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Fifty years of eutrophication and lake restoration reflected in sedimentary carbon and nitrogen isotopes of a small, hardwater lake (South Germany)

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ABSTRACT

This study analyses the response of the carbon and nitrogen isotopic composition of sedimentary organic matter to rapid human-induced eutrophication and meromixis as well as subsequent restoration efforts [in-lake phosphorus (P)-Precipitation, P-remediation of the well inflow and multiannual destratification] in a 46-yr sediment core sequence (1963-2009) from Fischkaltersee, a small hard-water lake (S-Germany). In addition, the sediment record was compared with detailed data on water column chemistry during almost (1977-2009) the recorded history of eutrophication and trophic recovery of the named lake. While the onset of eutrophication resulted in an abrupt positive excursion (+2.4‰), the overall reaction of $\delta^{13}C_{SOM}$ *to ongoing eutrophication and meromixis as well as to permanent hypolimnion aeration and trophic recovery is a continous negative trend (-3.7‰) with the most depleted signatures (-38.8‰) present in the youngest part of the core. This negative trend was not influenced by multiannual hypolimnion aeration, which although oxygenating bottom waters (>2 mg* O_2 L^{-1}*), did not reverse the increasing anoxis in the sediment, as is indicated by an declining Mn/Fe ratio. Hence, we conclude that in Fischkaltersee* $\delta^{13}C_{SOM}$ *was controlled by photoautotrophic input only during an early phase in the eutrophication process. The signal of intensifying microbially mediated carbon cycling processes in the sediment,* i.e. *methanogenesis and methanotrophy, was superimposed on the primary productivity signal by crossing a certain TP threshold (approx. TP=0.04 mg* L^{-1}*). Sedimentary* $\delta^{15}N$ *values exhibit an overall increase (+3.4‰) in reaction to the eutrophication process, while trophic recovery produces a continous decrease in the signal (-2.7‰). Linear correlation of* $\delta^{15}N$ *to nitrate utilisation in the epilimnion, however, is rather weak (*R^2*=0.33). Comparison between sediment* $\delta^{15}N$ *values and water column data reveals that two negative shifts in the isotopic signal (-1‰/-0.6‰) around 1980 and 1984 respectively, can be attributed to the existence of significant amounts of ammonium (up to 2 mg* L^{-1}*) in the trophogenic zone. Coincident drops in nitrate utilisation (-20%/-53%) indicate phytoplankton assimilation of ammonium. As the artificial aeration did also not affect* $\delta^{15}N$*, we conclude that water column denitrification never contributed significantly to the sedimentary N isotope signal.*

Key words: $\delta^{13}C_{SOM}$*,* $\delta^{15}N$*, lacustrine organic matter, methanogenesis, denitrification, osterseen.*

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INTRODUCTION

Investigations of the carbon as well as the nitrogen isotopic composition of autochthonous organic matter have become standard tools for the reconstruction of lacustrine paleoproductivity (Hodell and Schelske, 1998; Brenner *et al*., 1999; Meyers, 2006; Drew *et al.,* 2008) as the combined analysis of the stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) of sediment organic matter (SOM) also offers the potential to identify organic matter (OM) sources (Mayr *et al*., 2005) or to reconstruct changes in the nutrient cycling (Heyng *et al*., 2012). Phytoplankton preferentially incorporates the lighter carbon isotope ^{12}C during assimilation (Farquhar *et al*., 1989). The resulting enrichment of ^{13}C in the dissolved inorganic carbon (DIC) pool in the surface water is proportional to the intensity of primary productivity. It is recorded in the biomass produced and deposited in the sediment thereafter (Teranes and Bernasconi, 2005). Primary productivity can be the dominant control of $\delta^{13}C_{SOM}$, therefore the latter has been widely used as a proxy indicator of eutrophication processes (McKenzie, 1985; Hollander and McKenzie, 1991; Brenner *et al*., 1999).

Marine studies (Sigman *et al*., 1999) revealed a strong relationship between the $\delta^{15}N$ values of SOM and the degree of surface water nitrate (NO_3^-) utilisation (thus, the intensity of primary productivity as well). This correlation seems to be somewhat weaker in lacustrine environments, as here the factor limiting primary productivity often is phosphorus rather than nitrogen (Wetzel, 2001), thus a sufficient consumption of the surface water N pool is the exception. When only a minor part of the dissolved inorganic nitrogen (DIN) pool of the surface water is consumed, its N isotopic composition will remain largely unaltered and an intensifying primary production will not be reflected in a corresponding increase in $\delta^{15}N_{SOM}$ (Teranes and Bernasconi, 2000).

Nevertheless, several studies proved the significance of a primary productivity effect on $\delta^{15}N_{SOM}$ in lacustrine environments (Teranes and Bernasconi, 2000; Talbot, 2001). However, the interpretation of $\delta^{13}C$ and $\delta^{15}N$ of SOM in terms of paleoproductivity can be complicated by a variety of processes in the rather complex lacustrine C- and N-cycles that can also have a strong impact on the C and N stable isotope ratios of SOM but are not necessarily correlated to the intensity of primary productivity. Antropogenically induced eutrophication often produces anaerobic conditions in the bottom waters and in the sediment which promote the intensification of microbially mediated processes. For instance, the formation (methanogenesis) and oxidation (methanotrophy) of methane as well as denitrification have the potential to impart strong changes in the isotopic signal of $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$, respectively (Finlay and Kendall, 2007), as the isotope fractionation effects associated with these processes are pronounced. This is obvious for microbial methane (-110‰ to -50‰; Whiticar, 1999), which is produced in enormous amounts in strictly anoxic zones of the water column or sediment (Nitzsche *et al*., 2009). Subsequently, a large part of this methane can be oxidized in the overlying oxic water layers, and thus be re-integrated into the epilimnetic DIC pool. As well, the microbial biomass itself can have a significant effect on the carbon isotopic signature of SOM, as bacterial OM and its metabolites are strongly depleted in ^{13}C (Whiticar, 1999).

Denitrification on the other hand, which is also a bacterially mediated process and essentially dependent on anoxic conditions, produces considerable enrichment of ^{15}N in the remaining DIN pool, as during the reduction of nitrate NO_3^- to nitrous oxide NO_2 and dinitrogen N_2, the forms of nitrogen bearing the lighter isotope ^{14}N are consumed more rapidly. In marine studies, the associated isotope effects ranged between +20‰ and +30‰ (Granger *et al*., 2008). Thus, dependent on the extent of anoxis in a lake, denitrification can be an important influence on $\delta^{15}N_{SOM}$, thus masking the effect of primary productivity.

Moreover, it is well known that the isotopic composition of the DIN pool can be significantly altered by the signal of external N loading to the lake, which is especially true for anthropogenically eutrophicated systems, as sewage and agricultural runoff can be considerably enriched in $\delta^{15}N$ (Talbot, 2001). Considering these processes, detailed knowledge about the biogeochemical conditions in the water column during the entire process of eutrophication is essential for studies of paleoproductivity based on $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$. In many cases such information is not available or has to be inferred from other proxy indicators, which can lead to inappropiate conclusions.

Therefore, field studies are needed to test the possible impact of these processes on $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$ by comparing detailed water column data with the sediment record produced during the same time period, which ideally should consist of all stages of anthropogenically induced eutrophication and also trophic recovery of a lake. As complete records containing both detailed sediment and water column data of the eutrophication process of a single lake are rare, this can also be achieved by applying a space-for-time approach, where recent sediment depositions of different lakes spanning a broad range of trophic stages are compared (Woodward *et al*., 2012).

In this study, we report on the effect of a period (ca. 46 yrs) of severe eutrophication as well as subsequent restoration measures on the sedimentary isotope signatures $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$ in Fischkaltersee, a small pre-Alpine hardwater lake in Bavaria, southern Germany. The main advantage of the site is the detailed knowledge about the lake chemistry during the various highly invasive restoration approaches. The latter were initated in reaction to the rather fast anthropogenically induced eutrophication of Fischkaltersee and consisted of chemical P-precipitation, followed by multiannual permanent and afterwards a period of intermittent destratification. Thus we are able to examine the effects of these lake restoration attempts in great detail both for the water column as well as for the sediment. This study might also be of relevance for the interpretation of sedimentary isotope values in terms of natural eutrophication.

METHODS

Site description

Fischkaltersee (47°46'52.54" N, 11°19'21.00" W) is a small head lake of a side chain of the pre-Alpine lake district Osterseen located in Bavaria, southern Germany (Fig. 1). Morphometric characteristics of Fischkaltersee are given in Tab. 1. The main surface inflow to the carbonate-rich kettle lake is an adjacent surface groundwater well with a mean delivery rate of ca. 5 L s^{-1} (Steinberg and Niesslbeck, 1981). Runoff from an agricultural area and increasing local sewage disposal in the nearby village of Staltach which both drained to the catchment of the well (Steinberg and Zimmermann, 1988) resulted in an rapid increase in trophic level starting in 1970 (Melzer, 1976; Steinberg and Fischer, 1982). However, ongoing investigations of a neighbouring lake in the side chain indi-

Tab. 1. Morphometric and hydrologic data of lake Fischkaltersee.

Surface area	0.034 km^2
Max. depth	11.2 m
Mean depth	5.7 m
Volume	1.8×10^5 m^3
Drainage area	0.3 km^3
Theoretical water retention time	143 d

cate that the original trophic state of those lakes might have been already altered by the mid of the 20th century (Braig, unpublished results).

In 1974, when the concentration of total phosphorus (TP) in the well water was 279 μg L^{-1}, Fischkaltersee had already become eutrophic with TP=40 μg L^{-1} and an periodically anaerobic hypolimnion (Melzer, 1976; OECD, 1982), but remained dimictic until 1975. From 1974 on (Steinberg and Fischer, 1982), the lake was also loaded with considerable amounts of salty water from a nearby street junction during annual snowmelt (up to 200 mg Cl$^-$ L^{-1}, Steinberg and Zimmermann, 1988). This salt load increased the stability of bottom water stratification to the point of meromixis: depth profiles of conductivity taken during the routine measurements reveal a constant mean difference of 251±76 μS cm^{-1} between bottom and surface waters until the onset of aeration. As a consequence, high concentrations of TP (2 mg L^{-1}), hydrogen sulfide H_2S (15 mg L^{-1}) and ammonium NH_4^+-N (22 mg L^{-1}) were measured in the anoxic monimolimnion of Fischkaltersee in 1979. By then, the TP input from the well had increased considerably to 450 μg L^{-1} (Steinberg and Bucksteeg, 1980) and remained high for most of the period of the following lake restoration program, as Staltach was not con-

