatomaceous ooze (classification according to Schnurrenberger et al. 2003). The use of isotopic and TOC/TN data for typifying contributions from different sources of sedimentary OM requires the preservation of the original geochemical signature during sedimentation, burial and early diagenesis. To investigate how TOC/TN and isotopic composition of OM changes during these processes, sediment traps were deployed in the centre of Laguna Potrok Aike (Fig. 1) during three subsequent periods between March 2003 and March 2005 (Table 1). Stable isotope analyses and TOC/TN ratios from sediment traps of Laguna Potrok Aike from two different depths (30 m and 90 m) are presented.

Microfossil records

Palynomorph and diatom sample preparations, counts and assemblages are reported in more detail in Wille et al. (2007). Here, only algal palynomorph and diatom concentrations were used for comparisons with OM composition modelled from stable isotope results. For diatom analyses, the samples were heated with hydrogen peroxide to oxidize organic material

Table 1 Elemental (TN, TOC) and isotopic composition ($\delta^{13}\text{C}_{\text{org}}$, $\delta^{15}\text{N}$) of sediment from traps deployed in two different depths (30 m, 90 m) in the centre of Laguna Potrok Aike between March 2003 and March 2005

Sample No.	Time interval	TN (wt. %)	TOC (wt. %)	TOC/TN _{molar}	$\delta^{13}\text{C}_{\text{org}}$ (‰)	$\delta^{15}\text{N}$ (‰)
30 m depth						
PAIS-217	13.03.03–27.02.04	0.30	2.71	10.49	–24.03	4.17
PAIS-229	01.03.04–12.12.04	0.39	3.11	9.27	–24.36	4.41
PAIS-231	12.12.04–11.03.05	0.18	1.58	10.50	n.a.	n.a.
PAIS-232	12.12.04–11.03.05	0.28	2.60	10.92	–24.48	n.a.
Mean		0.29	2.50	10.30	–24.29	4.29
SD		0.09	0.65	0.71	0.23	
90 m depth						
PAIS-219	13.03.03–27.02.04	0.34	2.84	9.67	–24.16	3.69
PAIS-230	01.03.04–12.12.04	0.38	3.13	9.55	–24.53	4.22
PAIS-233	12.12.04–11.03.05	0.31	2.75	10.52	–24.73	4.07
PAIS-234	12.12.04–11.03.05	0.29	2.68	10.84	–25.46	3.61
Mean		0.33	2.85	10.15	–24.72	3.90
SD		0.04	0.20	0.63	0.55	0.29

Note that two traps per depth were deployed during the last time interval

and mounted onto microscope slides following standard procedures (Battarbee 1986). Duplicated permanent slides for light microscopy were prepared with Naphrax[®]. Diatom valves were counted by adding a known volume of polystyrene microspheres to the final suspension as described by Battarbee and Kneen (1982).

For calculation of pollen percentages, two tablets of *Lycopodium* spore markers were added to each sediment sample (Stockmarr 1971). Samples were sieved and treated with HCl and KOH. After acetolysis (Faegri and Iversen 1989) the samples were sieved using ultrasonic treatment and pollen slides were mounted with paraffin. Pollen counts in each of the 242 pollen samples ranged between 300 and 500 grains, excluding aquatic taxa and spores (Wille et al. 2007).

Sediment accumulation rates for diatom frustules and algal palynomorphs, respectively, were calculated by multiplying concentrations by sediment accumulation rates. Sediment accumulation rates were determined as the product of sedimentation rates and dry density, which was determined by Haberzettl et al. (2007 and unpublished results).

Isotope mixing model and statistics

For modelling δ -values of organic matter mixtures of OM sources with different isotopic composition,

mixing models exist, which were used so far especially in ecological and food-web studies (e.g., Phillips and Koch 2002). Here we adapted these models for paleolimnological studies using the following approach.

The isotopic composition δ_{M} of a sedimentary sample consisting of multiple OM sources X, Y, ... , N can be described as:

$$\delta_{\text{M}} = f_{\text{X}}\delta_{\text{X}} + f_{\text{Y}}\delta_{\text{Y}} + \dots + f_{\text{N}}\delta_{\text{N}} \quad (1)$$

$$\text{with } 1 = f_{\text{X}} + f_{\text{Y}} + \dots + f_{\text{N}} \quad (2)$$

where f_{X} , f_{Y} , ..., f_{N} , are the carbon and nitrogen fractions, respectively, contributed by individual OM sources X, Y, ..., N. They are calculated as $f_{\text{X}} = x/(x + y + \dots + n)$ with x , y , ..., n being the weight percentages of any element of these sources (C or N in the range from 0 to 1) times the mass fraction of each individual OM source.

Mixing lines in $\delta^{13}\text{C}_{\text{org}}$ versus $\delta^{15}\text{N}$ space were first calculated for two-end members using Eq. 1. Four-end-member mixings were calculated from mixtures of two sources on each end of the mixing line. The relative proportions of these two OM sources forming a new end member were kept constant, but the proportions of each double-source mixture were varied for calculation of four-end-member mixing lines. These mixing lines were fitted to the observed regression lines given by the

sedimentary isotope data. Actually measured element concentrations of organic matter sources given in Table 2 were used for weighting mixing models except for soils, diatoms and cyanobacteria. Soil samples contained high fractions of minerogenic material, whereas diatomaceous ooze had high amounts of biogenic opal complicating mixing calculations. A TOC content of 50%, typical for soil OM (Schachtschabel et al. 1992), was thus assumed for the soil OM source and the corresponding N concentration was calculated from the given C/N ratio of the analysed soil (Table 2). The TOC content for diatoms was calculated as 54% from the Redfield Ratio given as stoichiometric ratios of C:H:O:N:P = 106:175:42:16:1 (Anderson 1995) and N concentration was calculated as well from the C/N ratio. The same TOC values as for diatoms were taken in the model for cyanobacteria, as the low measured TOC values around 27% imply some contamination of the samples with minerogenic matter. All statistical analyses were performed with the computer software Origin 7.5 (OriginLab, USA) using two-sided *t*-tests for all regression analyses.

Results

Sediment traps

Similar mean values between TOC/TN ratios of traps in 30-m (10.3 ± 0.7) and 90-m water depth (10.2 ± 0.6 ; Table 1) were found. The TOC/TN ratios of the trapped OM are indistinguishable from those of the uppermost 0.5 cm of the sediment core (10.5; core PTA02/4). The $\delta^{13}\text{C}_{\text{org}}$ values of the sediment traps ($-24.3\text{‰} \pm 0.2\text{‰}$ in 30 m and $-24.7\text{‰} \pm 0.6\text{‰}$ in 90 m water depth; Table 1) and the $\delta^{15}\text{N}$ values (4.3‰ in 30 m and $3.9\text{‰} \pm 0.3\text{‰}$ in 90 m water depth; Table 1) are also close to those of the uppermost sediment layer of the core (-24.2‰ for $\delta^{13}\text{C}_{\text{org}}$ and 3.7‰ for $\delta^{15}\text{N}$ of PTA02/4).

Composite profile from the lake centre

Lithologically, the sediments consist of partly laminated silts with minor amounts of sand, clay, carbonate, organic matter and biogenic silica (Fig. 2, detailed description in Haberzettl et al.

2007). As proposed by Haberzettl et al. (2007), four sections, two of them containing in situ tephra overlain by reworked tephra, were considered as event layers, and therefore, neither were included in the age model nor in data evaluations. These intervals are marked with gray bars in Fig. 2.

