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Impact of recent lake eutrophication on microbial community changes as revealed by high resolution lipid biomarkers in Rotsee (Switzerland)

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ABSTRACT

The effects of eutrophication on short term changes in the microbial community were investigated using high resolution lipid biomarker and trace metal data for sediments from the eutrophic Lake Rotsee (Switzerland). The lake has been strongly influenced by sewage input since the 1850s and is an ideal site for studying an anthropogenically altered ecosystem. Historical remediation measures have had direct implications for productivity and microbial biota, leading to community composition changes and abundance shifts. The higher sewage and nutrient input resulted in a productivity increase, which led predominantly to a radiation in diatoms, primary producers and methanogens between about 1918 and 1921, but also affected all microorganism groups and macrophytes between about 1958 and 1972. Bacterial biomass increased in 1933, which may have been related to the construction of a mechanical sewage treatment plant. Biomarkers also allowed tracing of fossil organic matter/biodegraded oil contamination in the lake. *Stephanodiscus parvus*, *Cyclotella radiosa* and *Asterionella formosa* were the dominant sources of specific diatom biomarkers. Since the 1850s, the cell density of methanogenic Archaea (*Methanosaeta* spp.) ranged within ca. 0.5–1.8 $\times$ 10^9 cells g^{-1} dry sediment and the average lipid content of Rotsee Archaea was ca. 2.2 fg iGDGTs $cell^{-1}$. An altered BIT index (BIT_{CH}), indicating changes in terrestrial organic matter supply to the lake, is proposed.

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1. Introduction

Due to human activity, such as land clearing, agriculture, forestry and urbanisation, nutrient cycling in ecosystems has been intensively altered, especially since the industrial revolution. The impact, along with climate change (Keeling et al., 2010), has profoundly altered natural biological communities in limnic, marine and terrestrial ecosystems (e.g. Vitousek et al., 1997; Smith et al., 1999). It has been estimated that human induced eutrophication has altered one third to one half of the land surface (Vitousek et al., 1997).

Today, the mechanisms of lake eutrophication are quite well understood (for an overview see Smith et al., 1999), with high nutrient loading fuelling productivity and biomass accumulation. Another factor is increased water column stratification, which leads more rapidly to O_2 depletion in the hypolimnion, which can even result in dead zones and mass mortality of species (Diaz and Rosenberg, 2008). The O_2 deficiency enhances the release of nutrients from the sediment, further increasing the nutrient cycling and bioavailability.

Because of the negative impact of eutrophication, water sewage treatment has had a dramatic improvement over the last decades, resulting in a general increase in surface water quality (Smith et al., 1999; Matzinger et al., 2010). At the same time, efforts to remediate affected water bodies have been less successful and have not always worked out as foreseen. For example, Matzinger et al. (2010) showed that the decrease in nutrient supply to lakes did not strongly reduce O_2 consumption rate in the water column because of remineralisation of organic matter (OM) in the sediment.

Another aspect is that complex system changes from chemical, physical and biological feedback mechanisms, that rule the system ecology of lakes, may result in 'tipping points' (Scheffer, 2010). These are critical transitions indicating the fragility of an ecosystem, resulting in dramatic changes in the abundance and composition of inhabiting organisms, either (algal) blooms or the extinction of species and the 'point of no return' (Scheffer, 2010). However,

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increased understanding of these mechanisms is often hampered by lack of historical data - investigations have typically only been started after severe cases of eutrophication, while hardly any prior physicochemical and biological data are available (Stadelmann, 1980; Scheffer, 2010). This lack is particularly for microbiological data, yet such biota play a central role during eutrophication. There is therefore a need for high temporal resolution reconstruction of microbial communities to improve the understanding of the 'natural' state, the onset and development of eutrophication, and subsequent remediation measures.

The aim of this study was to reconstruct the eutrophication history and the response of microbial biomass, using organic and inorganic proxies, in a small eutrophic Swiss lake. The relationship between biomarker concentration change and shift in microbial abundance was constrained, partly down to the species level, being supported by results from previous work on diatoms (Lotter, 1989) and methanogenic Archaea (Falz et al., 1999). Finally, we reevaluated the effectiveness of recovery activity and the implications for microbial communities after intensive sewage input to this ecosystem.

2. Material and methods

2.1. Study site and sample collection

Rotsee is a small (0.46 km^2) prealpine, monomictic and eutrophic lake with a maximal depth of 16 m (Fig. 1, Table 1). It formed after the retreat of the Reuss glacier after the last interglacial (Frey, 1907). Currently, it has a stable stratified water column with a strong chemocline between ca. 6 and 10 m and an anoxic hypolimnion for most of the year (Schubert et al., 2010). During the Holocene, the lake was mostly eutrophic and only partly mesotrophic, according to the past algal flora (Züllig, 1985).

The combination of the geographical and hydrological characteristics, together with the forested catchment, favours natural eutrophication (Bloesch, 1974), on which the anthropogenic nutrient enrichment since the 19th century (Stadelmann, 1980) has been profoundly superimposed. Since ca. 1850, the trophic state increased through sewage input and in 1920 the lake was classified as polytrophic (Bloesch, 1974; Stadelmann, 1980). Numerous blooms of *Oscillatoria rubescens* (today: *Planktothrix rubescens*, in German "Burgunderblutalge"), which turned the lake water red (Züllig, 1985). As a consequence of a canal construction from the Reuss River in the southwest corner of the lake in 1922 (Fig. 1), freshwater input increased (Kohler et al., 1984) and the water renewal time dropped from 3–4 to 0.4 yr (Lotter, 1989). However, recovery measures were unsuccessful because of continued nutrient supply from a nearby disposal site, temporal drying of the canal and the inability of the water inflow from the canal to initiate mixing (Bachmann, 1931; Stadelmann, 1980). After the completion of construction of an interceptor sewer in 1969 and a sewage treatment plant in 1974, the lake started to recover slowly (Stadelmann, 1980).