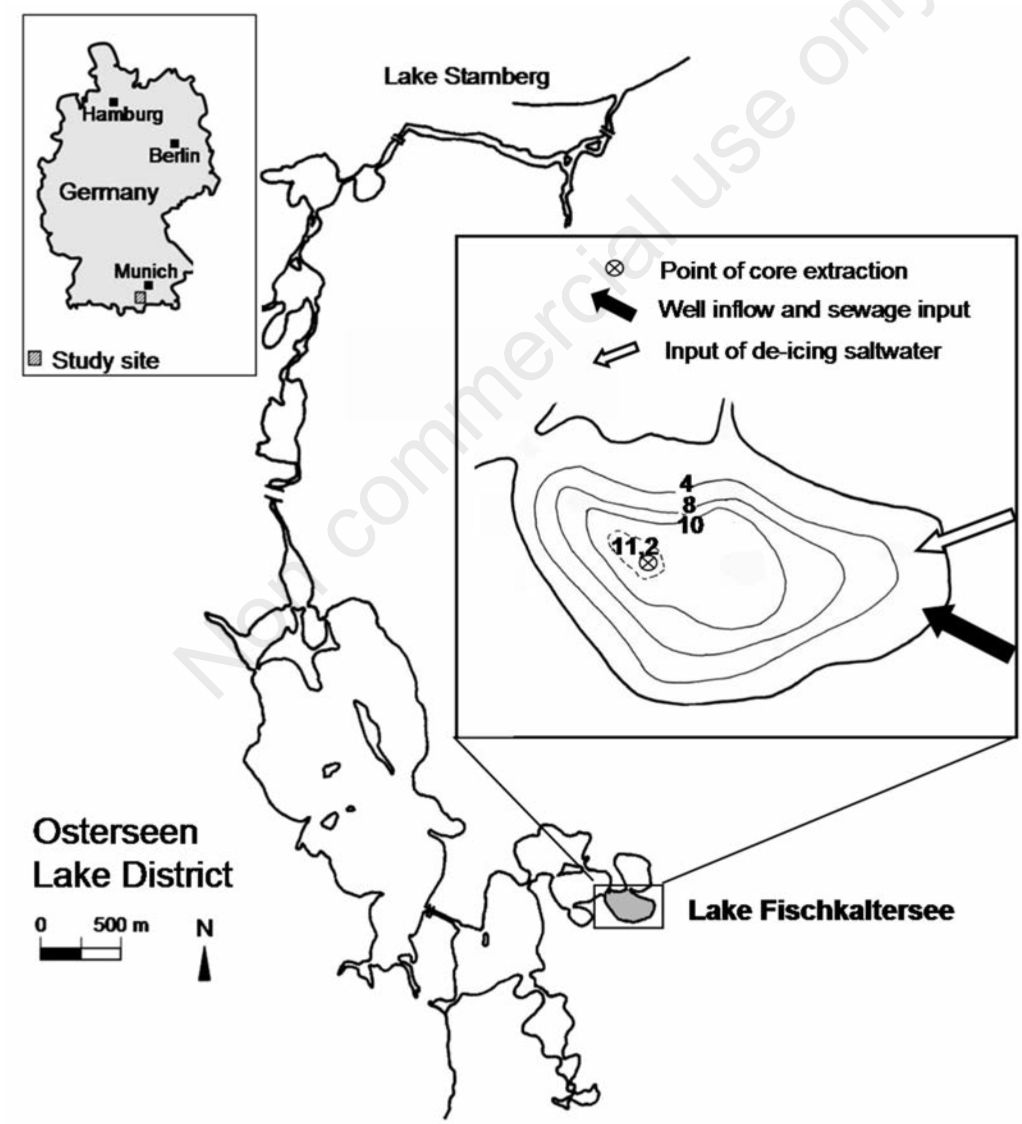

Fig. 1. Outline map of the geographic location of the Osterseen lake district and the position of the investigated lake, Fischkaltersee (grey filling). The bathymetric map shows the point of core extraction and the inflows of well water, sewage and de-icing saltwater to Fischkaltersee.

nected to a centralized sewage plant until 1981 (Steinberg and Zimmermann, 1988). In addition, considerable P-desorption from the saturated aquifer occurred afterwards (Steinberg and Zimmermann, 1988), so that TP concentrations of >100 μg L^{-1} in the trophogenic zone rendered the lake hypertrophic (OECD, 1982).

These circumstances gave reason to a scientifically motivated lake restoration program conducted and monitored by the State Office for Water Management of Munich (Steinberg and Bucksteeg, 1980). The program consisted of routine monitoring of water column parameters as well as highly invasive remediation measures. While sporadic water column data have been available since 1974, routine measurement of physical and chemical water column parameters began in 1977 and was conducted biweekly until 1993 and bimonthly until 2000. From then on, measurements were only conducted in 2005 and 2008. Remediation measures began in late December of 1979 with a phosphorus precipitation measure: Overall, 14 tons of aluminium hydroxide [$(Al_2(OH)_{3.36}Cl_{2.13}(SO_4)_{0.25}$; Steinberg and Bucksteeg, 1980] were pumped into different depths of the lake on two consecutive days, producing a continuous, 10 to 70 mm thick layer of aluminium-hydroxide-P-complex (*alumn*; Wauer, 2006) over the entire lake sediment (Steinberg and Bucksteeg, 1980; Steinberg and Fischer, 1982). At first, this measure seemed to be successful, as the concentration of TP was reduced by more than 50% in the trophogenic zone immediately after the restoration measure (Steinberg and Bucksteeg, 1980). Furthermore, the biomass of the phytoplankton was reduced by 90% via coprecipitation. However, only a few weeks after the treatment TP concentrations in the trophogenic zone rose to 50 μg L^{-1} and polytrophic phytoplankton communities developed again. To fight the algal blooms and to establish oxic, P-retaining conditions at the sediment-water interface, a system of hypolimnetic aeration was established for permanent destratification of Fischkaltersee, starting in May 1980. However, this treatment was not effective, as it resulted in a doubling of viable biomass of primary producers, a fivefold increase in plate counts of heterotrophs and also common oxygen depletion at the sediment-water interface (Steinberg and Schrimpf, 1982). The permanent destratification was maintained until 1984 and changed into an intermittent mode from 1985 onwards, as problems with phytoplankton blooms continued. In conjunction with P-restoration of the well inflow, a rhythm of 21 days of aeration followed by a break of one week, led to a continuous decrease in both TP and biomass concentrations (Steinberg and Zimmermann, 1988), so that from 1993 until 2000, aeration was only performed in spring and autumn to support natural circulation. After 2000, all remediation measures were stopped. Today, Fischkaltersee is in a mesotrophic, dimictic state with TP=29 μg L^{-1}.

Field and laboratory methods

In August 2009, a 48 cm long gravity core (FIS 8/09) was recovered from the western section of the deepest basin of Fischkaltersee (Figs. 1 and 3) using an UWITEC gravity corer. The core was stored at 4°C in the dark until further processing. In the laboratory, the core was split lengthwise in two halves that were photographed and described lithologically. Non-destructive X-ray fluorescence (XRF) scanning (Mo tube, 200-μm step size) of one split-core surface was carried out at 0.2 mm resolution with an ITRAX XRF core scanner (Cox Analytics, Mölndal, Sweden) (Lüder *et al*., 2006; Croudace *et al*., 2006). After XRF analysis, both halves of the core were sampled continuously and volumetrically in slices of 1 cm. The resulting subsamples were weighed and freeze-dried for determination of dry density and water content. Macroscopic remains of terrestrial plants were removed prior to further analyses. Subsamples of one core half were used for determination of ^{210}Pb and ^{137}Cs activity concentrations (Nehyba *et al*., 2011). Briefly, a γ-ray spectrometer equipped with a high-purity Germanium well detector (Canberra, 36.6% relative efficiency) was used to detect the activity concentrations of ^{210}Pb and ^{137}Cs. The activity of unsupported (excess) ^{210}Pb was calculated by subtracting ^{226}Ra activity, which is in equilibrium with the (supported) ^{210}Pb present in the sediment minerals, from total ^{210}Pb activity. Conventional dating models (Kirchner, 2011) did not provide concise $^{210}Pb_{excess}$ sediment chronologies covering the entire core. Thus, ages were determined in a two-step approach as follows: first, linear interpolations between reference points of known deposition date (core surface, ^{137}Cs peaks, alumn layer) resulted in estimating mean time-invariant sedimentation rates. Second, the assumption of the rates being time-invariant was checked by fitting the Constant Initional Concentration (CIC) model (Krishnaswamy *et al*., 1971) to the unsupported ^{210}Pb concentrations between the individual time markers used for interpolation. Since the CIC model assumes that that the sedimentation rate is constant, any systematic deviation with depth between measured predicted concentrations will indicate a time trend of the sedimentation rates, whereas mere scattering of measured excess ^{210}Pb around its predicted concentrations confirms that our assumption of a mean time-invariant sedimentation rate is reasonable.

Subsamples of the other core half were homogenized in a mortar prior to isotopic and elemental analysis. Prior to homogenization all macroscopic remains were removed. For determination of total nitrogen (%TN) and its isotope ratio R ($^{15}N/^{14}N$), ca. 8 mg of bulk sediment were weighed into tin capsules and combusted at 1080°C in an element analyzer (NC 2500, Carlo Erba, Milano, Italy) coupled to an isotope-ratio mass spectrometer (IRMS, DeltaPlus, Thermo-Finnigan). Prior to the analysis of total organic carbon content (%TOC) and its isotope ratio R ($^{13}C/^{12}C$) in the IRMS, subsamples of ca. 3.3 mg were weighed into silver cups and subsequently treated in situ with small (50 µL) amounts of 3% hydrochloric acid (HCl) at 80°C to remove all carbonate. This step was repeated until no further effervescence occurred. Then all samples were treated with 150 µL 20% HCl and dried for 2 h (Nieuwenhuize *et al.,* 1994; Ryba and Burgess, 2002; Kennedy *et al*., 2005). Isotope ratios R are reported as per mill in the delta notation ($\delta^{13}C/\delta^{15}N$) against the international reference standard VPDB (carbon) and AIR (nitrogen) respectively, where

$$\delta^{13}C_{sample}, \delta^{15}N_{sample}=(R_{sample}/R_{standard}-1)\times 1000$$

Precision derived from peptone standards analysed concurrently with samples is 0.10‰ (one standard deviation of >65 standards) for both $\delta^{13}C$ and $\delta^{15}N$.

Comparisons using our own sediment standard showed good agreement between $\delta^{13}C_{SOM}$ of sediment (-33.40±0.14‰) treated with this in situ carbonate removal and values produced with a rinsing procedure (-33.16±0.15‰) (Mayr *et al*., 2005). We chose the *in situ* method, as additional precaution had to be taken in removing all carbonate from this carbonate-rich (>45%) sediment samples. At such high carbonate concentrations, acid fumigation methods often fail to remove all inorganic carbon (Kennedy *et al*., 2005), which is essential for a reliable determination of $\delta^{13}C$ of SOM.

Unhomogenized subsamples from nine stratigraphic horizons were selected for diatom analysis using standard techniques (Battarbee *et al.,* 2001). Briefly, 0.2 g of dry sediment sample were immersed in cold 30% H_2O_2 for 12 h, followed by boiling in hot (80-100°C) H_2O_2 for 5 h and a final addition of potassium dichromate $K_2Cr_2O_7$ for complete oxidation of organic matter. For removal of carbonates, small drops of 30% HCl were added to the remaining material. After cooling and pH-neutralisation, the diatom-rich residue was diluted, pipetted onto microscope coverslips and allowed to dry on a warming tray prior to mounting onto cover-slides with Naphrax. A minimum of 600 diatom valves was identified per sample at 1000x magnification using a Leica DM RBE microscope with DIC optics. Identifications were based on keys by Krammer and Lange-Bertalot (1986, 1988, 1991a, 1991b). The diatom index (DI) as a reference system for trophic level and TP (Tab. 2) was calculated according to Hofmann (1993) and Schaumburg (2004). It has been developed and calibrated on several Bavarian lakes and is calculated from abundance and trophic preferences of the different taxa of bentic diatoms present in a sample, where

$$DI=\frac{\sum_{i=1}^{n} H_i\times G_i\times T_i}{\sum_{i=1}^{n} H_i\times G_i} \qquad \text{(eq. 1)}$$

with H_i= relative abundance of taxon i, G_i= weighting factor for indicator quality of taxon i, T_i= trophic index of taxon i.