The record of Laguna Potrok Aike exhibits considerable isotopic variations. Total isotopic ranges are ca. 7‰ for both $\delta^{13}\text{C}_{\text{org}}$ (values between -21.72‰ and -28.65‰) and $\delta^{15}\text{N}$ (8.9‰ – 1.7‰) over the entire record (Fig. 2). A significant overall negative correlation ($r = -0.67$, $P < 0.0001$, $N = 497$) between $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ records is discernible. The TOC/TN-ratios range between 4.4 and 18.4 with highest values at the basal layers and lowest values in the middle sections of the record (Haberzettl et al. 2007). Increases in TOC/TN are positively correlated with TOC variations (Fig. 2). Moreover, $\delta^{13}\text{C}_{\text{org}}$ as well as $\delta^{15}\text{N}$ records are significantly correlated with TOC/TN values. Overall correlation of $\delta^{15}\text{N}$ versus TOC/TN is negative ($r = -0.42$, $P < 0.0001$, $N = 497$), whereas the overall correlation of $\delta^{13}\text{C}_{\text{org}}$ versus TOC/TN is positive ($r = 0.39$, $P < 0.0001$, $N = 515$). Although correlations between TOC/TN and isotopic ratios of both elements are significant, they are considerably weaker than the correlation between $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values. This is a consequence of the non-uniformity of the correlation in different sections of the sediment profile.

The isotopic records are characterized by distinct abrupt changes and long-term trends best visible in the $\delta^{15}\text{N}$ record. Changes in trends and abrupt shifts permitted subdivision of the sediment profile into five intervals (Fig. 2) described here from the base to the top of the profile. The first section A (1892–1132 cm sediment depth; 16,090–8470 cal. yrs BP) starts from lowest $\delta^{15}\text{N}$ and high $\delta^{13}\text{C}_{\text{org}}$ values and thereafter shows generally rising $\delta^{15}\text{N}$ and decreasing $\delta^{13}\text{C}_{\text{org}}$ values. The second section B (1131–678 cm; 8470–7390 cal. yrs BP) exhibits an abrupt increase in $\delta^{15}\text{N}$ values by ca. 2‰ and has highest, but most variable $\delta^{15}\text{N}$ values and lowest $\delta^{13}\text{C}_{\text{org}}$ values thereafter. The next section C (677–80 cm; 7360–1120 cal. yrs BP) exhibits uniformly decreasing $\delta^{15}\text{N}$ and increasing $\delta^{13}\text{C}_{\text{org}}$ values. A $\delta^{15}\text{N}$ minimum and $\delta^{13}\text{C}_{\text{org}}$ maximum separates section C and D. The $\delta^{15}\text{N}$ values increase in section D and the $\delta^{13}\text{C}_{\text{org}}$ values decrease again (79–18 cm; 1100–175 cal. yrs BP). The stratigraphically uppermost

Table 2 TOC, TN, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and TOC/TN of potential organic matter sources from the catchment areas of Laguna Potrok Aike (PTA) and Laguna Azul (AZU)

OM type/taxon	Location	TN (wt. %)	TOC (wt. %)	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	TOC/TN (molar)
Algal organic matter						
Diatomaceous ooze ^a	AZU03/5, 1 cm	1.6	13.5	-27.77	4.2	9.8
Diatomaceous ooze ^a	AZU03/5, 10 cm	1.8	14.0	-27.34	4.3	8.8
Diatomaceous ooze ^a	AZU03/5, 20 cm	1.9	15.0	-25.90	4.3	9.1
Diatomaceous ooze ^a	AZU03/5, 30 cm	1.9	14.7	-26.60	4.2	9.1
Diatomaceous ooze ^a	AZU03/5, 41 cm	1.7	13.1	-28.21	3.8	8.9
Diatomaceous ooze ^a	AZU03/5, 45 cm	2.0	15.5	-26.55	3.7	9.1
Diatomaceous ooze ^a	AZU03/5, 47 cm	2.0	14.7	-23.02	3.5	8.7
Diatomaceous ooze ^a	AZU03/5, 49 cm	2.0	15.3	-23.78	3.7	8.9
Diatomaceous ooze ^a	AZU03/5, 51 cm	2.1	16.0	-23.83	4.2	9.0
Diatomaceous ooze ^a	AZU03/5, 54 cm	1.8	14.5	-23.99	4.0	9.3
Diatomaceous ooze ^a	AZU03/5, 57 cm	1.8	14.2	-25.96	3.7	9.5
Diatomaceous ooze ^a	AZU03/5, 63 cm	2.1	15.3	-24.46	4.1	8.7
<i>Mean AZU</i>		1.9 (6.9 ^c)	14.7 (54 ^c)	-25.62	4.0	9.1
Cyanobacteria						
<i>Nostoc</i> sp. (PAIS 235)	PTA	4.3	26.8	-20.22	-0.8	7.3
Cyanobacteria from thermistor chain (PAIS 182)	PTA	2.6	27.3	-23.38	0.3	12.2
<i>Mean PTA</i>		3.4 (6.4 ^c)	27.1 (54 ^c)	-21.80	-0.3	9.8
Terrestrial vegetation						
<i>Berberis</i> sp. ^a	AZU	0.9	52.0	-28.27	0.5	65.6
<i>Festuca</i> sp. ^a	AZU	0.3	43.6	-25.23	-0.9	166.1
<i>Hordeum</i> sp. ^a	AZU	0.5	40.1	-26.00	-1.5	102.2
Brassicaceae ^a	AZU	1.8	42.5	-25.20	1.7	27.3
<i>Empetrum</i> sp. ^a	AZU	0.7	54.3	-26.31	-1.4	93.8
<i>Stipa</i> sp. ^a	AZU	0.6	42.7	-27.31	2.3	77.9
<i>Acaena</i> sp. ^a	AZU	0.7	46.5	-27.53	-1.3	80.4
Poaceae ^a	AZU	0.7	44.4	-24.56	10.8	77.6
<i>Berberis</i> sp. ^a	AZU	1.1	51.0	-26.88	-2.5	55.3
<i>Mean AZU</i>		0.8	46.3	-26.37	0.8	82.9
<i>Stipa</i> sp.	PTA	0.5	44.5	-25.83	3.4	100.1
<i>Adesmia</i> sp.	PTA	1.0	46.6	-25.20	-1.0	53.5
<i>Stipa</i> sp.	PTA	0.7	42.6	-27.82	4.2	76.4
Poaceae	PTA	0.8	40.8	-26.62	2.3	57.8
<i>Stipa</i> sp.	PTA	0.6	44.6	-26.02	0.9	90.4
<i>Caltha sagittata</i>	PTA	1.5	46.6	-24.50	3.7	35.7
<i>Mean PTA</i>		0.8	44.3	-26.00	2.2	69.0
Aquatic mosses						
<i>Drepanocladus perplicatus</i> ^b	PTA	1.8	n.a.	n.a.	1.6	n.a.
<i>Drepanocladus perplicatus</i>	PTA	0.9	42.1	-32.82	0.2	56.7
<i>Drepanocladus perplicatus</i>	PTA	0.9	40.3	-31.49	1.8	53.5
<i>Mean PTA</i>		1.2	41.2	-32.16	1.2	55.1