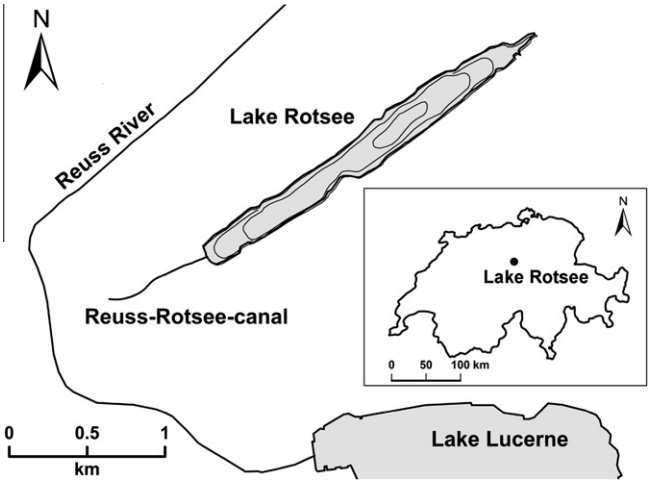

Fig. 1. Map with Rotsee, the Reuss River and its connection to Rotsee by the Reuss–Rotsee-canal (partly below ground level) and the northwest corner of Lake Lucerne. Inset map shows location of Rotsee.

Table 1
Hydrographical and limnological parameters for Rotsee (Bloesch, 1974; Kohler et al., 1984; Schubert et al., 2010; Züllig, 1985).

Parameter	Value	Unit
Drainage area	4.6	km^2
Surface area	0.46	km^2
Volume	0.0039	km^3
Max. depth	16	m
Mean depth	9	m
Residence time	0.44	yr
Trophic state	Eutrophic	
Lake mixing	Monomictic, holomictic (winter)	
Chemocline	6–10	m

A 56 cm long sediment core was recovered with a gravity corer in October 2009 from the centre of the lake at 16 m depth (GPS position N 47°4.251 E 8°18.955, WGS84). The core was sliced in continuous 1 cm intervals and frozen at −20 °C until analysis. Another 63 cm core was obtained from the same location in August 2010 for elemental analysis.

2.2. Age model

For core dating, ^{137}Cs and ^{210}Pb in freeze-dried and ground sediment were measured via γ spectrometry with a high purity Ge detector (Canberra GCW-3523) using the γ energy at 46.5 keV for ^{210}Pb and 661.7 keV for ^{137}Cs. Based on the Chernobyl accident and nuclear bomb test peaks in ^{137}Cs and a constant rate of supply (CRS) model, sedimentation (Appleby and Oldfield, 1978) and accumulation rates (Niessen et al., 1992) were calculated.

2.3. Bulk parameters

Total carbon (TC) and total nitrogen (TN) were measured on freeze-dried samples with a Thermo Quest CE Instrument NC 2500. Total organic carbon (TOC) was measured on decalcified samples. Total inorganic carbon (TIC) was calculated as the difference between TC and TOC. The errors for TC and TOC were ±0.1 wt.% and ±0.2 wt.% for TN. Additional TIC measurements with a Coulomat 5011 coulometer indicated that the method led to 0.5 wt.% higher TIC values, corresponding to 0.5 wt.% lower TOC values. C and N isotopic compositions ($\delta^{13}C$ and $\delta^{15}N$) of the OM were obtained with a GV Instruments IsoPrime isotope ratio mass spectrometry (IRMS) instrument, measured in the same run as for TOC and TIC. The $\delta^{13}C$ [‰ Vienna Peedee Belemnite (VPDB)] and $\delta^{15}N$ (‰ air) errors were up to ±0.3‰. The chlorin index (CI) and total chlorin concentration were determined according to Schubert et al. (2005). The analytical precision of the method was ca. 5% (Schubert et al., 2005).

2.4. Biomarker analysis

Ca. 5 g thawed sediment was extracted (×3) by way of ultrasonication with MeOH and dichloromethane (DCM): 1 × 10 ml MeOH, 1 × 10 ml MeOH:DCM (1:1, v:v), 1 × 10 ml DCM. For quantification, a known mixture of 5α-cholestane, C_{19} *n*-alcohol and $C_{19:0}$

fatty acid (FA) was added to the extract. Water was removed in a separation funnel with NaCl (20 ml, 5%). The extract was run over a Cu column to remove elemental S and over a column filled with Na_2SO_4 to remove traces of water. Samples were saponified (3 h, 80 °C) with 6% KOH in MeOH. Neutrals were extracted (x 3) with hexane and dried with Na_2SO_4 while the acid fraction was extracted from the aqueous phase after the addition of 6 M HCl. The neutrals were divided into apolar and polar fractions via liquid chromatography over NH_2 columns (Hinrichs et al., 2003). The polar fraction was derivatised [1 h, 80 °C, with N,O-bistrimethylsilyltrifluoroacetamide (BSTFA, Supelco)]. FAs were derivatised with 14% BF_3/MeOH (Sigma Aldrich) to produce the methyl esters (FAMEs). To identify multiple bond positions in FAs, an aliquot was derivatised with 2-amino-2-methylpropanol to form 2-alkenyl-4,4-dimethoxyloxazline (DMOX) derivatives (Spitzer, 1997).

The resulting fractions were examined using gas chromatography with flame ionisation detection [GC-FID; Carlo Erba HRGC 5160 Mega Series, VF-5 column (60 m × 0.25 mm inner diameter (i.d.) × 0.25 μm film thickness (f.t.)], He carrier gas at 1.0 ml min^{-1}). The samples were also examined using a gas chromatography-mass spectrometry (GC-MS) instrument (GC8000Top Finnigan Voyager, electron impact ionisation, Agilent HP-5 column, 30 m × 0.32 mm i.d. × 0.25 μm f.t., He carrier gas at 1.0 ml/min).

Glycerol dialkyl glycerol tetraethers (GDGTs) were analysed using a fraction of the total extract, dissolved in hexane/isopropanol (1:1, v:v) and filtered with 0.45 μm PTFE filters prior to analysis via high performance liquid chromatography (HPLC) in a manner similar to that described by Hopmans et al. (2000). For quantification, a synthesised C_{46} GDGT standard was added to each sample prior to analysis (Huguet et al., 2006). Analysis was performed with a Thermo Surveyor LC system coupled to an LCQ Fleet ion trap mass spectrometer, as described by Bechtel et al. (2010). Isoprenoid GDGTs (isoGDGTs) were named according to Schouten et al. (2009) and for branched GDGTs (brGDGTs) the nomenclature from Weijers et al. (2007) was used. Ethers in the polar fraction were cleaved prior to carbon isotopic analysis (Kohnen et al., 1992; Blumenberg et al., 2004). No derivatisation was necessary. For compound specific carbon isotopic analysis of the cleaved ethers, an Agilent GC 6890N with a combustion furnace using copper oxide coupled to a micromass IsoPrime mass spectrometer (Restek Rxi-5ms column, 60 m × 0.32 mm i.d. × 0.25 μm f.t.) was used. The GC oven temperature programme was: 70–130 °C at 20 °C min^{-1}, then to 320 °C (held 20 min) at 4 °C min^{-1}. He was the carrier at 1.0 ml min^{-1}.