From the comprehensive water column dataset produced during the lake restoration program, the following physical and chemical parameters were selected and are presented as four values per year where available:

TP, concentration of chlorophyll a (Chl a), bottom water temperature (T_{11m}), oxygen content in 0 m and 11 m depth ($O_{2\ 0m,\ 11m}$), nitrate-N concentration in 0 m and 11m depth (NO_3^--$N_{\ 0m,\ 11m}$), ammonium-N concentration in 0 m and 11 m depth (NH_4^+-$N_{\ 0m,\ 11m}$). TP and Chl a were calculated as a whole lake average applying a volume weighted function to the respective concentrations in the individual depths. The degree of NO_3^- utilisation in the phototrophic zone NO_3^- utilisation was calculated as the relative depletion of NO_3^--N in 0 m depth within each annual productivity cycle (Lehmann *et al*., 2004):

$$NO_3^-\ \text{utilisation}=\{1-([NO_3^--N]_{min}/[NO_3^--N]_{max})\}\times 100 \qquad \text{(eq. 2)}$$

Dissolved inorganic nitrogen DIN-N was also calcu-

Tab. 2. Diatom index (Hofmann, 1993) and ascribed trophic state *vs.* approx. TP corridors (OECD, 1982).

Diatom index	trophic state	TP (OECD, 1982)
1.00-1.99	oligotrophic	>0.01 mg L^{-1}
2.00-2.49	oligo-mesotrophic	
2.50-3.49	mesotrophic	0.01-0.035 mg L^{-1}
3.50-3.99	meso-eutrophic	
4.00-5.00	eutrophic	0.035-0.1 mg L^{-1}
Not defined	hypertrophic	>0.1 mg L^{-1}

lated as a whole lake average sum of the concentrations of NO_3^--N and NH_4^+-N. All figures were produced with the program OriginPro 8.5 (OriginLab).

RESULTS

Chronology

The chronology for FIS 8/09 based on activity concentrations ^{137}Cs and the alumn layer as a chronological mark is shown in Fig. 2. First, a tentative core chronology was inferred from the ^{137}Cs tracer by linear interpolation between reference points of known deposition date, *i.e.* core surface, alumn layer and the two ^{137}Cs peaks in 1963 (weapons testing) and 1986 (Chernobyl accident). While the ^{137}Cs peak (808 Bq kg^{-1}, 26-27 cm) above the alumn layer (1980) clearly can be attributed to the fall-out of the Chernobyl accident in May 1986, the first rise of ^{137}Cs activity concentration is much smaller (73.4 Bq kg^{-1}) and located in the lowermost sample which raises some doubt in its significance. However, the ratio of the peak concen-

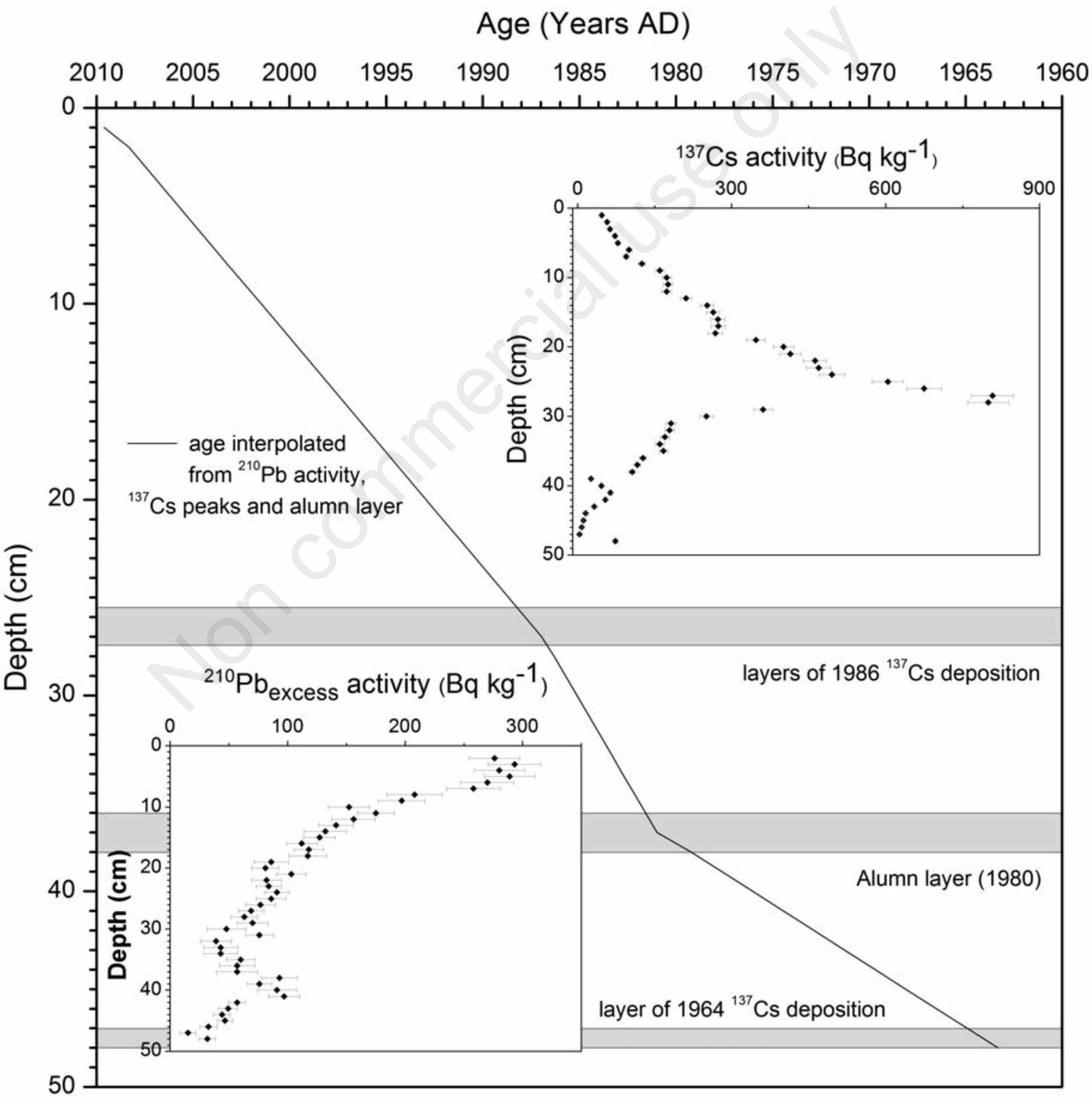

Fig. 2. Age-depth model for core FIS 8/09 based on linear interpolation between reference points of known deposition date: core surface (0-1 cm, 2009), alumn layer (36-37.5 cm, 1980) and layers of ^{137}Cs deposition (47-48 cm, 1963; 26-27 cm; 1986). Detail graphs show the depth distribution of ^{137}Cs (above) and $^{210}Pb_{excess}$ (below) activity in the core FIS 8/09. Error bars indicate two standard deviations.

trations of about 11:1 confirms that the lower peak originates from the weapons fallout maximum, since it rather accurately reflects the ratio of deposition rates of both events: integrating the Chernobyl derived ^{137}Cs present in the core gives a total deposition of 28.5±1.5 kBq m^{-2} (decay corrected to May 1986), compared to the average atomic weapons fallout deposition of about 3 kBq m^{-2} in Germany (UNSCEAR, 2000).

Interpreting the ^{210}Pb activity profile is not straightforward. Application of the Constant Rate of Supply (CRS) model, which allows for varying sedimentation rates, requires the total excess ^{210}Pb inventory of a core which is not available. The Constant Initial Concentration (CIC) model, which assumes time-invariant sedimentation rates, fits very well to the activity profile measured, if the 0-16 cm and the 16-49 cm sections are evaluated separately, indicating a change in the sedimentation regime at this depth. For the 0-16 cm section, however, a ^{210}Pb based chronology is in conflict with the reference points of known deposition date, and thus must be judged as unreliable. In contrast, the ^{210}Pb based sedimentation rate derived from the lower core section is in close agreement with its ^{137}Cs based value. This not only confirms our ^{137}Cs based chronology, but also its assumption of a time-invariant sedimentation rate. With the alumn layer as time reference, the ^{210}Pb chronology derived from the lower core section assigns the year 1995±2.6 to the change in the ^{210}Pb sedimentation regime. This agrees well with the time of a major change in lake treatment (stop of aeration in 1993) which may have influenced the ^{210}Pb geochemistry in the lake. Our chronology results in a total core age of ~46 a, so the sediment contained in FIS 8/09 covers the entire eutrophication history described here, which is supported also by the obtained core data (*e.g.* diatoms).

Core lithology, X-ray fluorescence data and lake history phases

The most prominent feature of the core FIS 8/09 is the translucent, colloidal layer of very high water content (89%) in 36-37.5 cm depth (Fig. 3), compared to an average of 77% in the rest of the core. It is the layer of the alumn-phosphorus complex deposited during the artificial P-precipitation in December 1979, which is confirmed by coincident peaks of Al- and P-counts from XRF scans (Supplementary material). This layer was also attributed to the P precipitation event in an earlier sediment study of Fischkaltersee conducted one year after the restoration measure (Steinberg and Fischer, 1982). Therefore, it represents a chronostratigraphic marker layer dividing the core into a homogenous upper and a more heterogenous lower zone (Fig. 3). The homogenous upper part of the core (0-36 cm) consists of brownish-grey silts of high water content and with many macroscopic pores. These silts are interrupted by weak, irregular carbonate concretions and macroscopic plant remains. The zone directly below the alumn-layer is composed of several alternating laminae of brown-beige and light-grey silt (37.5-40.5 cm). The homogenous lower part (40.5-48 cm) of FIS 8/09 consists of light-grey, fine-grained silt. High Ca-counts derived from XRF-scans indicate carbonate contents significantly higher than in the upper zone (Fig. 3).

Based on the well-known history of eutrophication, restoration efforts and the chronology introduced above, both water column data and sediment proxies can be subdivided into six phases (Figs. 3, 4, 5):

A) 1963-1976 early eutrophication
B) 1976-1980 eutrophication and meromixis
C) 1980-1984 P-precipitation and permanent destratification
D) 1985-1993 intermittent destratification
E) 1993-2000 aided circulation
F) 2000-2009 no restoration measures

Comparison between water column data and sediment proxies

Since routine measurements did not begin until 1977, water column data (Fig. 4) for phase A (1963-1976) is scarce. Available data show an increase in TP around 1975 (0.035 to 0.045 mg L^{-1}) and comparatively moderate NH_4^+-N concentrations in the hypolimnion (max. 0.21 mg L^{-1}), which was still oxic in February 1975 (73% oxygen saturation).

In the sediment proxy record (Fig. 5), phase A is characterised by a minor increase of the DI (2.5 to 2.9) indicating an change in trophic state from almost oligo-mesotrophic to mesotrophic, but with values significantly lower than in the whole record following thereafter. The δ^{13}C signature remains constant until 1971, when it exhibits a sharp and isolated positive excursion (-32.7‰) which is followed by a decline reaching a plateau with more negative values (-36.5‰) until 1981. δ^{15}N rises from a low of 3.4‰ to a plateau of 4.5‰ around 1970 and reaches a peak at 1977 (6.2‰). Percentages of TOC and TN remain relatively constant (averages of 0.3% and 2.6%, respectively) until the end of phase B (1979) when there is a pronounced rise in both, followed by a continuous increase until maximum values (0.6% and 5.7%, respectively) are reached in the topmost part of the core. The TOC/TN ratio oscillates between 7.6 and 12.5 (average 10.2) without exhibiting a clear trend. The ratio of Mn/Fe is a proxy linked to oxidation/reduction processes and therefore an indicator of anoxic conditions in lake sediments (Wersin *et al.*, 1991; Zhu *et al.*, 2009). In the FIS 8/09 core, the Mn/Fe values (Fig. 5) exhibit a decline from 1969 towards the core top. Between 1983 and 1986, this otherwise continuously declining trend is interrupted by a minor increase.