Table 2 continued

OM type/taxon	Location	TN (wt. %)	TOC (wt. %)	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	TOC/TN (molar)
Submerged aquatic macrophytes						
<i>Myriophyllum</i> sp. ^a	AZU	1.5	45.6	−8.87	3.5	35.6
Characeae, 2 m depth ^a	AZU	1.1	43.4	−14.85	−1.4	44.3
<i>Potamogeton</i> sp., 1.5 m depth ^a	AZU	1.9	48.7	−7.11	−16.5	30.6
<i>Myriophyllum</i> sp., 2 m depth ^a	AZU	1.7	47.5	−8.13	−7.0	33.1
Mean AZU		1.6	46.3	−9.74	−5.4	35.9
<i>Potamogeton</i> sp.	PTA	1.5	36.0	−14.49	1.5	28.1
<i>Potamogeton</i> sp.?	PTA	1.5	41.1	−11.62	1.6	32.8
Plant debris	PTA	1.2	46.5	−14.93	2.1	45.9
<i>Potamogeton</i> sp.?	PTA	1.1	38.6	−12.86	0.7	39.2
<i>Myriophyllum</i> sp.	PTA	0.9	36.5	−10.10	2.8	46.6
<i>Myriophyllum</i> sp., 2 m depth	PTA	1.7	47.5	−11.33	3.7	33.3
<i>Potamogeton</i> sp., 2 m depth	PTA	1.3	48.4	−12.54	1.7	43.5
Cf. <i>Ruppia</i> sp., 1.5 m depth	PTA	1.5	35.8	−16.12	2.5	28.3
Mean PTA		1.3	41.3	−13.00	2.1	37.2
Soils						
Soil, slope ^a	AZU	1.3	16.4	−26.64	4.9	14.9
Soil, crater rim ^a	AZU	0.9	10.9	−25.63	3.0	14.5
Soil, crater slope ^a	AZU	0.7	7.3	−25.91	3.1	12.9
Soil, crater rim ^a	AZU	0.7	10.3	−25.86	2.4	16.8
Soil crater floor ^a	AZU	0.2	2.4	−23.76	5.2	11.4
Soil, crater slope ^a	AZU	0.6	6.8	−25.48	6.8	13.3
Soil on tephra ring ^a	AZU	0.8	9.9	−24.57	3.3	15.1
Mean AZU		0.7	9.1	−25.41	4.1	14.1
Soil above till	PTA	0.4	3.8	−24.98	n.a.	12.5
Soil above sediment	PTA	0.1	1.4	−24.95	n.a.	11.7
Humous soil, uppermost 10 cm	PTA	0.2	1.8	−23.98	8.2	13.5
Humous soil, 60–70 cm	PTA	0.3	2.8	−25.41	8.7	12.3
Soil, uppermost layer	PTA	0.2	2.3	−24.62	6.0	11.8
Soil	PTA	0.1	0.9	−25.35	4.6	11.9
Soil	PTA	0.4	4.2	−24.98	7.5	12.5
Soil	PTA	0.4	4.1	−25.49	7.7	13.2
Mean PTA		0.2 (4.7 ^c)	2.7 (50 ^c)	−24.97	7.1	12.4

^a Data from Mayr et al. (2005)

^b Subfossil moss from exposed lake sediment

^c Values in brackets give estimated TOC and TN values of pure OM used for model calculations (see Material and Methods for explanation)

n.a.: not analyzed

Data for diatomaceous ooze are from various depths of sediment core AZU03/5 from Laguna Azul (Mayr et al. 2005)

core section E is short, but was analysed in high resolution allowing to separate it from the preceding unit. It covers the period 175 to −48 cal. yrs BP (17–0.5 cm). In this section the trends are reversed

again: $\delta^{13}\text{C}_{\text{org}}$ values increase whereas $\delta^{15}\text{N}$ values decrease towards the present.

Correlations of $\delta^{13}\text{C}_{\text{org}}$ versus $\delta^{15}\text{N}$ data calculated for each unit separately are significant for all units

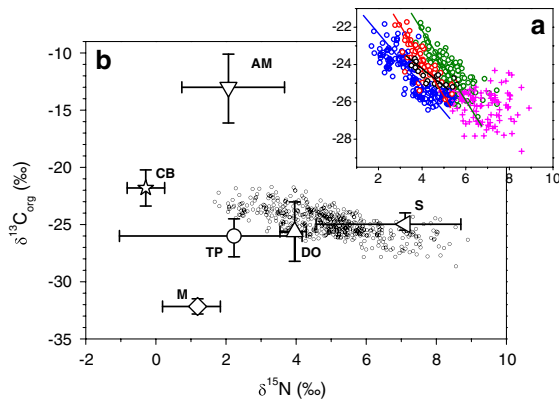


Fig. 3 Sedimentary $\delta^{13}\text{C}_{\text{org}}$ versus $\delta^{15}\text{N}$ values of units A (blue), B (magenta), C (green), D (red) and E (black). Correlation patterns are shown in the insert (a) and data are compared to isotopic and geochemical signatures of modern samples from potential OM sources (b), the latter given as means (large symbols) and total ranges (bars). AM: aquatic macrophytes, TP: terrestrial vascular plants, M: aquatic mosses, S: terrestrial soils, DO: diatomaceous ooze, CB: cyanobacteria. All OM source data are from Laguna Potrok Aike except for DO which is from Laguna Azul. More details are given in the text and in Table 2

despite of section B (Fig. 3a). Units A, C, D and E have similar negative slopes of their linear regression lines and the correlation coefficients are generally higher than for the total data set (section A: $r = -0.81$, $P < 0.001$, $N = 145$; section C: $r = -0.72$, $P < 0.001$, $N = 166$; section D: $r = -0.80$, $P < 0.001$, $N = 62$; section E: $r = -0.77$, $P = 0.001$, $N = 18$). Furthermore, ranges of $\delta^{13}\text{C}_{\text{org}}$ are similar between the two major units C and A, but $\delta^{15}\text{N}$ values are shifted by ca. 1.5‰ to higher values in C relative to A (Fig. 3a). In contrast, the correlation between $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ is not statistically significant for unit B (section B: $r = -0.17$, $P = 0.08$, $N = 106$) in which the lowest $\delta^{13}\text{C}_{\text{org}}$ and highest $\delta^{15}\text{N}$ values occur.

Comparably high correlation coefficients are observed for $\delta^{13}\text{C}_{\text{org}}$ versus TOC/TN correlations in units A, C and D (Fig. 4a; $r = -0.81$, $P < 0.001$, $N = 145$ for unit A; $r = -0.72$, $P < 0.001$, $N = 166$ for unit C; $r = -0.80$, $P < 0.001$, $N = 62$ for unit D). In contrast, $\delta^{13}\text{C}_{\text{org}}$ and TOC/TN values of units B and E are characterized by weak or non-significant negative correlations ($r = -0.35$ and -0.11 , respectively).

The negative correlations between $\delta^{15}\text{N}$ and TOC/TN of units A, C and D (Fig. 5a) are also highly

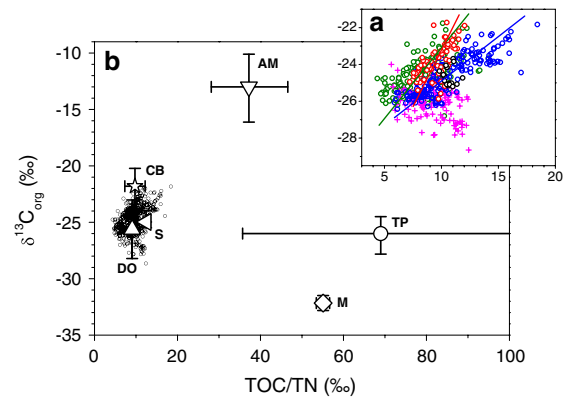


Fig. 4 Sedimentary $\delta^{13}\text{C}_{\text{org}}$ values versus TOC/TN ratios of units A, B, C, D and E. Correlation patterns are shown in the insert (a) and data are compared to isotopic and geochemical signatures of modern samples from potential OM sources (b). For further explanations see Fig. 3

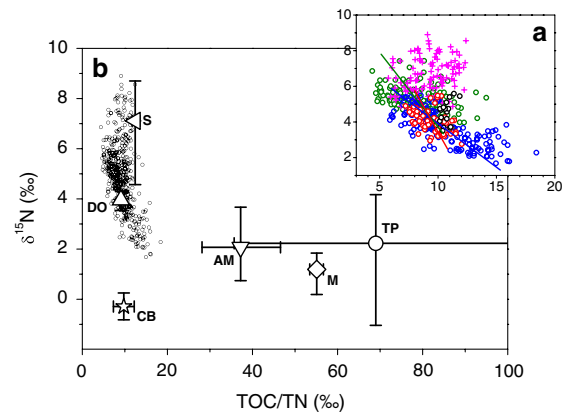


Fig. 5 Sedimentary $\delta^{15}\text{N}$ values versus TOC/TN ratios of units A, B, C, D and E. Correlation patterns are shown in the insert (a) and data are compared to isotopic and geochemical signatures of modern samples from potential OM sources (b). For further explanations see Fig. 3

significant ($r = -0.74$, $P < 0.001$, $N = 145$ for unit A; $r = -0.42$, $P < 0.001$, $N = 166$ for unit C; $r = -0.45$, $P < 0.001$, $N = 62$ for unit D), whereas units B and E have weak positive correlations ($r = 0.28$, $P < 0.001$, $N = 106$ for unit B; $r = 0.48$, $P = 0.040$, $N = 18$ for unit E).