The precision of the biomarker analysis was 10%, whereas the error for GDGTs was within 15%. The analytical error for compound specific $\delta^{13}C$ values was 1–2‰.

2.5. XRF core scanning

Relative elemental concentration was determined for the 2010 core, which was cut lengthwise and the surface allowed to dry at room temperature for 24 h. One half of the core was measured with the AVAATECH X-Ray Fluorescence Core Scanner at ETH Zurich, Switzerland, at excitation energy of 10 and 30 kV, respectively with a resolution of 0.3 mm for 30 s at each point (Richter et al., 2006). The units are XRF counts (peak area). The precision was ca. 2–3%, depending on the element.

2.6. Diatom analysis

Diatom samples were prepared from 2–4 cm intervals using standard techniques, including processing with H_2O_2 (30%) and HCl (10%). Between 300 and 400 valves were counted and identified for each sample and diatom accumulation rate was calculated using the evaporation tray technique (Battarbee et al., 2002).

2.7. Definition of BIT_{CH} index

A changed branched and isoprenoid tetraether index (BIT_{CH} index) was defined as:

$$\begin{aligned} BIT_{CH} &= \text{brGDGTs/isoGDGTs} \\ &= ([\text{GDGT-III}] + [\text{GDGT-II}] + [\text{GDGT-II-b}] + [\text{GDGT-II-c}] \\ &\quad + [\text{GDGT-I}] + [\text{GDGT-I-b}] + [\text{GDGT-I-c}])/([\text{GDGT-0}] \\ &\quad + [\text{GDGT-1}] + [\text{GDGT-2}] + [\text{GDGT-3}] + [\text{crenarchaeol}] \\ &\quad + [\text{crenarchaeol regio isomer}]) \end{aligned}$$

with:

(a) brGDGTs (Weijers et al., 2007): [GDGT-III], *m/z* 1050; [GDGT-II], *m/z* 1036; [GDGT-II-b], *m/z* 1034; [GDGT-II-c], *m/z* 1032; [GDGT-I], *m/z* 1022; [GDGT-I-b], *m/z* 1020; [GDGT-I-c], *m/z* 1018.

(b) isoGDGTs (Schouten et al., 2009): [GDGT-0], *m/z* 1302; [GDGT-1], *m/z* 1300; [GDGT-2], *m/z* 1298; [GDGT-3], *m/z* 1296]; [crenarchaeol], *m/z* 1292; [crenarchaeol regio isomer], *m/z* 1292].

3. Results and discussion

3.1. Sedimentation rate and age model

A precise age model was a prerequisite for a high resolution biomarker and trace metal record of Rotsee sediment. Since the core was only rarely laminated and mostly uniform brown-black in colour, radionuclides, i.e. ^{137}Cs and ^{210}Pb, were used for dating (Fig. A1; Supplementary online material). The former showed increased activity at 9–10 cm and 18–19 cm corresponding to the Chernobyl accident in 1986 and the peak in nuclear bomb tests in 1963, respectively. The resulting sedimentation rate was calculated as 0.40 cm yr^{-1} using ^{137}Cs. Using ^{210}Pb dating, a similar sedimentation rate of 0.35 cm yr^{-1} was found. Using an average sedimentation rate of 0.38 cm yr^{-1}, the core contained ca. 150 yr of lake history. The age model (Fig. A1) could be calibrated with higher TOC concentration at 33–34 cm via the high productivity event before 1922 (Lotter, 1989). The match with the age model of Lotter (1989) supports the high precision of the age model. Hence, biomarker sampling resolution of 1 cm gave a resolution of ca. 4 yr.

3.2. Eutrophication and sewage input history of Rotsee

TOC ranged between 4.3 and 6.8 wt.% within the core, with accumulation rate between 3.1 and 4.9 g cm^{-2} yr^{-1} (Fig. 2). At ca. 33–34 cm (1918–1921) and 15–18 cm (1961–1969), TOC accumulation rate maxima indicated times of higher productivity. The peak at 33–34 cm seemed to be a result of a nutrient supply induced trophic regime shift before the canal construction in 1922 (Lotter, 1989). The change became evident from re-analysis of phytoplankton samples from Bachmann (1931) in Lotter (1989), so the connection to the Reuss River was not the main driver of the higher productivity.

At the beginning of the 1960s, eutrophication peaked. The decreasing productivity since the end of the 1960s was a direct result of the construction of an interceptor sewer, preventing direct sewage supply to the lake from the surrounding urban area (Stadelmann, 1980). However, Reuss River water was still rich in nutrients, but this ended in 1974 after the construction of a sewage treatment plant (Stadelmann, 1980). Between 3 and 14 cm (1972–2001), TOC accumulation remained stable and decreased only in the recent lake sediment. Two explanations are likely: Non-point source input of nutrients from agriculture, which continued to fuel

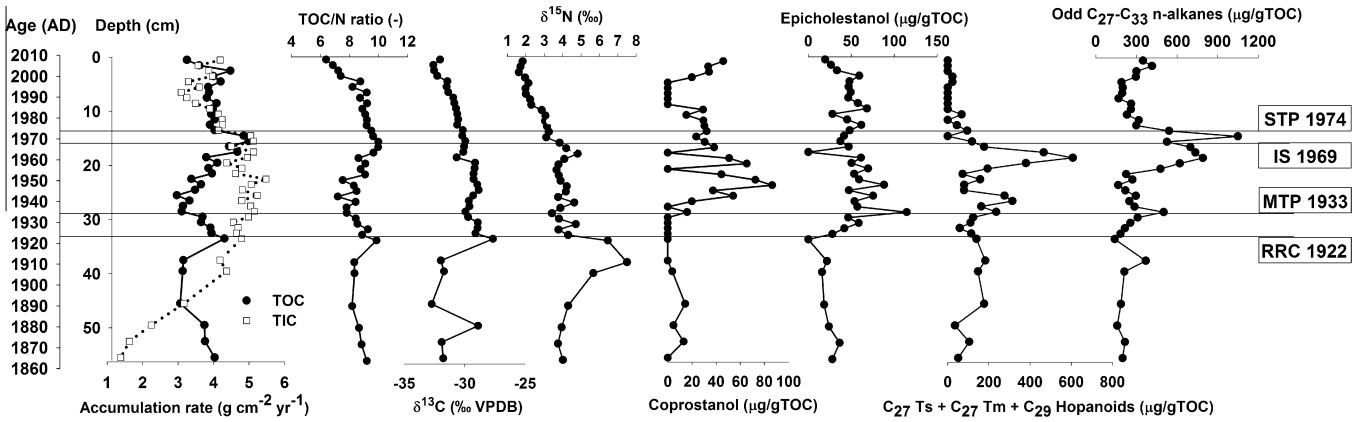

Fig. 2. Bulk parameters for core and profiles of coprostanol, epicholestanol, sum of C_{27} Ts, C_{27} Tm and C_{29} hopanoids and sum of odd C_{27}-C_{33} *n*-alkanes, plotted vs. sediment depth and age (AD). RRC, Reuss–Rotsee-canal; MPT, mechanical sewage treatment plant; IS, interceptor sewer; STP, sewage treatment plant (in all cases with the time of completed construction).