In phase B (1976-1980), in which routine measurements of water column data began, concurrent peaks in TP (max. 0.178 mg L^{-1}) and Chl a (max. 122 mg L^{-1}) (Fig. 4) agree well with an expressed rise in DI indicating a change from mesotrophic to an eutrophic state (2.9 to 4.0) in the sediment core data (Fig. 5). Constant water temperature (5.6°C) as well as O_2 and NO_3^--N concentrations below detection limit at the bottom of the lake indicate a meromictic state at least from 1977 on. Most noticeable are also extreme NH_4^+ concentrations (max. 22.29 mg L^{-1} NH_4^+-N) that were detected in the monimolimnion from 1977 on and began to extend into surface waters thereafter. By then, NH_4^+ was present in the trophogenic zone in significant amounts (max. 2.06 mg L^{-1} NH_4^+-N) and surface water nitrate utilisation (NO_3^- utilisation) experienced a drop of 20%. At the same time, the positive trend of $\delta^{15}N$ exhibits a pronounced gap to a minimum (5.3‰) in 1981 (Fig. 5).

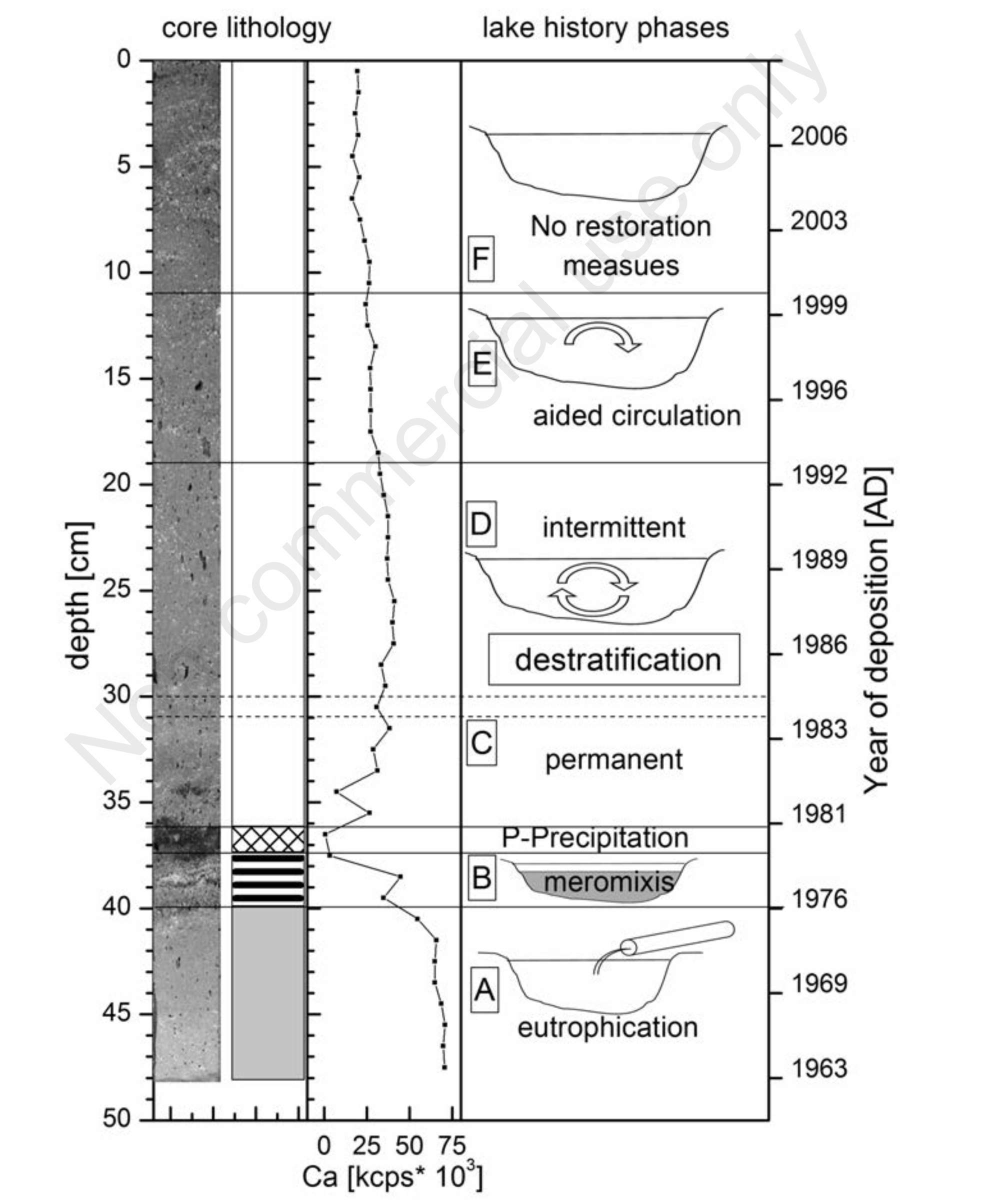

Fig. 3. Photograph of half-core surface, core lithology (left panel) and depth profile of XRF-derived Ca counts (middle panel, indicated as kilocounts per second) of core FIS 8/09. The right panel shows the corresponding phases of lake history and the years of sediment layer deposition, according to the age-depth model.

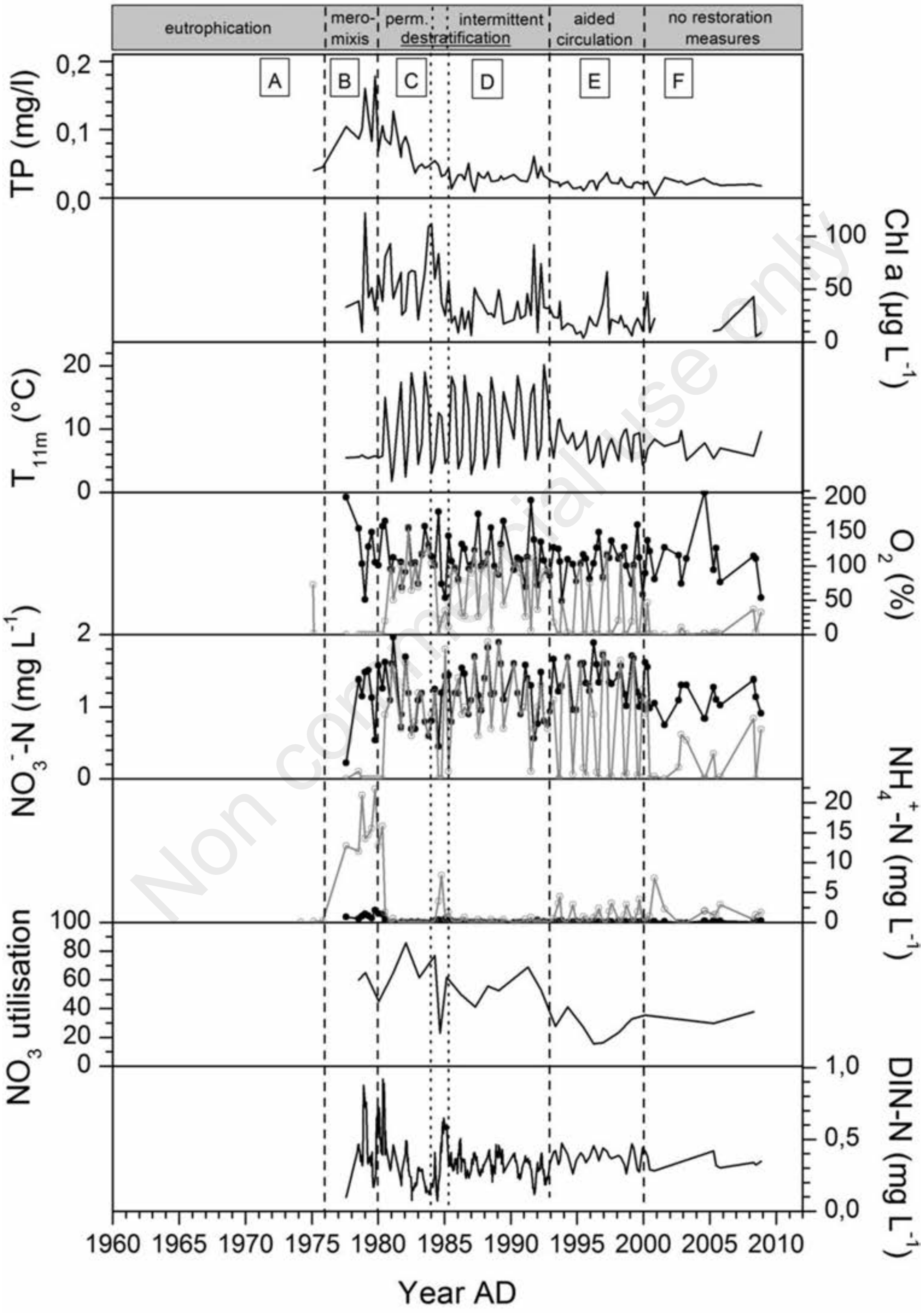

Fig. 4. Record of historic water column data containing physical (T_{11m}, O_2) and chemical (concentrations of TP, Chl a, $NO_3^-{}_{0m,\,11m}$, $NH_{4\,0m,\,11m}$, NO_3 utilisation, DIN) parameters. For O_2, NO_3^- and NH_4 closed circles and black lines represent 0 m values and open circles and grey lines 11 m values. The different phases of lake history are separated through vertical dashed lines.