Geochemical results from the shallow water core (PTA03/6)

Figure 6 compares the uppermost part of the sediment record from the 100-m-deep lake centre to the

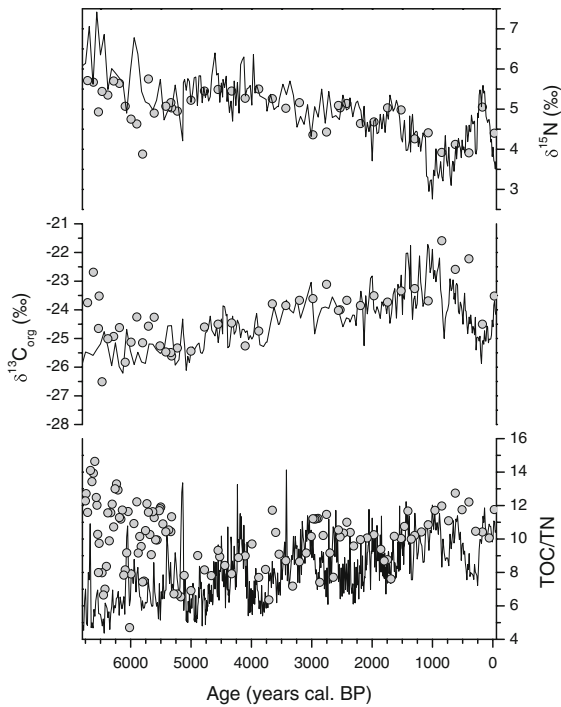


Fig. 6 TOC/TN, $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ curves of the sediment core from 30 m water depth (PTA 03/6, gray circles; TOC/TN and $\delta^{13}\text{C}_{\text{org}}$ from Haberzettl et al. 2008) compared to the records from the lake centre (PTA02/4, PTA03/12, PTA03/13, black lines), both versus their respective time scales. Only the undisturbed upper part of core PTA03/6 is shown

$\delta^{13}\text{C}_{\text{org}}$, $\delta^{15}\text{N}$ and TOC/TN records of the undisturbed upper part of core PTA03/6 from 30 m water depth. Both records are plotted versus their independent time scales. The sediment core closer to the shore (PTA03/6) shows marked differences from the core that was taken at the lake centre in the section immediately above the erosional unconformity (ca. 6790–5500 cal. yrs BP). For this time interval, higher TOC/TN ratios and $\delta^{13}\text{C}_{\text{org}}$ values in core PTA03/6 compared to core PTA03/12&13 are observed. After ca. 5500 cal. yrs BP, however, both records compare well in absolute values and in relative fluctuations within the dating uncertainties.

TOC/TN and isotopic signatures of potential OM sources

$\delta^{13}\text{C}_{\text{org}}$, $\delta^{15}\text{N}$ and TOC/TN of different samples of OM from diatoms, cyanobacteria, soils, vascular plants (aquatic macrophytes, terrestrial plants) and aquatic mosses are given in Table 2. High carbon

isotope values clearly separate the aquatic macrophytes from other sources (Figs. 3b, 4b) and reflect their ability to extensively utilize bicarbonate (HCO_3^-), which is enriched in ^{13}C relative to dissolved CO_2 (Mook et al. 1974). In the pH range of Laguna Potrok Aike (8.7–9.0) bicarbonate is the predominating dissolved inorganic carbon (DIC) species (Wetzel 2001), favouring the growth of HCO_3^- utilizing photoautotrophs such as *Myriophyllum* and *Potamogeton* (Sand-Jensen 1987), which are the dominating aquatic macrophytes in Laguna Potrok Aike. Active uptake of bicarbonate by cyanobacteria (Espie et al. 1991) might explain the relatively high $\delta^{13}\text{C}_{\text{org}}$ values of the cyanobacteria samples from Laguna Potrok Aike (Figs. 3b, 4b). In contrast, the low $\delta^{13}\text{C}_{\text{org}}$ of diatomaceous OM from Laguna Azul, which has a similar pH to Laguna Potrok Aike (8.3–9.0, Mayr et al. 2005), implies that diatoms in these lakes are not able to utilize bicarbonate extensively, but take up preferentially the limited amount of dissolved CO_2 . Aquatic mosses revealed very low $\delta^{13}\text{C}_{\text{org}}$ values (around -32‰) indicating no utilization of bicarbonates at all. Terrestrial plant samples have $\delta^{13}\text{C}$ values between -24.5‰ and -28.3‰ (Table 2) and are thus within the typical range of C_3 plants (Ehleringer 1991). Terrestrial plants, soils and diatomaceous organic matter cannot be distinguished further by their carbon isotope signatures, but TOC/TN ratios allow separating soils (11.4–16.8) and diatomaceous organic matter (8.7–9.8) from terrestrial plants, aquatic macrophytes and aquatic mosses all with TOC/TN higher than 27 (Figs. 4b, 5b). Cyanobacteria have TOC/TN ratios overlapping with those of soils and diatom OM.

The nitrogen isotope signatures (Figs. 3b, 5b) separate potential OM sources with low values (means between -0.3‰ and 2.2‰ : cyanobacteria, terrestrial plants, aquatic macrophytes and mosses), intermediate values (diatomaceous organic matter, mean of 4.0‰), and highest values (soils, mean of 7.1‰). While TOC/TN ratios and $\delta^{13}\text{C}$ values of potential OM sources from Laguna Azul and Laguna Potrok Aike are generally in the same range, $\delta^{15}\text{N}$ means differ between both sites by as much as 7.4‰ (submerged aquatic macrophytes), 1.4‰ (terrestrial vegetation) and 3.0‰ (soils; Table 2). Different parent rocks and soil development in the catchment areas (predominantly Quaternary and Neogene

sediments covered by humic soils at Laguna Potrok Aike, but Quaternary basaltic rocks and tephra with thin soil cover at Laguna Azul) may explain the different nitrogen isotope signatures at the two sites. $\delta^{15}\text{N}$ ranges allow distinguishing terrestrial plants and soils surrounding Laguna Potrok Aike (Table 2). Potrok Aike soils vary between 4.6‰ and 8.7‰ and do not overlap with diatomaceous OM from Laguna Azul (3.5–4.3‰). Although, the representativeness of the $\delta^{15}\text{N}$ values of diatomaceous OM of Laguna Azul for Laguna Potrok Aike can be debated considering the inter-site $\delta^{15}\text{N}$ differences observed for other OM sources, these data certainly provide the best approximation at this stage. The low $\delta^{15}\text{N}$ values (0.28‰ and -0.79 ‰) of cyanobacteria collected in Laguna Potrok Aike demonstrate the ability of various taxa of this group to utilize molecular nitrogen (Wada and Hattori 1976; Macko et al. 1987). The isotope fractionation associated with N_2 fixation is typically small (-2.1 ‰ to $+0.05$ ‰; Wada and Hattori 1976; Wada 1980) explaining their $\delta^{15}\text{N}$ values close to that of atmospheric nitrogen (0‰ by definition).