productivity, or redissolution and resuspension of nutrients and OM. The latter explanation implies that, although the nutrient input to the lake was reduced, nutrient redissolution from the lake sediment still fuelled productivity, similar to observations for other Swiss lakes (Matzinger et al., 2010). The continued nutrient supply explains the still conspicuous eutrophic character of the lake.

TIC increased consistently from the lower end of the core (1.4 g cm^{-2} yr^{-1}), towards ca. 33–34 cm (4.8 g cm^{-2} yr^{-1}, Fig. 2) and remained almost constant to 17–18 cm (4.3–5.1 g cm^{-2} yr^{-1}). Above this, TIC decreased to ca. 3.1 g cm^{-2} yr^{-1} at 5–6 cm, before reaching 4.2 g cm^{-2} yr^{-1} at the top of the core. The higher TIC values between ca. 17 and 34 cm (1918–1964) are in agreement with the elevated trophic state (Bloesch, 1974; Lotter, 1989). Bloesch (1974) and Lotter (1989) showed that TIC (and therefore carbonate precipitation) was related to productivity. Use of accumulation rate prevents potential bias of the TOC as a result of dilution by way of enhanced carbonate deposition (Stein, 1991).

TN, between 0.5 to almost 1.0 wt.%, coincided with the TOC profile, with higher values at ca. 17–20 cm and 29–34 cm. The much higher TOC (4.3–6.8 wt.%) and TN (0.5–1.0 wt.%) values (Fig. 2) vs. other Swiss lakes (Bechtel and Schubert, 2009) such as the oligotrophic Lake Brienz (0.4–1 wt.% TOC, <0.1 wt.% TN) and the eutrophic Lake Lugano (1.1–3.2 wt.% TOC, 0.1–0.4 wt.% TN) may be explained by Rotsee's higher nutrient input, higher productivity, shallow maximum depth and anoxic hypolimnion.

The $\delta^{13}C$ values for TOC were mostly <−31‰ before the beginning of the 1920s (Fig. 2) and increased to −27.6‰ at ca. 33–34 cm (1918–1921), which might be related to the increased productivity, leading to more enriched $\delta^{13}C$ values at that time. Since then, they have remained quite constant, likely overall due to the high extent of eutrophication. However, the values decreased again since the 1960s/1970s, reaching −32.0‰ in the surface sediment (Fig. 2), possibly related to a continuous recovery from eutrophication. The carbon isotope signal therefore also traces the trends in eutrophication and recovery during the lake's history. One complication in using $\delta^{13}C$ values with sediments is the so-called Suess effect. Burning $\delta^{13}C$ depleted fossil fuel in conjunction with industrialisation led to a shift in the isotopic ratio for atmospheric CO_2, which rose to −1.7‰ in 2004, compared with preindustrial values (McCarroll and Loader, 2004). Carbonate and OM deposited after the beginning of industrialization could therefore be influenced. Hence, if a lake is in equilibrium with the atmosphere, like e.g. the Great Laurentian Lakes, this has to be taken into account, since it would decrease the $\delta^{13}C$ value of the deposited OM (Meyers, 2006). However, Lake Rotsee is not in equilibrium with the atmosphere due to the mixing into the surface water of liberated dissolved inorganic carbon derived from OM degradation. Additionally, other factors like variation in the extension of blooms and precipitation of calcareous nanoplankton have a much stronger influence on the isotopic signal in the productive zone. We therefore think that the Suess effect is of minor importance in Lake Rotsee and have therefore not corrected the $\delta^{13}C$ TOC values.

The $\delta^{15}N$ values (Fig. 2) increased from the bottom of the core (4.0‰) to a clear maximum between 33 and 38 cm (max. 7.5‰), then decreased again upwards to the sediment surface (1.8‰). The values are within the range (Heaton, 1986; Hoefs, 2009) for soil OM (0‰ to +9‰), fertiliser (−4‰ to +4‰) and manure and septic waste (sewage, 0‰ to +25‰). Shifts in the latter potential source might in particular strongly increase $\delta^{15}N$, which might lead to large excursions in the isotopic signature. Although these different sources cannot be distinguished on the basis of $\delta^{15}N$ values alone, the decrease in $\delta^{15}N$ from the 1920s until 2009 may indicate reduced sewage and nutrient input. In contrast, the increasing $\delta^{15}N$ values until the 1920s are indeed likely an indication of increasing sewage input, which is known to have taken place since the mid-19th century (Kohler et al., 1984). N fixation and/or denitrification might also have led to the decrease in $\delta^{15}N$ values since the 1920s. However, N fixation is low in eutrophic systems because nitrogen is not limited (Canfield et al., 2005), so it seem to have hardly affected the $\delta^{15}N$ values in Rotsee. While no isotopic data for NO_3^- were available for the water column, the values in the sediment can trace water column nitrification-denitrification. Denitrification in the sediment of lakes proceeds until completion, which results in similar nitrogen isotopic signatures in the water column and sediment, also hardly affecting the $\delta^{15}N$ composition (Lehmann et al., 2003). Therefore, source changes (especially sewage supply) are the most likely reason for the observed shifts in the $\delta^{15}N$ signal.

Other sewage input indicators are thought to be coprostanol and epicholestanol (Mermoud et al., 1985; Bull et al., 2002), which were also found in Rotsee (Fig. 2). However, coprostanol can originate from mammals (Sherwin et al., 1993), so animal waste can be another source, which is likely due to surface runoff from nearby livestock farming north of the lake. Epicholestanol is more likely an indicator of bacterial alteration in the lake (Cordeiro et al., 2008), which might indicate higher bacterial activity during lake eutrophication, especially since the 1920s, and culminating at ca. 1933. Sewage input began in the mid-19th century and ceased in 1974 with the construction of a treatment plant. Both markers, still observed in the surface sediment, are therefore apparently not clear sewage indicators in Rotsee.