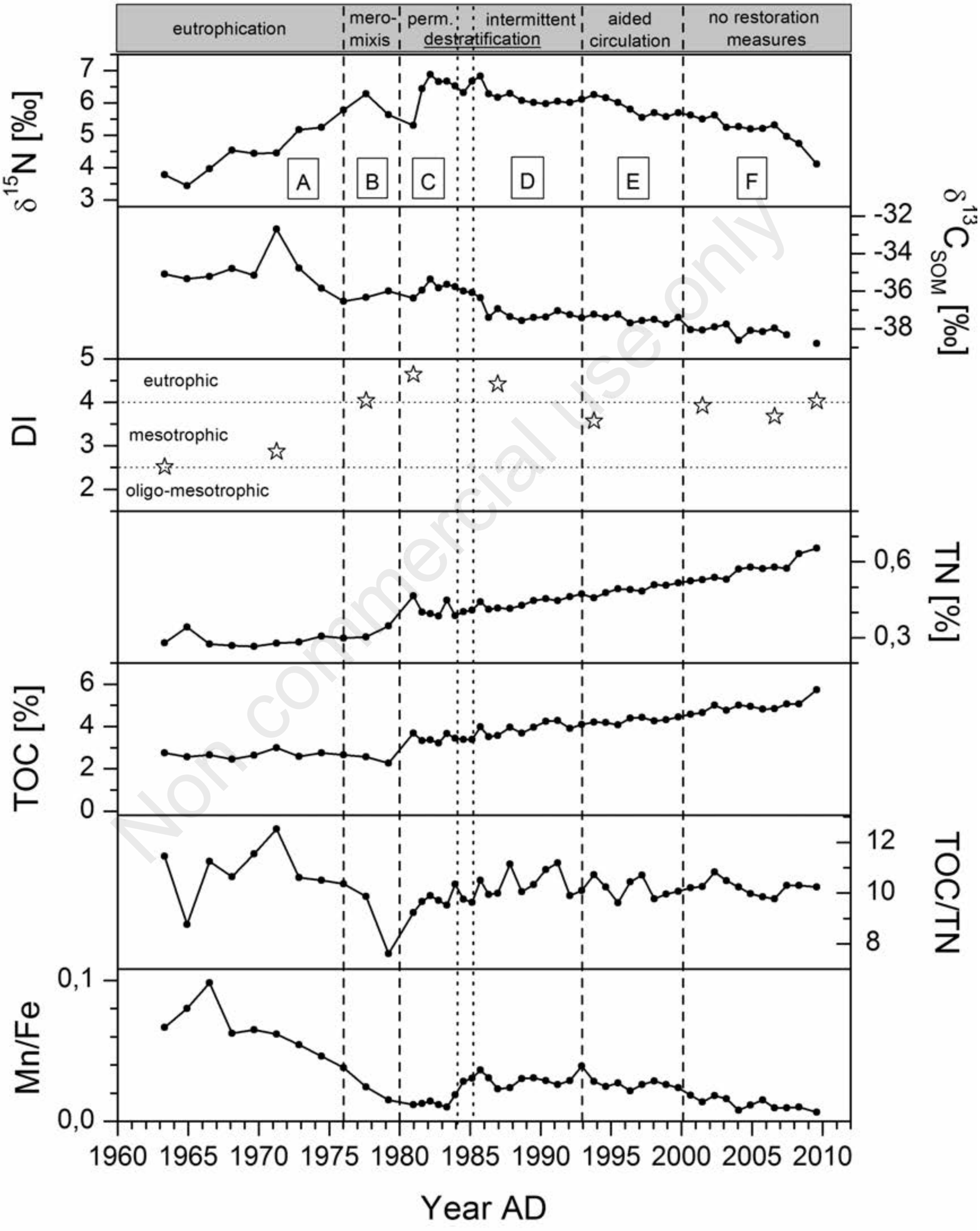

Fig. 5. Isotopical ($\delta^{15}N$, $\delta^{13}C_{SOM}$), biological (DI), geochemical (TOC, TN, TOC/TN) and XRF-derived (Mn/Fe) data of core FIS 8/09. This chrono-stratigraphic profile was produced by applying the age-depth model to the core parameters of FIS 8/09.

Core signals and water column data of phase C (1980-1984) are characterized by the impact of continuing eutrophication and the onset of restoration efforts. The P-precipitation measure in December 1979 managed to lower TP significantly (>50%), but only temporary, as 14 months later TP rose again to a maximum of 0.127 mg L^{-1}. The efficacy of the permanent destratification by hypolimnion aeration, which was initiated in April 1980, is clearly visible in the extreme seasonal variations of water temperature (1.8-19°C) at the lake bottom. As well, the O_2 concentration never fell below 50% in the whole lake from 1981 until 1984. The aeration produced an initial peak in the DIN concentration, which soon was followed by a continuous decline. Concurrent with this, there is an elimination of NH_4^+ at the lake bottom as well as in upper water layers (NH_4^+-N>0.14 mg L^{-1}) and a uniform concentration of NO_3^- in the whole water column (0.7-1.7 mg L^{-1} NO_3^--N). In phase C, $\delta^{15}N$ also rises sharply to a maximum of 6.9‰ and then declines to 6.3‰ in 1984. At the same time, the signal of $\delta^{13}C_{SOM}$ exhibits a minor increase (1.1‰) followed by a decreasing trend lasting to the core top (-38.3‰) (Fig. 5). At the end of this phase, Chl a reaches a distinct peak (112.3 mg L^{-1}), indicating expressed algal blooms, while TP decreases continuously (Fig. 4). From 1984 to 1985, aeration ceased for one year and NH_4^+ accumulated again (7.9 mg L^{-1} NH_4^+-N). Likewise, NO_3^- vanished at the lake bottom, but NO_3^- utilisation dropped from a maximum of 85% to 23%. Concurrently, there is a slight elevation in $\delta^{15}N$ (+0.5‰).

Phase D (1985-1993) follows the aeration gap and is characterized by an overall decline in Chl a concentration (61.76 to 31.73 mg L^{-1}) and DI values (4.42 to 3.57) (Figs. 4, 5). After a $\delta^{15}N$ maximum (6.8‰) in 1985, both isotope curves show a gradual decline. Still, at the end of phase D, there are concurrent peaks in Chl a (92.15 mg L^{-1}) and NO_3^- utilisation (68.75%), and despite the ongoing intermittent destratification by artificial aeration, both oxygen and nitrate concentrations in the bottom waters are often markedly lower than in surface water layers. In phase E (1993-2000), $\delta^{13}C_{SOM}$, $\delta^{15}N$, TP, DI, Chl a and NO_3^- utilisation continue their negative trend. At the lake bottom, NO_3^- vanishes and NH_4^+ concentrations rise concurrently on a seasonal time scale. The limited effect of the aided circulation is visible in a considerably lower bottom water temperature (5-10°C). In Phase F (2000-2009) all restoration measures ceased and monitoring of water column data was only conducted in 2000, 2005 and 2008. The cessation of restoration activities resulted in a depletion of oxygen in the hypolimnion. In this period, neither $\delta^{15}N$ nor DI reached their respective levels of the beginning of the record (3.4 *vs* 4.1‰ and 2.52 *vs* 4.04), while $\delta^{13}C_{SOM}$ exibits the lowest signature of the record at the core top (-38.9‰).

DISCUSSION

History of eutrophication and restoration efforts

The Fischkaltersee record offers a unique possibility to compare a well-documented history of multiple anthropogenic impact, rapid eutrophication and subsequent restoration efforts with its sedimentary imprints. The lake is part of the Osterseen lake district and most of these lakes were still in an oligotrophic state in the 1960s (Melzer, 1976). Nevertheless, some lakes might already have been affected by moderate human-induced eutrophication at that time. Ongoing investigations of an lake in close proximity of Fischkaltersee indicate that the main process of eutrophication of those lakes could have started as early as 1950. Thus, the original, oligotrophic state of Fischkaltersee might already have have been altered at the onset of the rapid eutrophication described here.

This is supported by the DI value at the core bottom, which indicates a trophic level significantly lower than in the entire record following thereafter. Melzer, who was the first to investigate the lake's limnology in 1974, described ongoing sewage inflow and a highly eutrophicated but still dimictic lake (Melzer, 1976). Later, stratigraphic investigations of the concentrations of TP, Chl a and several elements (*i.e.*, Mn, Al, Pb, Cd) in the sediment dated the onset of the rapid eutrophication described here to the early 1970s (Steinberg and Fischer, 1982) and confirmed its rather fast progression. This agrees very well with the slight elevation in DI around 1971 and its rapid increase until 1981 present in our sediment core. Therefore, the entire sedimentation of the phase before the onset of the rapid eutrophication of Fischkaltersee as well as the phase of pollution and restoration efforts following thereafter is contained in the sediment record presented here.

Because of the discharge of salty water during annual snowmelt to the lake, Fischkaltersee switched to a meromictic status in 1975 (Steinberg and Bucksteeg, 1980), but Mn/Fe indicates that the surficial sediments already became increasingly anoxic from 1970 on. This is a common result of intensified primary productivity and subsequent high OM- and P-sedimentation, which create a lasting depletion of dissolved oxygen in the sediment (Gächter and Wehrli, 1998). It is important to note that this condition intensified in the sediment of Fischkaltersee and prevailed up to the end of our investigation in 2009. Moreover, it was not significantly altered by the hypolimnion aeration, whether permanent or intermittent. As the aerator used in Fischkaltersee was mounted on a steel rack approx. 1 m above ground (Steinberg and Schrimpf, 1982), both the bubble plume and the resulting water current never came into direct contact with the sediment surface, where - despite an oxic bottom water zone (>2 mg L^{-1} O_2) - anoxic conditions prevailed. This is in concordance with the findings of many aeration experiments (Fast and Tyler, 1981; Bailey-Watts *et al.,* 1987; Gächter and Wehrli, 1998; Grochowska and Gawronska, 2004; Teranes and Bernasconi, 2000). As well, it is evident from the O_2 data of the water column that bottom waters in Fischkaltersee turned hypoxic very quickly each time the aeration ceased. In conjunction with the extreme temperature elevation in the bottom water zone during summer (max. +13.4°C), this is of great relevance for both isotopic signals in the sediment of Fischkaltersee. As the village of Staltach was connected to a centralized sewage plant in 1981 (Steinberg and Zimmermann, 1988), both the N and P load to the lake peaked around that time and so did their respective concentrations in the water column. However, despite the gradual decline of sewage inflow and treatment efforts, the state of Fischkaltersee before the onset of the rapid eutrophication described here could not be re-established until present day which is obvious from the DI.

Sedimentary δ^{13}C

Many studies attributed the controlling biogeochemical influence over $\delta^{13}C_{SOM}$ mainly to the extent of primary productivity in the phototrophic zone of a lake (Hodell and Schelske, 1998; Brenner *et al*., 1999; Meyers and Teranes, 2001; Meyers, 2006; Choudhary *et al*., 2009; Choudhary *et al*., 2010). During assimilation, phytoplankton discriminates against ^{13}C (Farquhar *et a*l., 1989). As a consequence, a ^{13}C enrichment in the remaining epilimnetic DIC pool develops, when the ^{13}C-depleted biomass is removed from the epilimnion via sedimentation. This can occur on a seasonal or multiannual time scale as DIC pools are replenished with ^{13}C-depleted carbon when biomass is remineralized again. However, periods of pronounced primary productivity and subsequent fixation of biomass in the sediment will be recorded as a $\delta^{13}C_{SOM}$ increase. Therefore, $\delta^{13}C_{SOM}$ has widely been interpreted as a proxy of primary productivity (Lücke *et al.,* 2003).

It is evident from the data presented above that in Fischkaltersee the profile of $\delta^{13}C_{SOM}$ cannot be solely explained by primary productivity changes. $\delta^{13}C_{SOM}$ is not correlated with the development of epilimnetic primary productivity or any of its sedimentary proxies (DI, Chl a, TP) in the later stages of eutrophication of Fischkaltersee. With the exception of the defined positive excursion in 1971 during the onset of eutrophication, the overall reaction of $\delta^{13}C_{SOM}$ to eutrophication as well as to all restoration efforts is a continuous negative trend. This is shown by the most depleted $\delta^{13}C_{SOM}$ signatures (minimum -38.8‰) in the youngest samples of the record, when Fischkaltersee was already in a state of trophic recovery. Even before the onset of the rapid eutrophication in 1970, the isotopic signature of organic carbon in the sediment $\delta^{13}C_{SOM}$ was constant but quite ^{13}C-depleted (average -35.1‰). These rather low values are more negative than common $\delta^{13}C_{SOM}$ signatures of lacustrine algal matter and also lake sediment (Meyers and Teranes, 2001), but are in good agreement to the isotopic signature $\delta^{13}C_{SOM}$ (-30 to -37‰) encountered by the investigation of Teranes and Bernasconi 2005 in the sediment of hypereutrophic Baldeggersee, Switzerland. The authors of this study found the $\delta^{13}C_{SOM}$ profile to be caused by variations in the relative input of both ^{13}C-enriched photoautothropic and microbial biomass, which is known to have a much more depleted signature.