Using all information available, diatomaceous ooze, cyanobacteria and soils can be clearly distinguished from OM of vascular plants (aquatic macrophytes and mosses, terrestrial plants) by means of their TOC/TN ratios. $\delta^{13}\text{C}$ values on the upper end of the scale allow discrimination of OM derived from aquatic macrophytes and cyanobacteria from terrestrial plants, diatomaceous ooze and soils with intermediate $\delta^{13}\text{C}$ values and aquatic mosses with lowest $\delta^{13}\text{C}$ values. The nitrogen isotope signatures allow differentiating

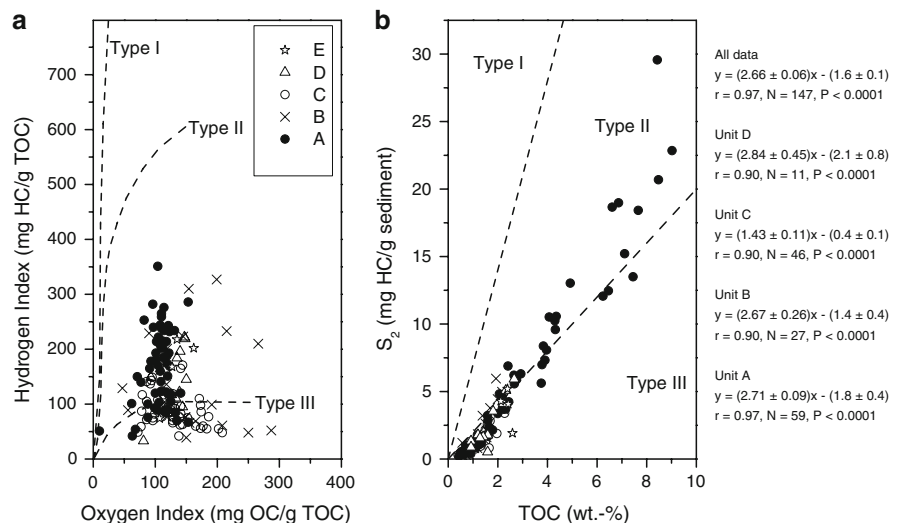
soil OM from all other OM sources. The comparison with isotopic signatures of various sources implies that the sediment OM consists of a complex mixture of different OM sources and cannot be explained by a simple two-end-member mixing model. However, the sedimentary isotopic and TOC/TN data also imply that aquatic mosses and terrestrial plants can be rejected as major OM contributors a priori as sedimentary data plot far from these sources.

Rock Eval results

HI values are, on average, highest in the lower part of unit A (average 168 mg HC/g TOC), decline towards unit B (average 137 mg HC/g TOC) in which they are variable, and are lowest in unit C (average 90 mg HC/g TOC) (Fig. 2). In units D and E, HI values increase again (averages 145 mg HC/g TOC and 166 mg HC/g TOC, respectively). Unit A and B exhibit large HI variations of about 300 mg HC/g TOC, whereas unit C is characterized by generally lower and less variable HI values which tend to rise towards units D and E. OI values are rather uniform throughout the record (average 122 mg OC/g TOC, standard deviation 38 mg OC/g TOC) with the exception of higher variability in the upper part of unit B and the lower part of unit C (Fig. 2).

HI values are plotted versus OI values in a Van-Krevelen-type plot (Fig. 7a) along with the evolution pathways of kerogen. These pathways were originally established for oil and gas exploration purposes and classify kerogens into three different types (Tissot and

Fig. 7 Rock Eval data of the sedimentary record from the centre of Laguna Potrok Aike given as (a) Van-Krevelen-type plot, (b) S_2 versus TOC plot. The units of Fig. 2 are distinguished by different symbols



Welte 1978; Espitalié et al. 1977, 1985). Type I, II and III kerogens of lacustrine sediments were attributed to waxy organic matter, algal organic matter and vascular-plant organic matter, respectively (Meyers and Teranes 2001). Sedimentary kerogens of the Laguna Potrok Aike record plot close to the type III pathway or lie between the pathways of type II and III (Fig. 7). No major differences are observed for the distribution of data from the various units in the Van-Krevelen-type diagram, albeit unit B includes OI values higher than all other data. Matrix effects can bias Rock Eval data due to absorption of hydrocarbons, e.g., on clay mineral surfaces. The definition of the mean hydrocarbon content via the slope of the regression line in a plot of hydrocarbon amount relative to sediment mass (S_2) versus TOC helps to overcome this problem (Langford and Blanc-Valleron 1990; Ariztegui et al. 2001). Figure 7b gives the S_2 versus TOC data of Laguna Potrok Aike and the fields of the kerogen types as well as the regression-line equations of all data and of the respective units. The intercept of the regression through all data is 1.6% TOC and gives the mean TOC content that has to be exceeded before hydrocarbons are detected, because a certain amount of TOC is absorbed to the matrix, especially to clay minerals (Langford and Blanc-Valleron 1990). The mean HI value is calculated as ten times the slope of the regression line in a S_2 versus TOC plot (Langford and Blanc-Valleron 1990). The resulting matrix-corrected mean HI value is 26.6% and thus considerably higher than 16.8% given by the uncorrected Rock Eval data. The matrix-corrected HI values of units A, B and D agree within their error margins with this average value, but the matrix-corrected value of unit C is significantly lower (14.3%, see regression equations next to Fig. 7b). Moreover, a lower matrix absorption effect is observed as indicated by an intercept value closer to zero (0.4% TOC). Only four values exist for unit E and therefore the Rock Eval data cannot be taken into consideration for evaluation and, thus, regression data are not given in Fig. 7.

Discussion

Origin of sedimentary OM

The $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ values of the sediment traps from Laguna Potrok Aike are close to those of the

uppermost sediment layer of the cores. Thus, the sediment-trap data document no substantial modifications of TOC/TN ratios and isotope values of Laguna Potrok Aike's sediments during the processes of early diagenesis and can be assumed to reflect the original geochemical composition of deposited particulate OM. These observations are in accordance with other sediment-trap studies demonstrating that the original TOC/TN ratios and isotopic composition of particulate organic matter are well preserved in lake sediments after deposition (Meyers 1994; Meyers et al. 1995; Hodell and Schelske 1998; Teranes and Bernasconi 2000). Nevertheless, there are other experimental data and field studies which show that diagenetic effects may alter TOC/TN ratios and isotope values ($\delta^{13}\text{C}_{\text{org}}$, $\delta^{15}\text{N}$) under certain conditions (Best et al. 1990; Lehmann et al. 2002). The similar isotope values of OM trapped at different depths indicate a rather homogeneous pelagic OM sedimentation. The strong similarity of the central core record (PTA03/12&13) with the record from the shallower water (PTA03/6) after 5500 cal. yrs BP further testifies uniform basin-wide sedimentation processes. Therefore, two main prerequisites (preservation of the original OM composition and a basin-wide sediment homogeneity) for a comparison of isotopic values and TOC/TN ratios of the sediments with those of potential OM sources are fulfilled and the use of a fingerprint approach for interpretation of the data is applicable.

In some studies isotopic variations in sedimentary organic matter were related to isotopic changes in the inorganic N or C sources taken up by phytoplankton that subsequently sedimented at the lake bottom (e.g., McKenzie 1985; Gu et al. 1996). Because preferential uptake of light carbon during photosynthesis can lead to heavy isotopic enrichment of algal OM, isotopic change in sedimented OM of algal origin is indicative of changes in paleoproductivity. The sediments of Laguna Potrok Aike, however, cannot be attributed to algal OM alone. Only the isotopic and TOC/TN sedimentary data in the upper part of unit A are in accordance with the geochemical signatures of diatomaceous organic matter. In all other core sections the scatter of the sedimentary data, their correlation patterns and the Rock Eval results are not consistent with an exclusive algal origin of sedimentary organic matter. Moreover, the isotopic signatures themselves point to changes in the organic matter composition.

For instance, the extremely low $\delta^{15}\text{N}$ values in the lower part of unit A and the extraordinary high values in unit B cannot be explained with organic matter signatures of entirely algal origin. These points evidence varying contributions of supplementary OM sources in almost all core sections. Especially at the beginning of unit A, during the Lateglacial period between 16,100 and 12,400 cal. yrs BP, and in the course of unit C during the Late Holocene (1650–570 cal. yrs BP), the $\delta^{15}\text{N}$ values are lower (down to 1.68‰) and the $\delta^{13}\text{C}$ values and TOC/TN ratios are higher (up to -21.72‰ and 18.42, respectively) than the ranges observed for diatomaceous ooze in the dataset from Laguna Azul (Table 2) in particular, and for algal OM in general (e.g., Elser et al. 2000). A positive correlation between $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ would be expected if variations of these parameters were driven by changes in aquatic primary productivity (Gu et al. 1996; Finlay and Kendall 2007). In fact, a negative correlation was observed in units A, C, D and E whereas unit B exhibits no significant correlation (Fig. 3). The fingerprint approach implies that during periods with high $\delta^{13}\text{C}_{\text{org}}$ values and low $\delta^{15}\text{N}$ values significant amounts of aquatic macrophyte and/or cyanobacterial OM were deposited, even though algal OM was still a major sedimentary OM component. On the other hand, the high $\delta^{15}\text{N}$ values in unit B imply that, in addition to diatomaceous ooze, soil OM is a major constituent for this stratigraphic level.