The two C_{27} isomers Ts (18α-22,29,30-trinorneo-hopane) and Tm (17α-22,29,30-trinor-hopane; much less abundant than Ts)

and C_{29} hopanoids (Seifert and Moldowan, 1978), tracers for petroleum contamination, were found, with peaks at 25–29 cm (1932–1942) and 17–20 cm (1956–1964, Fig. 2). The *n*-alkane carbon preference index (CPI, defined by Bray and Evans, 1961) also showed some lower values here (1.9–3.2, Fig. A2) although high maturity material like fossil OM or petroleum shows typical values close to 1 (Peters et al., 2006), which were not observed in this part of the core.

Previous studies indicate that the presence of these hopanoids, together with tricyclopolyprenanes, strongly suggests a contribution from fossil OM and/or biodegraded oil (Seifert and Moldowan, 1978; Behrens et al., 1998). However, the low abundance of tricyclopolyprenanes and the CPI values (>1) show that the contamination remained low. The decrease in these hopanoids at the beginning of the 1970s and the peak in the sum of odd C_{27}-C_{33} *n*-alkanes at 13–20 cm (1956–1974) indicate that the sewage treatment plant in 1974 effectively reduced the oil supply to the lake. The saturated hydrocarbons cannot be a result of the reduction in biohopanoids by H_2S since the end products of such a pathway remain partially unsaturated (Hebting et al., 2006).

3.3. Terrestrial OM sources

Aquatic and terrestrial OM sources were distinguished on the basis of TOC/N values, specific terrigenous biomarkers, trace metal profiles and distributions of FAs, *n*-alkanes and *n*-alcohols.

The molar TOC/N ratio showed values between 6 and 10 (Fig. 2), indicating a predominance of aquatic OM sources (Meyers and Ishiwatari, 1993). In contrast, specific terrigenous biomarkers were detected, such as lupeol, β-amyrin and amyrenone (Brassell and Eglinton, 1983), but the concentrations were too low for quantification.

The maximum at *n*-$C_{16:0}$ FA suggests predominantly autochthonous OM input to the sediment, in line with TOC/N values <10 (Fig. 2). In contrast, the maxima in the C_{17}, C_{23}, C_{25} and C_{27} *n*-alkanes and C_{16}, C_{22} and C_{26} *n*-alcohols indicate both aquatic and terrestrial sources (Meyers and Ishiwatari, 1993). The high abundance of C_{23} and C_{25} *n*-alkanes and C_{22} *n*-alcohol indicate a significant contribution from submerged and/or floating macrophytes (Ficken et al., 2000).

Other proxies for terrigenous input are the relative content of Fe, K and Ti, the covariance of which indicates that these trace metals have a similar detrital source (Tribovillard et al., 2006). They show a general decrease until about 1922 (Fig. 3), which we interpret to be primarily the result of dilution of detrital input by an increasing input of autochthonous material resulting from eutrophication and related higher productivity. The fluxes may have remained constant over time. Ti intensity decreased to the detection limit after 1922 (Fig. 3).

These trace metals correlate well with the ratio of branched (br) and isoprenoid (iso) GDGTs (Fig. 3). The correlation is in line with observations that indicate that brGDGTs originate from catchment soil (e.g. Weijers et al., 2007, Bechtel et al., 2010). Even though all the proxies indicate that most of the sediment material is of autochthonous aquatic origin, the BIT index (Hopmans et al., 2004) would lead to a contrasting conclusion. Below 33 cm, the BIT index shows highest values between 0.98 and 1.0 and decreases to 0.9 at 28–29 cm. From 26 cm to the core top, the index is between 0.93–0.96. If interpreted in the classical way (Hopmans et al., 2004), one would conclude that Rotsee sediment OM has a primarily terrigenous source. As concluded before (Bechtel et al., 2010) BIT index values can, however, be primarily ruled by the input of crenarchaeol, instead of by the input of brGDGTs. Indeed, the lower BIT value at 28–29 cm is due to a higher crenarchaeol concentration at that depth (Fig. 6). In lake settings, crenarchaeol is much less an indicator of aquatic archaeal input than it is in marine settings (Blaga et al., 2009), for which the BIT index was developed, and this may be especially the case in systems with a strong CH_4 cycle. The original BIT index deliberately excluded the other isoGDGTs because their source is considered more diverse, including methanogenic and methane-oxidising Archaea. If however, as is the case of Rotsee, a larger part of aquatic archaeal production is related to the CH_4 cycle, inclusion of the other isoGDGTs in the ratio should better reflect the relative input of allochthonous and autochthonous OM. Indeed, two alternative BIT indices, (i) the sum of all brGDGTs over the sum of all isoGDGTs (BIT_{CH}; definition in Section 2.7) or (ii) the ratio of a single brGDGT to GDGT-0, show much higher and more reasonable sensitivity to changes in the allochthonous supply from the lake catchment (Fig. 3).

Besides dilution by autochthonous OM input as a cause for the relative changes in detrital input to the lake, this may of course also be caused by real changes in detrital input. Pfister (1999) observed that from 1828 to 1895 the frequency of extreme flood events in the Reuss River increased, although at that time it was

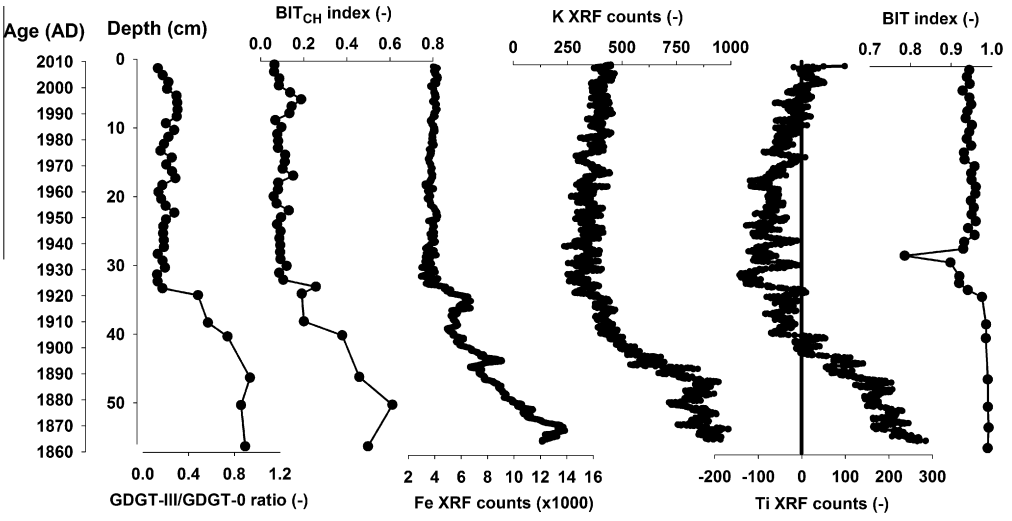

Fig. 3. Terrestrial input to the lake, traced via the ratio of branched GDGT-III/GDGT-0 (1050/1302), sum of branched to sum of isoprenoid GDGTs (BIT_{CH} index) and the XRF counts of Fe and K as running average of 9, XRF counts of Ti plotted as running average of 20 and BIT index according to Hopmans et al. (2004). All profiles are plotted vs. sediment depth and age (AD).