Likewise, the $\delta^{13}C_{SOM}$ record of Fischkaltersee cannot be derived from the input of photoautotropic biomass alone, whose carbon isotopic signature typically is about -28‰ (Meyers and Lallier-Verges, 1999). Particularly in eutrophicated lacustrine environments such low δ^{13}C signatures have been associated with significant influence of ^{13}C-depleted OM derived from heterotrophic sources (Lehmann *et al*., 2004; Teranes and Bernasconi, 2005; Daskalou *et al*., 2009), as the excess availability of nutrients not only increases primary productivity, but also OM sedimentation and subsequent microbial reworking processes (Liikanen and Martikainen, 2003). Together with the resulting anoxic conditions in the water column and/or sediment, eutrophication produces ideal conditions for an expansion of the heterotrophic community and the associated carbon cycling processes, *i.e.* sulfate reduction, denitrification, chemoautotrophy, methanogenesis and methanotrophy (Hollander and Smith, 2001; Liikanen and Martikainen, 2003). Among those, the formation of methane in the anoxic part of the sediment and its subsequent oxidation in the upper water column and reintegration into the DIC pool play a key role for the isotopic signal $\delta^{13}C_{SOM}$ in the sediment: Microbial methane typically is quite depleted in δ^{13}C (-110‰ to -50‰) (Whiticar *et al.* 1986; Whiticar 1999) and significant amounts (up to 50%) of the sedimenting carbon are recycled into methane (Fallon *et al*., 1980; Kelly and Chynoweth, 1981). Methanotrophic processes that oxidize CH_4 and thus reintegrate it into the epilimnetic DIC pool add another step of additional isotopic depletion, as the associated fractionation effect is -16‰ to -30‰ (Summons *et al*., 1994). This process can be of quantitative significance: Ogrinc *et al.* (2002) found that in lake Bled, a carbonate-rich, subalpine lake in Slovenia, up to 78% of DIC in pore water originates from methanogenesis.

Recently, it has been shown using data from 50 lakes in western Ireland that, depending on the extent of bottom water anoxis, methane production in anaerobic lake sediments can be of greater influence on sedimentary $\delta^{13}C_{SOM}$ than primary production (Woodward *et al*., 2012). Smith and Hollander (2001) introduced a conceptual model on the response of $\delta^{13}C_{SOM}$ to cultural eutrophication: for a wide TP range (approximately 0.05 to 0.175 mg L^{-1}), they attribute the dominating influence on the carbon isotopic signal to the extent of microbial carbon cycling processes in the lake (*i.e.,* methanogenesis and methanotrophy), which are superimposed on the signal of the photoautotrophic biomass. Therefore, a negative isotopic trend in sedimentary carbon is predicted following eutrophication in the TP range named above. The isotopic signal of primary productivity processes will control $\delta^{13}C_{SOM}$ only when TP is below or above the proposed TP thresholds, which were interpolated from water column data and $\delta^{13}C_{SOM}$ profiles of two lakes of different degrees of eutrophication. This model is consistent with the $\delta^{13}C_{SOM}$ profile observed in Fischkaltersee: as the eutrophication process proceeded exceptionally fast here, it is reasonable to assume that the lower TP threshold, above which microbial input will dominate, was crossed rather quickly already in the 1970s. Thus, the impact of the intensifying primary productivity on the $\delta^{13}C_{SOM}$ signal in the sediment was constrained to the defined positive excursion of $\delta^{13}C_{SOM}$ in 1971. From 1971 on, the almost continuous decline in the signal indicates an increasing imprint of ^{13}C-depleted microbial processes on the sediment, either uncoupled to epilimnetic primary productivity via sedimentation of depleted heterotropic biomass or coupled through methanogenesis, subsequent oxidation and reintegration in the surface water DIC pool.

Although no data is available on the isotopic composition of DIC or the extent of methane production in Fischkaltersee, insight into the interactions of primary productivity, methanogenesis and methanothrophy can be gained from an investigation on the pelagic bacteria population (0-11 m), which was conducted before the onset of artificial aeration by Steinberg and Niesslbeck (1981). They found that bacteria population maxima preceded those of phytoplankton, the latter using DIC as substrate that originated from methane produced in the monimolimnion and sediment that was subsequently oxidized in upper water layers. This process is likely to have intensified through the artificial aeration, as the sediment remained anoxic, but oxygenated bottom waters allowed for a quantitative oxidation of the produced CH_4 all year round. Also, both OM sedimentation and bottom water temperature increased considerably, which has the potential to promote methanogenesis further, as methane production is known to be a direct function of both OM input and temperature (Kelly and Chynoweth, 1981). It is documented that the aeration in Fischkaltersee was accompanied by a fivefold increase in abundance of heterotrophs (Steinberg and Schrimpf, 1982).

The negative trend of $\delta^{13}C_{SOM}$ continues towards the youngest part of the sediment core. Consequently, during the course of the eutrophication of Fischkaltersee a TP threshold was crossed around 1971 and thereafter microbial processes dominated over the effect of primary productivity on carbon isotopes to the present day. $\delta^{13}C_{SOM}$ values further imply that TP never crossed an upper threshold, above which algal biomass again controls $\delta^{13}C_{SOM}$ (according to the conceptual model of Hollander and Smith, 2001). It is also interesting to note that the $\delta^{13}C_{SOM}$ signature of the sediment of Fischkaltersee was already more ^{13}C-depleted (average -35.1‰) in the period before the onset of the rapid eutrophication process (1963-1970) than it is in similar lakes (Drew *et al.,* 2008; Choudhary *et al*., 2009, Lu *et al.,* 2010). According to that, microbial carbon cycling has always provided a significant input to DIC and the sediment in Fischkaltersee.

Sedimentary $\delta^{15}N$

The $\delta^{15}N$ value of bulk sedimentary nitrogen has been used as a proxy of paleoproductivity in several investigations of lake eutrophication (Talbot, 2001). Analogous to carbon uptake, phytoplankton discriminates against the heavier isotope ^{15}N during DIN uptake (Sigman *et al.,* 1999), where the degree of isotopic fractionation depends on the assimilated N form (NO_3^- *vs* NH_4^+). Given a sufficient consumption of N in surface waters, the resulting depletion of ^{14}N will be reflected in a ^{15}N increase in the remaining DIN pool and of the subsequently produced photoautothrophic biomass. Marine studies revealed a strong positive correlation between $\delta^{15}N$ of phytoplankton and the extent of surface-water nitrate depletion, *i.e.* primary productivity (Altabet and Francois, 1994). But for freshwater systems, this correlation was considered to be rather weak, because lacustrine primary productivity is limited more by P than by N, so that the consumption of the DIN pool shows less impact on $\delta^{15}N$ of phytoplankton (Lehmann *et al*., 2004). However, Teranes and Bernasconi (2000) were able to confirm a positive correlation between $\delta^{15}N$ and primary productivity rates for the lacustrine environment of hypereutrophic Baldeggersee as well. They show that $\delta^{15}N$ of newly produced photoautotrophic biomass is positively correlated to the amount of nitrate depletion in surface waters and its signal is closely recorded in the weighted average N isotopic composition of sedimenting organic matter and consequently in $\delta^{15}N$ of sediment recently deposited.

The results of our investigation provide additional evidence that sedimentary $\delta^{15}N$ can be a useful record of the nitrate utilisation in the epilimnion of lakes. In Fischkaltersee, the profile of $\delta^{15}N$ corresponds well to the overall development of the eutrophication process, *i.e.* the intensity of primary productivity as is represented more accurately by Chl a and DI than by TP (Wetzel, 2001). When compared directly to NO_3^- utilisation, the relationship becomes obvious: $\delta^{15}N$ values are most enriched (+6.9‰) when NO_3^- utilisation was most pronounced (85%) in 1982. Nevertheless, the rather weak (R^2=0.33) linear correlation of NO_3^- utilisation and $\delta^{15}N$ (Fig. 6) reveals that the effect of primary productivity on $\delta^{15}N$ can be confunded by other influences: some precision of the correlation might be lost as well to the fact, that NO_3 utilisation was calculated for each individual year as the seasonal depletion of the surface water NO_3 pool, according to Lehmann *et al.* (2004). The $\delta^{15}N$ values on the other hand were obtained from sampling the sediment core in slices of 1 cm, which might not always represent the exact integrated mean of the respective time period.

As mentioned above, the fractionation effect during DIN assimilation depends on the N form incorporated. For ammonium the associated fractionation (ε=-10‰; Fogel and Cifuentes, 1993) has been shown to be larger than for nitrate assimilation, so that uptake of NH_4^+ will result in more depleted $\delta^{15}N$ of organic matter. Due to an extremely elevated ammonium concentration in bottom waters during the meromictic phase (phase B) and the aeration gap in the years 1984-1985, NH_4^+ was present in significant amounts in the phototrophic zone of Fischkaltersee at that time. Its direct uptake by primary producers is visible in concurrent drops of $\delta^{15}N$ as well as of NO_3^- utilisation during those periods.

Given this, we conclude that in Fischkaltersee both the intensity of surface water DIN utilisation and the form and isotopic composition of DIN assimilated by phytoplankton are the main controls on $\delta^{15}N$ of sedimentary organic matter. It is important to note that several other processes in the rather complex lacustrine N cycle have the potential to impart strong trends to the nitrogen isotopic signal in the sediment, which makes detailed knowledge about the underlying processes in the lake essential for the interpretation of the sedimentary $\delta^{15}N$ record.

The TOC/TN of SOM in Fischkaltersee is rather constant (10.2), but somewhat higher than expected for pure algal matter, which typically ranges between 7-9 (Meyers and Teranes, 2001). This might be a sign of active denitrification occurring during early sedimentation, because N-rich products are preferentially degraded (Meyers and Teranes, 2001, Lehmann *et al.*, 2002). Although a substantial amount of both C and N can be lost to early diagenesis after sedimentation (approx. 20% and 35%, respectively), it is encouraging for the interpretation of sedimentary $\delta^{13}C_{SOM}$ and $\delta^{15}N$ that the associated isotope effects are only minor (max. +1.5‰ and -0.7‰, respectively; Gälman *et al.*, 2009) and, thus the original signals are preserved. Nevertheless, denitrification in the water column is a source of considerable N loss to the DIN pool of a lake, which must also be considered in our interpretation, as it is associated with a potentially enormous en-