To further clarify to what extent the sediments were composed of supplementary OM sources other than diatomaceous ooze, the isotope correlation trends of the sedimentary units A to E were compared with the mixing lines between various sources in $\delta^{13}\text{C}_{\text{org}}$ versus $\delta^{15}\text{N}$ space (Fig. 8). The two-end-member mixing lines in the model presented in Fig. 8 are non-linear as isotopic values were weighted with the element concentrations of the sources (cf. Phillips and Koch 2002). With the exception of unit B, all sedimentary isotope data plot within the field spanned by aquatic macrophytes, cyanobacteria, diatomaceous ooze and soils. Data of unit B plot close to the mixing line between diatomaceous ooze and soil organic matter although a large part of the data has lower $\delta^{13}\text{C}_{\text{org}}$ values than both of these two sources. This implies either that the soil end member is insufficiently represented by the modern data set for unit B or that a presently unknown source contributed to the

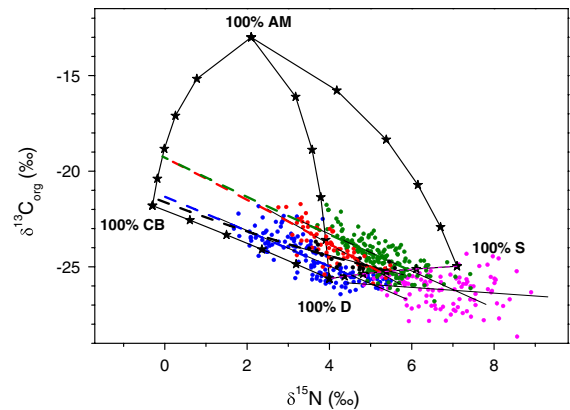


Fig. 8 Isotope mixing model in $\delta^{13}\text{C}_{\text{org}}$ versus $\delta^{15}\text{N}$ space for mixtures between diatom (D), soil (S), cyanobacteria (CB) and aquatic macrophyte (AM) OM. Stars on two-end-member mixing lines represent 20% intervals. The regression lines of the five units are given as thin lines. Each of the lines of units A, C, D, E coincides with a mixing line (bold line, colours as in Fig. 3) between a CB/AM mixture on the one side and a D/S mixture on the other side. The regression line of unit B is best explained by a two-end member mixing between D and S

OM or that one of the identified sources has been diagenetically overprinted. The bulk of data of all the other units do not plot on any of the two-end-member mixing lines. The regression lines of these units imply general mixtures of diatomaceous ooze and soil organic matter (DO/S) on the one end and cyanobacteria and aquatic macrophytes (CB/AM) on the other. Moreover the data points scatter considerably along the mixing lines inferred from the correlation trends. This implies that potentially the isotopic signature of single OM sources may have varied in time e.g., by physical and ecological constraints for OM production, or that proportions of the double end-members (DO/S and CB/AM, respectively) were not constant as assumed above. Therefore, the actual contributions of different sources cannot be quantified unambiguously. Nevertheless the mixing model can give a rough estimation about which sources potentially contributed to which extent to bulk OM in the respective time slices.

Under the assumption that the end points of the regression lines represent the end members of mixing lines between DO/S mixtures on the one side and CB/AM mixtures on the other side, new end-member mixtures including all four sources can be determined for every point on the regression line of every unit. The composition of each point on the regression lines

can then easily be estimated from DO/S-CB/AM mixture calculations. By doing so, relative changes in OM composition were determined and the long-term isotopic trends modelled. Following this approach, the sediment OM at the bottom of unit A consisted mainly of diatomaceous ooze (31%) and cyanobacterial OM (52%) with minor admixtures of soil (11%) and aquatic macrophyte (6%) OM. During the course of unit A, the diatom fraction steadily increased to 73%, whereas all other sources diminish except for soils (27%). At the base of unit B, the sedimentary OM consists predominantly of soil OM with some admixtures of diatoms. During unit C soil OM decreases from 75% to 54% and diatom OM from 25% to 18%. At the same time cyanobacteria and aquatic macrophyte OM increase from complete absence at the beginning to 18% and 10% at the end, respectively, according to the model estimations. Unit D starts with 26% diatom OM concentrations and admixtures of cyanobacteria (27%), soil (32%) and aquatic macrophytes (15%) and ends up with a mixture of 45% diatom and 55% soil OM. During the course of unit E, the diatom and soil fractions lower to 29% and 44%, respectively, and cyanobacterial OM increases to 26%.

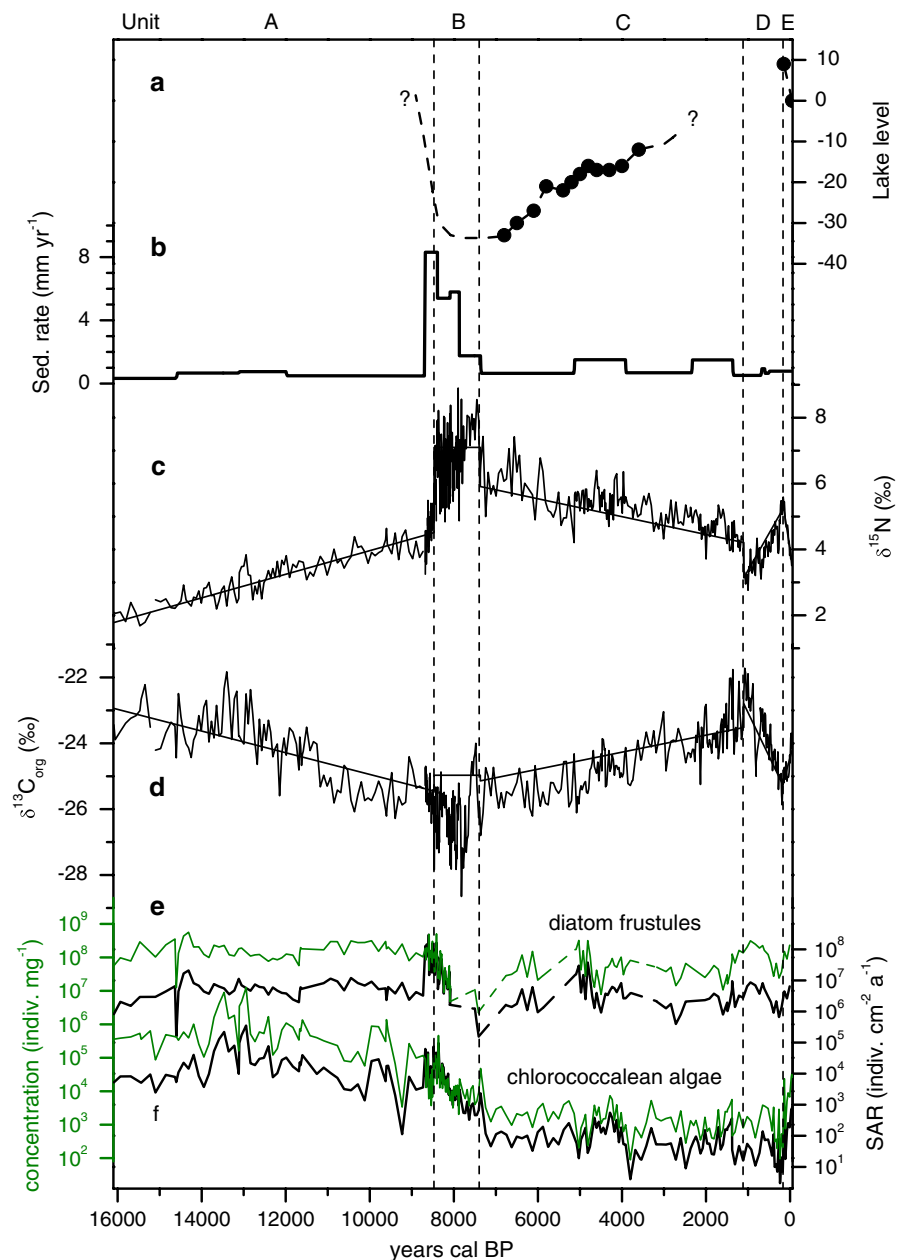
Although the geochemical datasets of OM sources used here are more extensive than in many other studies, they are still incomplete. Soils and other sources with lower $\delta^{13}\text{C}_{\text{org}}$ may exist in the catchment, and these were not sampled and analysed so far. Moreover the possibility of alteration of the original geochemical signal during deposition and early diagenesis may exist although we have no indications for this process at present. In spite of the discussed differences, however, there is in principle a high agreement between modelled and actual measured isotopic trends. The isotopic trends calculated using the input values of Table 2 reflect to a high degree the actual long-term trends in the records, with the exception of the $\delta^{13}\text{C}$ values of unit B, which are too high in the model (Fig. 9).