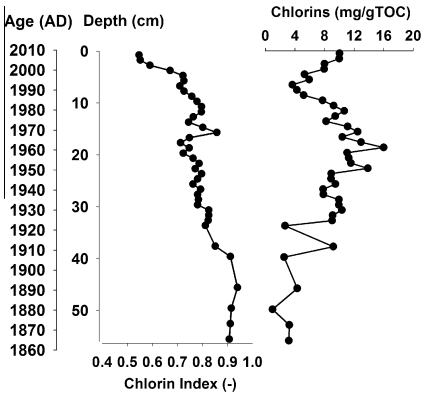

Fig. 4. Chlorin index and total chlorin concentration vs. sediment depth and age (AD).

not connected to Rotsee and therefore had no direct relationship. However, precipitation in the Swiss Alps was on average 28% higher during fall than in the period between 1901 and 1960. In the 20th century, extreme floods decreased in abundance, which could have resulted in lower erosional input from the catchment to the lake. However, such an increase in flood events since the 1970s (Schmocker-Fackel and Naef, 2010) is not apparent from the profiles of Fe, K and BIT_{CH}, although the Ti profile may show such a signal (Fig. 3). We therefore conclude that these profiles most likely indicate a dilution of terrigenous detrital input by aquatic input. Profiles (Figs. 2 and A3) of the sum of long chain FAs (C_{24}-C_{30}), *n*-alkanes (C_{27}-C_{33}) and *n*-alcohols (C_{24}-C_{32}) do not show a trend comparable to the Fe, K, Ti counts and BIT_{CH} (Fig. 3). In contrast, these compounds indicate that terrestrial input into the lake remained relatively constant.

3.4. Input and degradation of sedimentary OM

The chlorin index (CI) is a qualitative parameter estimating OM "freshness" and degradation. The lowest value (0.55) was in surface sediment (Fig. 4), indicating relatively fresh OM (Schubert et al., 2005). However, fresh chlorophyll would show values of ca. 0.2, suggesting that chlorophylls reaching the sediment are partly degraded in the water column. With increasing sediment depth the index increased up to 0.94 (Fig. 4), close to that of inert material (1.0).

The concentration profile of total chlorins (Fig. 4) has been used to reconstruct palaeoproductivity (Schubert et al., 2005). In contrast to the TOC, there was a maximum only at 18–19 cm (16 mg/g TOC), followed by a continuous decrease with depth. Together with the strong increase in total chlorins from 6–7 cm towards the sediment surface and the rapid increase in CI values with depth, the absence of a peak at ca. 33–34 cm could be due to degradation (Fig. 4).

3.5. Impact of eutrophication on microbial community changes

3.5.1. Primary producers

While C_{16} unsaturated FAs are generally related to algae and bacteria, C_{18} unsaturated FAs originate from algae, zooplankton and cyanobacteria (Volkman et al., 1980; Wakeham et al., 2007). Despite the non-specificity of these FAs, their changing abundance indicated changes in overall productivity within the lake. Because of significant correlation with the TOC and hopanoid profiles, the $C_{16:1(9)}$ FA (double bond at C-9) may originate from a mixed source of primary producers (peaks at 15–20 and 32–33 cm) and bacteria (peaks at 22–25 cm and 18–19 cm), whereas $C_{16:2(5,10)}$ FA is only related to productivity (Figs. 2 and A4).

Phytol (3,7,11,15-tetramethyl-2-hexadec-2-en-1-ol), an ubiquitous marker, can originate from chlorophylls in phytoplankton, but also from land plants, bacteriochlorophylls and cyanobacterial mats (Rontani and Volkman, 2003). However, peaks in the profile trace times of higher productivity, due to the similarity with the TOC profile (Fig. 5).

Ergosterol (24-methylcholest-7-en-3β-ol, C29:1Δ7; Fig. 5) has been found in fungi and yeast (Mille-Lindblom et al., 2004), but also in low amount in algae and protozoa (Raederstorff and Rohmer, 1987). The latter source is more likely, as indicated by the similarity in the depth profile to that for phytol (Fig. 5). Nonetheless, fungi could thrive on phytoplankton and/or bacterial biomass in the water column and sediment. They may play a crucial role in the cycling of nutrients and carbon, but knowledge about fungi in lakes is limited (Grossart et al., 2010).

Certain steroids were very abundant between 1958 and 1972. They (Figs. 5 and 7), specifically stigmasterol (24-ethylcholesta-5,22E-dien-3β-ol, C29:2Δ5,22E), stigmastanol (24-ethylcholestan-3β-ol, C29:0), campesterol (24-methylcholesterol, 24-methylcholest-5-en-3β-ol, C28:1Δ5), β-sitosterol (24-ethylcholest-7-en-3β-ol, C29:1Δ7), dinosterol (4,23,24-trimethylcholest-22E-en-3β-ol) and dinostanol (4,23,24-trimethylcholestan-3β-ol) can be related to higher productivity between 1958 and 1972 (Figs. 2, 5 and 7). The absence of a peak between 1918 and 1922 may be due to bad preservation, because of their high relative lability vs. other lipids (Hoefs et al., 2002).