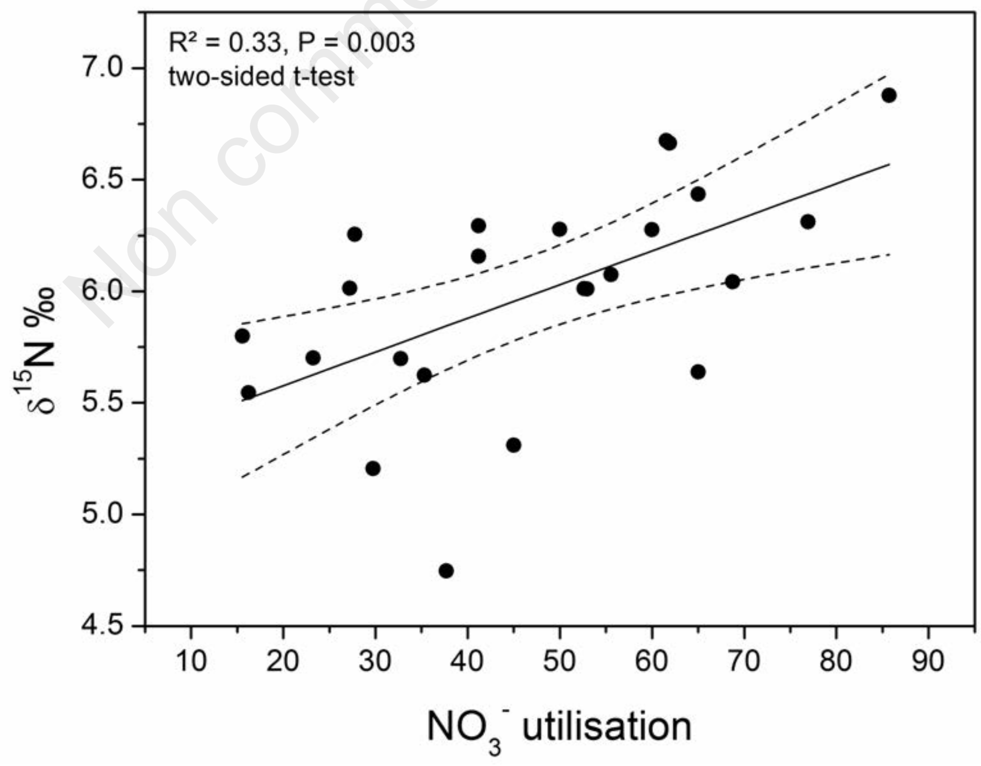

Fig. 6. $\delta^{15}N$ isotopic signature of FIS 8/09 *vs* NO_3^- utilisation in the epilimnion. Dotted lines indicate the confidence band for the given parameters of the linear correlation.

richment of ^{15}N in the remaining nitrate pool (+14 to +26‰; Teranes and Bernasconi, 2000) and the extent of this strictly anoxic process strongly depends on phases of stagnation. Hodell and Schelske (1998) interprete a contínous 6‰ increase in δ^{15}N in the sediment of lake Ontario as a sign of increased water column denitrification promoted by several meromictic episodes, which are the result of intensified primary productivity. Therefore, it is possible that the δ^{15}N increase in phase A was caused by increasing denitrification. However, if water column denitrification would have been the main cause for the δ^{15}N profile observed in Fischkaltersee, one would expect a strong drop of the signal once the hypolimnion aeration was initiated, as it eliminated anoxic zones in the water column. Thus we conclude that water column denitrification never has been the most significant influence to sedimentary δ^{15}N in Fischkaltersee.

Nevertheless, there is evidence for extensive denitrification in Fischkaltersee: in the first months following the onset of artificial destratification, there is a twofold increase in DIN (0.41 to 0.89 mg N L^{-1}). This is probably due to the oxidation of dissolved-organic nitrogen (DON) to nitrate, which appears in the hypolimnion from then on. During phase C, when permanent aeration would not allow for water column denitrification, DIN decreases considerably (0.89 to 0.07 mg N L^{-1}). This continuous decrease could be a result of denitrification in the anoxic sediment. As mentioned above, both the extreme increase in temperature and the oxygenation of bottom water layers are likely to have promoted microbial processes in the sediment, *i.e.* denitrification, as it depends on NO_3^- as a substrate and the activity of nitrification is known to be regulated by O_2 concentration (Grochowska and Gawronska, 2004; Jensen *et al.*, 1993).

Due to rate limitations caused by the transport therein, sediment denitrification is considered to exhibit only a minor isotopic fractionation (Brandes and Devol, 1997). Thus, although quantitatively of considerable importance, it would not influence the isotopic signature of DIN to the extent of water column denitrification (Teranes and Bernasconi, 2000). Increasing input of heterotrophic biomass could as well be responsible to a certain amount for the profile of sedimentary δ^{15}N in Fischkaltersee during 1963 to 1986, as it will also elevate δ^{15}N because there is an increase of 3 to 4‰ for each trophic level (Deniro and Epstein, 1981; Peterson and Fry, 1987). Therefore, especially the fivefold increase in abundance of heterotrophs which occurred as a result of the permanent destratification from 1980 on, could have contributed to the expressed increase in δ^{15}N thereafter. It is well known that human sewage as well as manure, both used as agricultural fertilizers, can be extremely enriched in ^{15}N (+5 to +20‰; Talbot, 2001), because land-based denitrification allows for an considerable ^{14}N loss.

Although neither the amount of the external N load nor its isotopic composition have been investigated during the anthropogenically induced eutrophication of Fischkaltersee, there is a good agreement between the overall profile of sedimentary δ^{15}N and the history of sewage input in Fischkaltersee: most enriched δ^{15}N signals in the sediment record appear between 1982 and 1986, while due to the launch of the local sewage plant, the external N load to the lake peaked around 1981. A slow decline of this input is likely as well because considerable subsequent desorption from the saturated aquifer is documented for the concurrent P input (Steinberg and Zimmermann, 1988). Therefore, despite a significant effect of epilimnetic nitrate utilisation by primary productivity, a factor Fischkaltersee could as well be the isotopic signature of the external N load.

CONCLUSIONS

In the past, primary productivity was thought to be the main biogeochemical influence controlling influencing δ^{15}N in $\delta^{13}C_{SOM}$, thus rendering the latter an ideal proxy indicator of paleoeuthropication. Particularly in anthropogenically eutrophicated systems this assumption might not always be valid. Here, the common anoxic conditions allow for an intensification of microbially mediated carbon cycling processes that have the potential to confund the effect of primary productivity on $\delta^{13}C_{SOM}$.

Based on their observations in two differently eutrophicated lakes, Smith and Hollander (2001) introduced a conceptual model which, for a certain TP range (approx. 0.05 to 0.175 mg L^{-1}), attributes the dominating impact on $\delta^{13}C_{SOM}$ to the extent of methanogenesis and methanotrophy in a lake. Since then, this effect has been confirmed to be of practical relevance (Woodward *et al*., 2012).

Our data provide additional conclusive evidence for the relevance of this model for $\delta^{13}C_{SOM}$ in anthropogenically eutrophicated lakes. In Fischkaltersee, its well-documented history of rapid eutrophication, multiple human impact and subsequent restoration efforts allows for a validation of the concept proposed by Smith and Hollander, particularly for the concept of P-thresholds controlling the dominant input to $\delta^{13}C_{SOM}$. Here, the impact of primary productivity on the carbon isotopic signature of SOM is constrained to the early phase of eutrophication (TP>0.04 mg L^{-1}). At higher TP concentrations, the intensity of microbial processes, *i.e.* methanogenesis and methanotrophy, becomes the dominating influence to $\delta^{13}C_{SOM}$.

It is important to emphasize that in Fischkaltersee $\delta^{13}C_{SOM}$ is not linearly related to the TP concentration in the water column, as this is an important implication constraining the applicability $\delta^{13}C_{SOM}$ for investigations on lacustrine paleoeutrophication. Other investigations considered the extent of stagnation and anoxis in the water column to control the extent of methanogenesis and therefore its impact on $\delta^{13}C_{SOM}$ (Teranes and Bernasconi, 2001). In Fischkaltersee, both the permanent as well as the intermittent destratification had no significant effect on the negative trend of $\delta^{13}C_{SOM}$. Our investigation reveals that water column anoxis is not necessarily a prerequisite for the domination of microbially mediated carbon cycling processes. Their influence on $\delta^{13}C_{SOM}$ can prevail as long as one compartiment, *i.e.* the surficial sediments, remains anoxic, which is a common result of increased OM sedimentation rates during eutrophication.

On the other hand, our results suggest that $\delta^{15}N$ is a useful indicator of lacustrine primary productivity even if its linear correlation to NO_3^- utilisation can be weakened by various other processes in the rather complex N cycle. However, because of this, a detailed knowledge about the underlying processes in the water column is essential for the interpretation of $\delta^{15}N$ in terms of paleoproductivity.

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REFERENCES

Altabet MA, Francois R, 1994. Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization. Glob. Biogeochem. Cy. 8:103-116.

Bailey-Watts AE, Wise EJ, Kirika A, 1987. An experiment in phytoplankton ecology and applied fishery management effects of artificial aeration on troublesome algal blooms in a small eutrophic loch. Aquac. Res.18:259-276.

Battarbee RW, Jones VJ, Flower RJ, Cameron NG, Bennion H, Carvalho L, Juggins S, 2001. Diatoms, p. 155-202. In: J.P. Smol, H.J. Birks, W.M. Last (eds.), Tracking environmental change using lake sediments. 3. Terrestrial, algal, and siliceous indicators. Springer.

Brandes JA, Devol AH, 1997. Isotopic fractionation of oxygen and nitrogen in coastal marine sediments. Geochim. Cosmochim. Ac. 61:1793-1801.

Brenner M, Whitmore TJ, Curtis JH, Hodell DA, Schelske CL, 1999. Stable isotope (delta C-13 and delta N-15) signatures of sedimented organic matter as indicators of historic lake trophic state. J. Paleolimnol. 22:205-221.

Choudhary P, Routh J, Chakrapani GJ, 2010. Organic geochemical record of increased productivity in Lake Naukuchiyatal, Kumaun Himalayas, India. Environ. Earth Sci. 60:837-843.

Choudhary P, Routh J, Chakrapani GJ, Kumar B, 2009. Biogeochemical records of paleoenvironmental changes in Nainital Lake, Kumaun Himalayas, India. J. Paleolimnol. 42:571-586.

Croudace IW, Rindby A, Rothwell RG, 2006. ITRAX: description and evaluation of a new multi-function X-ray core scanner. Geol. Soc. Spec. Publ. 267:51.

Daskalou V, Vreca P, Muri G, Stalikas C, 2009. Recent environmental changes in the shallow lake Pamvotis (NW Greece): evidence from sedimentary organic matter, hydrocarbons, and stable isotopes. Arch. Environ. Con. Tox. 57:21-31.

Deniro MJ, Epstein S, 1981. Influence of diet on the distribution of nitrogen isotopes in animals. Geochim. Cosmochim. Ac. 45:341-351.

Drew S, Flett I, Wilson J, Heijnis H, Skilbeck CG, 2008. The trophic history of Myall Lakes, New South Wales, Australia: interpretations using delta(13)C and delta(15)N of the sedimentary record. Hydrobiologia 608:35-47.

Fallon RD, Harrits S, Hanson RS, Brock TD, 1980. The role of methane in internal carbon cycling in lake Mendota during summer stratification. Limnol. Oceanogr. 25:357-360.

Farquhar GD, Ehleringer JR, Hubick KT, 1989. Carbon isotope discrimination and photosynthesis. Annu. Rev. Plant Phys. 40:503-538.

Fast AW, Tyler PA, 1981. The reestablishment of Meromixis in Hemlock Lake, Michigan, after artificial destratification. Int. Rev. Ges. Hydrobio. 66:665-674.

Finlay JC, Kendall C, 2007. Stable isotope tracing of temporal and spatial variability in organic matter sources to freshwater ecosystems, p. 283-333. In: R. Michener and K. Lajtha (eds.), Stable isotopes in ecology and environmental science. Blackwell Publ.

Fogel ML, Cifuentes LA, 1993. Isotope fractionation during primary production, p. 73-98. In: M.H. Engel and S.A. Macko (eds.), Organic Geochemistry. Plenum Press.

Gächter R, Wehrli B, 1998. Ten years of artificial mixing and oxygenation: no effect on the internal phosphorus loading of two eutrophic lakes. Environ. Sci. Technol. 32:3659-3665.

Gälman V, Rydberg J, Bigler C, 2009. Decadal diagenetic effects on delta C-13 and delta N-15 studied in varved lake sediment. Limnol. Oceanogr. 54:917-924.

Granger J, Sigman DM, Lehmann MF, Tortell PD, 2008. Nitrogen and oxygen isotope fractionation during dissimilatory nitrate reduction by denitrifying bacteria. Limnol. Oceanogr. 53:2533-2545.