The modelling results can be further tested by comparison with other geochemical data and microfossil records from Laguna Potrok Aike (Fig. 9). Quantitative information about algal concentrations in the Laguna Potrok Aike sediment record comes from palynological and diatomological investigations (Wille et al. 2007). As evidenced by their resistant

cell walls, all algal palynomorphs recorded in pollen slides belong to chlorococcalean green algae with a predominance of *Pediastrum kawraiskyi* during the Late Glacial and the Early Holocene and *Botryococcus* cf. *braunii* and *Pediastrum boryanum* occurring in lower amounts (Wille et al. 2007). Algal palynomorph concentrations are extremely high (up to 2.3×10^6 counts per ml sediment) in the Late Glacial and the Early Holocene (unit A) and decrease substantially at about the same time when sedimentation rates increase drastically around 8470 cal. yrs BP (Fig. 9). Thereafter, algal palynomorph concentration remains low and never exceeds 8.8×10^3 individuals per ml. Similar to algal palynomorph amounts, diatom concentrations are high throughout the Late Glacial and the Early Holocene (up to 5.6×10^8 frustules per mg) and decrease rapidly around 8400 cal. yrs BP to concentrations as low as 2.1×10^6 frustules per mg (Fig. 9). Unlike algal palynomorphs, however, diatom concentration recovers until 6700 cal. yrs BP at latest (2.8×10^7 frustules per mg) and remains high with fluctuations.

The results of microfossil quantifications confirm our interpretations based upon TOC/TN values and isotopic data. In units A and C, diatom concentrations are rather high (on average 1.7×10^8 frustules per mg in unit A and 0.9×10^8 frustules per mg in unit C) and agree with the inference from isotopic fingerprints that diatomaceous ooze is one of the most important OM constituent during all periods, except of unit B. Decreasing algal concentration (both diatoms and chlorococcalean green algae) between 8400 and 7400 cal. yrs BP (unit B) is consistent with a high OM input from lake-external sources (i.e., soils). Sediment accumulation rates (SAR) for both diatom frustules and algal palynomorphs belonging to chlorococcalean green algae were calculated to determine whether algal productivity actually decreased in unit B or lower diatom concentrations reflect dilution due to higher rates of sedimentation from external sources. These data (Fig. 9) imply that diatom productivity in the first half of unit B was even higher than before and therefore almost complete absence of diatom OM and other sources during unit B is likely caused by dilution effects. In fact the sedimentation rate is more than ten-fold higher during the deposition of unit B than during the preceding unit (Fig. 9), supporting a dilution effect.

Fig. 9 Lake level variations (a), sedimentation rate (b), $\delta^{15}\text{N}$ values (c), $\delta^{13}\text{C}_{\text{org}}$ values (d) and algal microfossil records (e, f) of the sediment record from the centre of Laguna Potrok Aike (compiled from cores PTA02/4, PTA03/12, PTA03/13). Confirmed lake-level stands given in meters above or below present-day lake level are ascertained from seismic investigations and radiocarbon dated lake-level terraces (Haberzettl et al. 2005, 2008; Anselmetti et al. in press) and given as bold lines. Dashed lines give assumed lake levels with no accurate dating (Anselmetti et al., in press). Modelled isotope values from mixing lines in Fig. 8 are shown as thin lines in the isotope curves. Diatom and algal palynomorph concentrations (green curves) and their accumulation rates (SAR, black curves) base on microfossil counts presented in Wille et al. (2007) in detail. Major gaps in the diatom concentration due to missing data are given as dashed lines. Time intervals of units A–E are given on top. For further explanations see text



At first sight, the Rock Eval analyses seem to disagree with the OM composition inferred from TOC/TN, isotopic and microfossil records. None of the data points in Fig. 7a plot close to the type I pathway, which originally was referred to as lipid-rich kerogen of lacustrine environments with high HI and low OI such as algal and microbial material (Tissot and Welte 1978). The HI values typify kerogens of all units of the Laguna Potrok Aike record either as type III or as a mixture of type II

and III. Type II kerogens were originally related to marine sediments with contributions of OM derived from phytoplankton, zooplankton and microorganisms, whereas type III kerogen was related to terrestrial vascular plants (Tissot and Welte 1978). However, this original classification established for mature rocks may not be valid for young Quaternary sediments. More recent publications (Meyers and Teranes 2001; Lüniger and Schwark 2002) suggest that HI values of 250–600 mg HC/g TOC (and thus

type II kerogen) are characteristic of immature Quaternary lacustrine kerogen of algal origin. Following these approaches, the sedimentary kerogens of Laguna Potrok Aike are of vascular plant origin (type III) or a mixture between vascular plants and algal OM (type II). The S_2 versus TOC plot (Fig. 7b) clearly shows an increase of type II kerogen with rising TOC. Accordingly, type II kerogens would predominate in sections with high TOC, especially in unit A. This is in partial agreement to the results obtained from the two-isotope modelling approach used to characterize OM composition. As outlined above, these results imply a predominance of diatom OM in the upper parts of unit A and D.

Discrepancies between OM composition inferred from Rock Eval analysis and other methods can be related also to alterations of HI and OI values during and after deposition. Organic matter oxidation decreases the hydrogen content of hydrocarbon-rich material such as algal OM and increases its oxygen content (Meyers and Teranes 2001). Changes in water depth or lake circulation may have caused variable oxygenation of profundal zones. For example, some of the major HI variations in the sediment record of Lake Malawi were attributed to periodic oxygenation at the lake floor (Filippi and Talbot 2005). A trend towards lower Fe/Mn ratios in the Early Holocene was interpreted as the result of a prevalence of more oxic conditions at the bottom of Laguna Potrok Aike during this period (Haberzettl et al. 2007), which is in agreement with lower corrected HI values in unit C than in units A and B (Fig. 6b). A plausible explanation for a higher oxygenation of the lake bottom during the Early Holocene at Laguna Potrok Aike is an enhanced lake circulation pattern induced by more wind stress. An intensification of the Southern Hemispheric Westerlies is evidenced for the Holocene at various places in southernmost South America (Lamy et al. 2001; Jenny et al. 2003; Gilli et al. 2005). At Laguna Potrok Aike, the increase of allochthonous pollen input from Andean forests suggests that an intensification to modern wind conditions started at 9200 cal. yrs BP (Mayr et al. 2007), i.e., shortly before the beginning of sedimentary unit B. These changes in wind intensities may have affected the mixing of the lake and thus oxic conditions at the lake bottom. For that reason, Rock Eval data of original OM sedimentary sources of Laguna Potrok Aike may have been

modified by varying oxidation due to changes in the mixing conditions of the lake.

Linkages between OM composition and hydrological changes

The TOC/TN ratios and isotope variations of the short core PTA02/4 from Laguna Potrok Aike that covers the last 1600 years of the much longer record presented here were previously interpreted as changes in the mixture between aquatic macrophyte and algal OM (Haberzettl et al. 2005). These parameters were then used as proxy for shoreline proximity. Enhanced input of OM from aquatic macrophytes was thought to take place preferentially during low lake levels, because then their shallow-water habitats advance towards the coring location (Haberzettl et al. 2005). Radiocarbon-dated, outcropping lacustrine deposits supported this hypothesis. Mammal bones deposited in fluvio-lacustrine sediments exposed up to 9 m above present lake level were dated to AD 1670–1965 and point to a high lake-level stand during a period probably time-equivalent to the “Little Ice Age” in the Northern Hemisphere (Haberzettl et al. 2005).