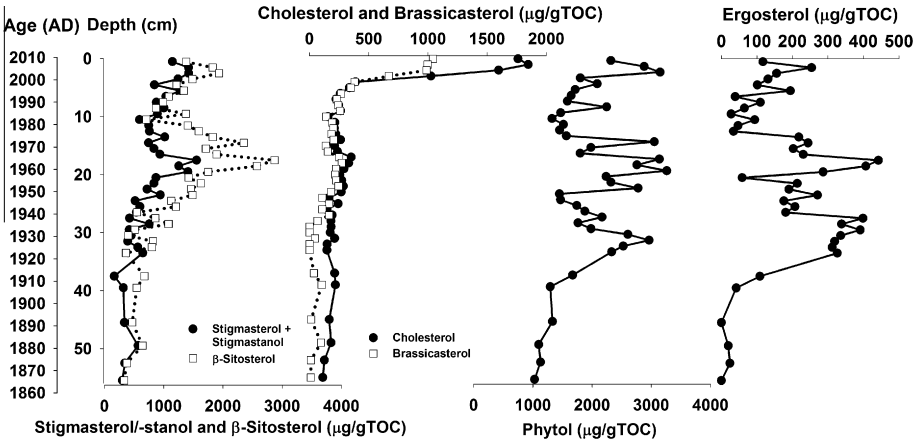

Fig. 5. Concentration of sterols, stanols and phytol vs. sediment depth and age (AD).

Because of the good match with higher TOC values between 1958 and 1972 (Fig. 2), stigmasterol and stigmastanol (Fig. 5) are interpreted as being derived mainly from phytoplankton in Rotsee, although a vascular plant source cannot be excluded (Volkman, 1986).

Similarly, brassicasterol (24-methylcholesta-5,22E-dien-3β-ol, C28:2Δ5,22E) and 24-methylcholesterol (Fig. 5) likely originate predominantly (Section 3.5.3) from algae (cf. Orcutt and Patterson, 1975; Volkman, 2003), but a contribution from higher plants cannot be excluded (Volkman, 2003). The match with cholesterol (cholest-5-en-3β-ol, C27:1Δ5), an algal/phytoplankton and zooplankton biomarker (Volkman, 1986; Volkman et al., 1998), suggests a similar origin. However, cholesterol and brassicasterol strongly decreased within the upper 5 cm, to ca. 21% and 37%, respectively (Fig. 5). Because of the high degree of degradation, the exact source of brassicasterol remains uncertain in Rotsee. A diatom source was not evident by comparison with diatom accumulation rates.

β-Sitosterol (Fig. 5) is the major sterol of emersed macrophytes (Ficken et al., 2000) and is often used as an indicator for higher plant input (Volkman, 1986). A high concentration peak was observed between 14 and 20 cm. The biomass of emersed aquatics probably increased as a result of the higher productivity. This is supported by the increased relative abundance of mid-chain *n*-alcohols and C_{23} and C_{25} *n*-alkanes at that depth (Fig. A3).

3.5.2. Bacteria and Thaumarchaeota

Hopanoids can be used as bacterial indicators (Rohmer et al., 1984), except for the hopanes discussed in Section 3.2. The peaks for C_{30} and C_{31} hopane at 28–31 cm (1926–1934) and 21-β-bishomohopan-32-ol between 25 and 29 cm (1932–1942) suggest a higher abundance of bacterial biomass and greater bacterial reworking of OM between 1926 and 1942 (Fig. 6). The higher abundance of straight and branched alkanes at 28–29 cm also indicates higher bacterial biomass at that time. Hopan-29-ol, C_{32}-bishomohopanol and C_{31}-homohopanol were detected, but could not be quantified because of the low abundance. The higher bacterial activity is further suggested by an epicholestanol peak at ca. 1933 (Fig. 1; Section 3.2).

After another hopanoid maximum in the 1960s, following the primary productivity during the eutrophication maximum, the abundance decreased, which could be a combination of biomass reduction due to reduced nutrient supply and the low extent of degradation of their precursors in the upper sediment. The depth dependent differences when comparing different hopanoids suggest distinct unequal sources. Based on biomarker data alone, a clear source distinction within the bacteria is not possible.

At 27–28 cm (1934–1937) crenarchaeol is on average five times more abundant vs. the rest of the profile, with a trend of increasing concentration starting at ca. 1922 (Fig. 6). As crenarchaeol originates from Thaumarchaeota, (NH_4^+ oxidising Archaea (Pitcher et al., 2011), the high abundance of crenarchaeol suggests a higher oxidation rate. It is not clear why Thaumarchaeota are only more abundant at this depth, because the trophic state was in general very high, at least between the 1920s and 1970s (Stadelmann, 1980; Kohler et al., 1984). However, the close match with bacteria between 1934 and 1937 suggests that a higher amount of NH_4^+ was supplied to the lake, which may have promoted Thaumarchaeota. The crenarchaeol maximum coincides with the construction of a mechanical sewage treatment plant in 1933 (Stadelmann, 1980), which would suggest a causal relationship. However, the mechanical water treatment should not have affected NH_4^+ content (Tchobanoglous et al., 2004). Either the biomass of bacteria and Thaumarchaeota might have increased due to a higher remineralisation rate for nutrients and OM during water treatment or these organisms were not removed in the treatment plant and entered the lake.

3.5.3. Diatoms

A description of the diatom assemblage in Rotsee was given by Bachmann (1931) and Lotter (1989). To compare the results, diatom accumulation rate was reinvestigated. In total, 71 different species were determined. Seven species *Stephanodiscus parvus*, *Cyclotella comensis*, *Asterionella formosa*, *Fragilaria crotonensis*, *Fragilaria ulna var. acus*, *Stephanodiscus hantzschii*, *Cyclotella comta/radiosa* represented at least 64% of all the diatoms. Several species represent the most dominant sources for certain biomarkers. It was not, however, possible to exclude other less abundant diatoms and/or other microorganisms as sources of these biomarkers.

The pentaunsaturated $C_{20:5(5,8,11,14,17)}$ FA (Fig. 7) is assumed to originate from diatoms (Volkman et al., 1998). The good correlation between the di- and tri-unsaturated FAs, $C_{18:2(9,12)}$ and $C_{18:3(5,9,12)}$, with the $C_{20:5(5,8,11,14,17)}$ FA (R^2 0.69 and 0.76, respectively) suggests the same origin for all three FAs (Fig. A5). All three were sparse before 1918, most abundant between 1918 and 1924, and then continuously decreased (Fig. A5). The increase in the upper 5 cm could be a degradation pattern, as FAs are easily decarboxylated (Hoefs et al., 2002). The correlation with *A. formosa* (R^2 0.46 for $C_{20:5}$, 0.37 for $C_{18:3}$, 0.48 for $C_{18:2}$) and *C. radiosa* (R^2 0.33 for $C_{20:5}$, 0.28 for $C_{18:3}$, 0.43 for $_{C18:2}$) seems to confirm them as the predominant source of these FAs. However, di- and triunsatu-