Grochowska J, Gawronska H, 2004. Restoration effectiveness of a degraded lake using multi-year artificial aeration. Pol. J. Environ. Stud. 13:671-681.

Heyng AM, Mayr C, Lücke A, Striewski B, Wastegard S, Wissel H, 2012. Environmental changes in northern New Zealand since the Middle Holocene inferred from stable isotope records (δ15N, δ13C) of Lake Pupuke. J. Paleolimnol. 48:351-366.

Hodell DA, Schelske CL, 1998. Production, sedimentation, and isotopic composition of organic matter in Lake Ontario. Limnol. Oceanogr. 43:200-214.

Hofmann G, 1993. [Aufwuchs-Diatomeen in Seen und ihre Eichung als Indikatoren der Trophie]. [PhD Thesis in German]. Goethe-Universität ed., Frankfurt: 241 pp.

Hollander DJ, McKenzie JA, 1991. CO2 control on carbon-isotope fractionation during aqueous photosynthesis: a paleo-pCO2 barometer. Geology 19:929-932.

Hollander DJ, Smith MA, 2001. Microbially mediated carbon cycling as a control on the delta C-13 of sedimentary carbon in eutrophic Lake Mendota (USA): new models for interpreting isotopic excursions in the sedimentary record. Geochim. Cosmochim. Ac. 65:4321-4337.

Jensen K, Revsbech NP, Nielsen LP, 1993. Microscale distribution of nitrification activity in sediment determined with a shielded microsensor for nitrate. Appl. Environ. Microb. 59:3287-3296.

Kelly CA, Chynoweth DP, 1981. The contributions of temperature and of the input of organic-matter in controlling rates of sediment methanogenesis. Limnol. Oceanogr. 26:891-897.

Kennedy P, Kennedy H, Papadimitriou S, 2005. The effect of acidification on the determination of organic carbon, total nitrogen and their stable isotopic composition in algae and marine sediment. Rapid Commun. Mass Sp. 19:1063-1068.

Kirchner G, 2011. 210Pb as a tool for establishing sediment chronologies: examples of potentials and limitations of conventional dating models. J. Environ. Radioactiv. 102:490-494.

Krammer K, Lange-Bertalot H, 1986. [Bacillariophyceae. 1. Naviculaceae]. [Book in German]. Gustav Fisher Verlag, Stuttgart: 876 pp.

Krammer K, Lange-Bertalot H, 1988. [Bacillariophyceae. 2. Bacillariaceae]. [Book in German]. Gustav Fisher Verlag, Stuttgart: 596 pp.

Krammer K, Lange-Bertalot H, 1991a. [Bacillariophyceae. 3. Centrales, Fragilariaceae, Eunotiaceae]. [Book in German]. Gustav Fisher Verlag, Stuttgart: 576 pp.

Krammer K, Lange-Bertalot H, 1991b. [Bacillariophyceae. 4. Achnanthaceae Kritische Ergänzungen zu Navicual (Lineolatae) und Gomphonema]. [Book in German]. Gustav Fisher Verlag, Stuttgart: 437 pp.

Krishnaswamy S, Lal D, Martin JM, Meybeck M, 1971. Geochronology of lake sediments. Earth Planet. Sc. Letters 11:407-414.

Lehmann MF, Bernasconi SM, Barbieri A, McKenzie JA, 2002. Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis. Geochim. Cosmochim. Ac. 66:3573-3584.

Lehmann MF, Bernasconi SM, Barbieri A, Simona M, McKenzie JA, 2004. Interannual variation of the isotopic composition of sedimenting organic carbon and nitrogen in Lake Lugano: a long-term sediment trap study. Limnol. Oceanogr. 49:839-849.

Liikanen A, Martikainen PJ, 2003. Effect of ammonium and oxygen on methane and nitrous oxide fluxes across sediment-water interface in a eutrophic lake. Chemosphere 52:1287-1293.

Lu YH, Meyers PA, Eadie BJ, Robbins JA, 2010. Carbon cycling in Lake Erie during cultural eutrophication over the last century inferred from the stable carbon isotope composition of sediments. J. Paleolimnol. 43:261-272.

Lücke A, Schleser GH, Zolitschka B, Negendank JFW, 2003. A Lateglacial and Holocene organic carbon isotope record of lacustrine palaeoproductivity and climatic change derived from varved lake sediments of Lake Holzmaar, Germany. Quaternary Sci. Rev. 22:569-580.

Lüder B, Kirchner G, Lucke A, Zolitschka B, 2006. Palaeoenvironmental reconstructions based on geochemical parameters from annually laminated sediments of Sacrower See (northeastern Germany) since the 17th century. J. Paleolimnol. 35:897-912.

Mayr C, Fey M, Haberzettl T, Janssen S, Lucke A, Maidana NI, Ohlendorf C, Schabitz F, Schleser GH, Struck U, Wille M, Zolitschka B, 2005. Palaeoenvironmental changes in southern Patagonia during the last millennium recorded in lake sediments from Laguna Azul (Argentina). Palaeogeogr. Palaeocl. 228:203-227.

McKenzie JA, 1985. Carbon isotopes and productivity in the lacustrine and marine environment, p. 99-118. In: W. Stumm (ed.), Chemical processes in lakes. J. Wiley & Sons.

Melzer A, 1976. [Makrophytische Wasserpflanzen als Indikatoren des Gewässerzustandes oberbayerischer Seen, dargestellt im Rahmen limnologischer Untersuchungen an den Osterseen und den Eggstätt-Hemhofer Seen (Oberbayern)]. [Book in German]. Cramer, Vaduz: 195 pp.

Meyers PA, 2006. An overview of sediment organic matter records of human eutrophication in the Laurentian Great Lakes region. Water Air Soil Poll. 6:453-463.

Meyers PA, Lallier-Verges E, 1999. Lacustrine sedimentary organic matter records of Late Quaternary paleoclimates. J. Paleolimnol. 21:345-372.

Meyers PA, Teranes J, 2001. Sediment organic matter, p. 239-269. In: W.M. Last and J. Smol (eds.), Tracking environmental change using lake sediments. 2. Physical and geochemical methods. Springer.

Nehyba N, Nývlt D, Schkade U, Kirchner G, Franců E, 2011. Depositional rates and dating techniques of modern deposits in the Brno reservoir (Czech Republic) during the last 70 years. J. Paleolimnol. 45:41-55.

Nieuwenhuize J, Maas YEM, Middelburg JJ, 1994. Rapid analysis of organic-carbon and nitrogen in particulate materials. Mar. Chem. 45:217-224.

Nitzsche HM, Czegka W, Hanisch C, Zerling L, Junge FW, 2009. The potential for releasing methane from artificial lakes in Central Germany - a (13)C study. Isot. Environ. Health S. 45:231-246.

OECD, 1982. Eutrophication of waters. Monitoring, assessment and control. Organisation for Economic Co-operation and Development Publ., Paris: 154 pp.

Ogrinc N, Lojen S, Faganeli J, 2002. A mass balance of carbon stable isotopes in an organic-rich methane-producing lacustrine sediment (Lake Bled, Slovenia). Glob. Planet. Change 33:57-72.

Peterson BJ, Fry B, 1987. Stable isotopes in ecosystem studies. Annu. Rev. Ecol. Syst. 18:293-320.

Ryba SA, Burgess RM, 2002. Effects of sample preparation on the measurement of organic carbon, hydrogen, nitrogen, sulfur, and oxygen concentrations in marine sediments. Chemosphere 48:139-147.

Schaumburg J, Colling M, Schlösser I, Köpf B, Fischer F, 2005. [Ökologische Typisierung von Phytoplankton]. [Book in German]. Bayerisches Landesamt für Wasserwirtschaft, Munich: 61 pp.

Sigman DM, Altabet MA, McCorkle DC, Francois R, Fischer

G, 1999. The delta N-15 of nitrate in the Southern Ocean: consumption of nitrate in surface waters. Glob. Biogeochem. Cy. 13:1149-1166.

Steinberg C, Bucksteeg K, 1980. Testing of aluminium precipitation as a lake restoration method. Vom Wasser 55: 47-61.

Steinberg C, Fischer KM, 1982. [Untersuchungen der obersten Sedimentschichten des Fischkaltersees]. [Book in German]. Bayerische Akademie der Wissenschaften. Kommission für Bayerische Landesgeschichte ed.

Steinberg C, Niesslbeck P, 1981. Bacterioplankton affected by phosphorus precipitation treatment in a polytrophic lake. Z Wasser Abwass For 14:43-46.

Steinberg C, Schrimpf A, 1982. [Auswirkungen einer künstlichen Volldurchmischung auf das Geschehen im Fischkaltersee]. [Book in German]. Bayerische Akademie der Wissenschaften. Kommission für Bayerische Landesgeschichte ed.

Steinberg C, Zimmermann GM, 1988. Intermittent destratification - a therapy measure against cyanobacteria in lakes. Environ. Technol. Lett. 9:337-350.

Summons RE, Jahnke LL, Roksandic Z, 1994. Carbon isotopic fractionation in lipids from methanotrophic bacteria - relevance for interpretation of the geochemical record of biomarkers. Geochim. Cosmochim. Ac. 58:2853-2863.

Talbot MR, 2001. Nitrogen isotopes in paleolimnology, p. 401-439. In: W.M. Last and J. Smol (eds.), Tracking environmental change using lake sediments. 2. Physical and geochemical methods. Springer.

Teranes JL, Bernasconi SM, 2000. The record of nitrate utilization and productivity limitation provided by delta N-15 values in lake organic matter. A study of sediment trap and core sediments from Baldeggersee, Switzerland. Limnol. Oceanogr. 45:801-813.

Teranes JL, Bernasconi SM, 2005. Factors controlling delta C-13 values of sedimentary carbon in hypertrophic Baldeggersee, Switzerland, and implications for interpreting isotope excursions in lake sedimentary records. Limnol. Oceanogr. 50:914-922.

UNSCEAR, 2000. Sources and effects of ionizing radiation. UNSCEAR 2000 report to the general assembly. I. Sources. United Nations Scientific Committee on the Effects of Atomic Radiation ed., New York: 654 pp.

Wauer G, 2006. [Der Einfluss von Fällmittelkombinationen auf die P-Retention in Sedimenten geschichteter Seen]. [PhD Thesis in German]. Humboldt-Universität zu Berlin Publ., Berlin: 123 pp.

Wersin P, Hohener P, Giovanoli R, Stumm W, 1991. Early diagenetic influences on iron transformations in a fresh-water lake sediment. Chem. Geol. 90:233-252.

Wetzel RG, 2001. Limnology: lake and river ecosystems. Academic Press, San Diego: 1006 pp.

Whiticar MJ, 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. Chem. Geol. 161:291-314.

Whiticar MJ, Faber E, Schoell M, 1986. Biogenic methane formation in marine and fresh-water environments - Co2 reduction vs acetate fermentation isotope evidence. Geochim. Cosmochim. Ac. 50:693-709.

Woodward CA, Potito AP, Beilman DW, 2012. Carbon and nitrogen stable isotope ratios in surface sediments from lakes of western Ireland: implications for inferring past lake productivity and nitrogen loading. J. Paleolimnol. 47:167-184.

Zhu LP, Zhen XL, Wang JB, Lu HY, Xie MP, Kitagawa H, Possnert G, 2009. A similar to 30,000-year record of environmental changes inferred from Lake Chen Co, Southern Tibet. J. Paleolimnol. 42:343-358.