The new isotope model that considers two more OM sources allows a more differentiated reconstruction of OM deposition processes in the lake. Contemporary to the most recent highstand, the sediment OM of the central core reveals $\delta^{15}\text{N}$, $\delta^{13}\text{C}_{\text{org}}$ and TOC/TN values which are in the range of diatomaceous organic matter with some admixture of soil organic matter. Immediately before (1650–570 cal. yrs BP), isotopic and TOC/TN data point to a relatively higher amounts of aquatic macrophyte debris and cyanobacterial OM admixed to diatomaceous and soil OM. Based also on other proxies (mainly inorganic carbon contents and Ti), this interval was attributed to a dry period (“Medieval Climate Anomaly”, MCA; Haberzettl et al. 2005). However, a period with a much more pronounced low lake-level stand has been substantiated recently by radiocarbon dates and seismic investigations (Haberzettl et al. 2008; Anselmetti et al., in press) outranging the MCA lake level lowstand at Laguna Potrok Aike by far. An unconformity was detected basin-wide by seismic investigations. It forms a terrace level about 30 m below the present-day lake level at the coring site of PTA03/6 (Haberzettl et al.

2008). A minimum age for this extremely low lake level was derived from correlations between seismic profiles and radiocarbon-dated sediment cores. Accordingly, the extreme low lake-level stand occurred shortly before 6790 cal. yrs BP, as continuous sedimentation on the lake-level terrace commenced during that time (Haberzettl et al. 2008). Notably, in the core from the lake centre a section of 6.5 m was deposited in only about 1400 years in the period 8700–7300 cal. yrs BP representing the phase of extremely high sedimentation rates. Probably this period reflects the time with the lowest lake level stand and intensified soil erosion from the crater slopes. Increased soil OM input coincides with markedly higher sedimentation rates and high Ti concentrations, a measure of allochthonous sediment input (Haberzettl et al. 2007; Mayr et al. 2007) during this time interval (Fig. 9). Most likely, the period of the extreme low lake-level stand therefore corresponds to the geochemically characterized unit B discussed here, in which soil OM predominates, whereas contributions from other OM sources, in particular aquatic macrophytes and cyanobacteria, were negligibly low due to dilution effects.

Probably extremely dry conditions prevailed during the low lake-level stand and the vegetation cover was thinned supporting erosion of soils by wind and surface runoff. Moreover, a lower lake level could have resulted in deeper incisions of the episodic creeks during sporadic heavy rainfalls which would carry eroded soil material into the lake. Thus, the anomalously high $\delta^{15}\text{N}$ signatures of unit B could provide information about the timing and exact duration of this extreme period. Accordingly, the driest probable period during the Holocene in the catchment area of Laguna Potrok Aike occurred from about 8500 to 7400 cal. yrs BP.

One reason for this drought period could have been the already mentioned increase in west wind strength. The lowermost lake level occurs within a period of maximum west wind intensity as suggested by enhanced deposition of long-distance transported Andean forest pollen (Mayr et al. 2007). Additionally, enhanced wave erosion could have contributed eroded littoral material to the lake during the formation of the presently submerged lake level terrace. These eroded lacustrine sediments were predominantly of Last-Glacial age and had different

OM origin and geochemical signatures (Haberzettl et al. 2008). It can be assumed that the reworked material mixed with currently produced algal OM and eroded soil and finally was redeposited in the lake centre as illustrated also in the extreme sedimentation rates during this period (Fig. 9). The deposition of older carbon from soils and re-worked lacustrine deposits is manifested in radiocarbon age reversals detected for this section (Haberzettl et al. 2007).

The assumption of Haberzettl et al. (2005) of predominance of algal OM in the Laguna Potrok Aike record during comparatively wet phases may still be valid given the new data from the much longer record. However, the sedimentary composition is more complex than previously assumed and cannot be explained by two-end-member mixing models alone. Moreover, sedimentary responses to drier climatic conditions apparently were different during the previously inferred MCA than during the inferred extremely dry period between 8500 and 7400 cal. yrs BP.

An extensive discussion about the likely reasons for changes in the proportions of OM from cyanobacteria versus diatoms goes beyond the scope of this article. Nevertheless it should be mentioned that changes in the nutrient budget or depositional processes may be responsible for these long-term shifts. Regarding the first argument, a main factor determining whether cyanobacteria, algae or aquatic macrophytes dominate in a lake is nutrient availability (Tilman et al. 1982; Vitousek and Howarth 1991). Nitrogen rather than phosphorus is apparently limiting phytoplankton growth in present-day Laguna Potrok Aike (Zolitschka et al. 2006). Nitrogen-fixing cyanobacteria have a competitive advantage over non-fixing phytoplankton organisms under such low N/P conditions as in Laguna Potrok Aike (Tilman et al. 1982). Nitrogen fixation itself can be limited by supply of other nutrients and energetic, ecological and physical constraints (Vitousek and Howarth 1991). At Laguna Potrok Aike, nitrogen limitation may be coupled to N-influx from external sources and variable extents of dust deposition, surface inflow, permanent groundwater inflow and precipitation might have had an influence on the nitrate supply to the lake. Additionally, short-term lake-level fluctuations due to rapid hydrological changes might have supplied varying amounts of

aquatic macrophyte/cyanobacterial versus algal OM. The presence of aquatic macrophyte OM for certain sediment sections could be explained by rapidly falling lake levels, which can cause massive mortality among aquatic macrophytes or even their complete extinction at respective depth levels, as reported for a shallow tropical lake (Havens et al. 2001). On the other hand, light attenuation due to enhanced phytoplankton growth (Krause-Jensen and Sand-Jensen 1998) and generally high loads of suspended particles can further diminish aquatic macrophyte populations for longer periods (Schelske et al. 1995; Kenney et al. 2002). However, which of these factors indeed played a role for variations of OM composition in Laguna Potrok Aike remains the object for further studies.

Conclusion

The applied geochemical fingerprint approach and the correlation patterns of isotopic and geochemical data have demonstrated that the sediments of Laguna Potrok Aike consist mainly of diatom and soil OM with varying contributions of other OM sources during the last 16,100 years with the exception of the period between 8470 and 7400 cal yrs BP. More extensive investigations of the geochemical signatures of potential OM sources and inter-core comparisons suggest that, apart from diatoms, aquatic macrophytes, cyanobacteria and soil OM contribute to bulk OM to various extents at different time intervals. Between 16,100 and 8470 cal. yrs BP (unit A) trends towards gradually increasing $\delta^{15}\text{N}$ and decreasing $\delta^{13}\text{C}_{\text{org}}$ and TOC/TN values indicate a decrease of the OM fraction from cyanobacteria and a relative increase of diatoms. Thereafter, the nitrogen isotope composition of sediments deposited between 8400 and 7400 cal. yrs BP (unit B) implies increased input of soil OM during an extreme lake level lowstand. After 7400 cal. yrs BP generally decreasing $\delta^{15}\text{N}$ values and increasing $\delta^{13}\text{C}_{\text{org}}$ and TOC/TN values reflect a gradual decrease of soil OM deposition and relatively constant diatom OM deposition, but increasing contributions of cyanobacterial and to a lesser extent aquatic macrophyte OM. The last 1100 years are exceptional, because isotopic trends are reversed with regard to the period before, whereas TOC/TN ratios show no change. For that period

increases in diatomaceous and soil OM in the isotope mixing model reflect the response to a rising lake level culminating in the high lake-level stand during the so-called Little Ice Age. It was further demonstrated that the sediment cores from the submerged lake-level terrace in 30 m water depth and from the central basin exhibit similar isotopic and TOC/TN variations after the Mid-Holocene low lake level. This highlights the potential to synchronize isotopic variations in sediment cores basin-wide as has been demonstrated before at the smaller Patagonian lake of Laguna Azul (Mayr et al. 2005).

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