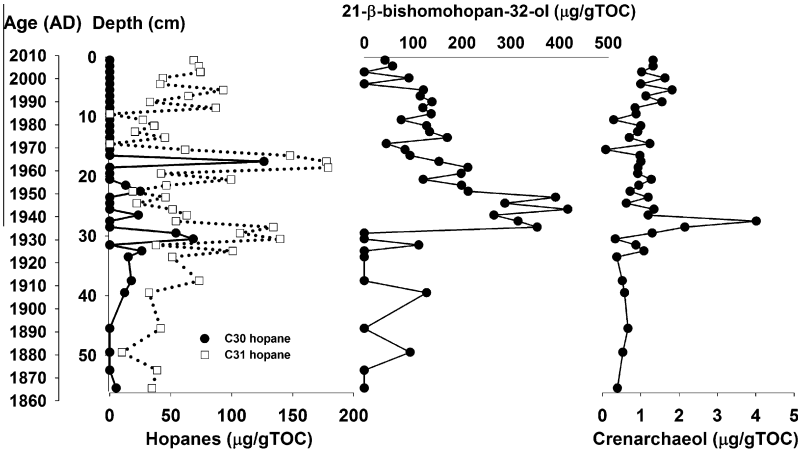

Fig. 6. Concentration of hopanoids and crenarchaeol vs. sediment depth and age (AD).

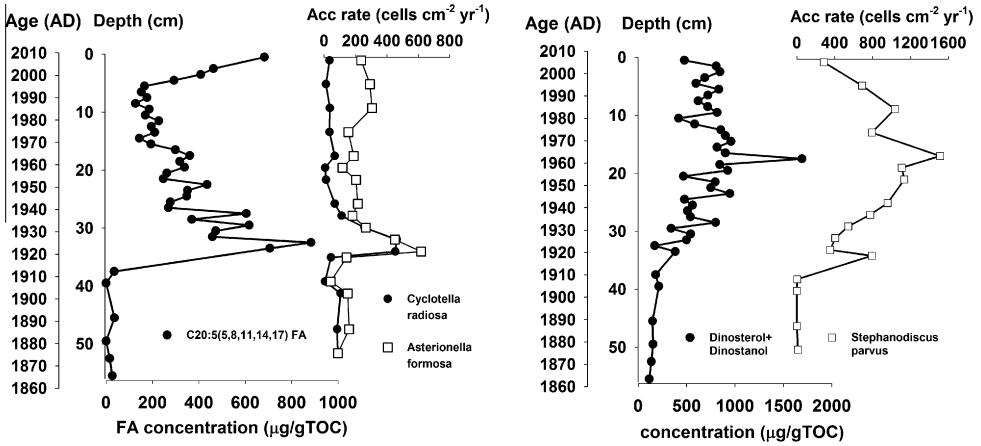

Fig. 7. Concentration of $C_{20:5(5,8,11,14,17)}$ FA and cell accumulation rate (acc rate) of *Cyclotella radiosa* and *Asterionella formosa* and profile of dinosterol/stanol with accumulation rate of *Stephanodiscus parvus* vs. sediment depth and age (AD).

rated FAs have also been referred to cyanobacteria and higher plants (Rezanka et al., 1983), which may explain the lower correlation between the diatoms and the $C_{18:2}$ and $C_{18:3}$ FAs.

The $C_{25:2}$ highly branched isoprenoid alkene (HBI; Fig. A6) is also known to be derived from diatoms (Volkman et al., 1998). In freshwater settings, only *Navicula sclesvicensis* has been reported to contain HBIs (Belt et al., 2001), but this diatom has not been found in Rotsee. The highest correlation with $C_{25:2}$ HBI could be found for *S. hantzschii*, but is only R^2 0.30, which suggests that other sources of this lipid need to be considered (Fig. A6).

Dinosterol and dinostanol were considered to be specific for dinoflagellates (Withers, 1983), but can also originate from diatoms (Volkman et al., 1993). Bachmann (1931) showed that dinoflagellates rarely occur in Rotsee. The deterministic $C_{22:6}$ FA for dinoflagellates (Volkman, 2003) is absent. Therefore, dinosterol and dinostanol are interpreted as being of diatom origin. The dinosterol/stanol profile matched the profiles for *S. parvus*, *F. crotonensis*, *Cyclotella pseudostelligera and Tabellaria fenestrata* together with the productivity maximum for 1958–1961 (18–19 cm; Figs. 7 and A7. However, cross plots indicate that the most dominant source seemed to be *S. parvus* (R^2 0.62, Fig. 7), also the most dominant of these diatoms in the lake since the 1920s due to the eutrophication. The low correlation for *F. crotonensis* (R^2 0.30) and *T. fenestrata* (R^2 0.28) suggests only a minor source of these lipids, while *C. pseudostelligera* (R^2 0.40) is unlikely to be a significant source because of its low accumulation rate.

24-Methylcholesterol can also be derived from dinoflagellates and diatoms (Orcutt and Patterson, 1975; Volkman, 2003). From the correlations, its main source could be *S. parvus* (R^2 0.45).

3.5.4. Methanogenic and methanotrophic Archaea

GDGT-0, the most dominant archaeal lipid, was used as a proxy for methanogenic Archaea. This proposed origin is supported by the fact that ca. 98% of archaeal biomass in the lake was methanogenic, with 91% consisting of *Methanosaeta* spp. (Falz et al., 1999). More evidence came from carbon isotope analysis after ether cleavage, with high $\delta^{13}C$ values between −36‰ and −21‰ for almost all ether cleaved GDGTs in the surface sediment, which is about the typical range of −35‰ to −22‰ for terrigenous, aquatic and also methanogenic archaeal lipids (Hinrichs et al., 2000), suggesting a predominantly methanogenic source. This is in contrast to much lower values, which can reach <−100‰ in marine settings, suggesting a predominantly methanotrophic origin (Hinrichs et al., 2000). On average, GDGT-0 showed a quite constant concentration of ca. 20 μg/g TOC, interrupted by a higher concentration during the productivity maxima, with ca. 42 and 83 μg/g TOC at 17–21 cm and 33–34 cm, respectively.

Based on reported data (Falz et al., 1999), GDGT-0 was used to estimate methanogen cell density in the lake sediment. The cell count was highest at the sediment surface and decreased continuously with depth, with ca. 3× lower cell density at 10 cm vs. the sediment surface (Falz et al., 1999). Through correlation of the cores, a concentration of 4.6×10^8 cells g^{-1} dry sediment of *Methanosaeta* spp. in the surface sediment corresponded to GDGT-0 concentration of ca. 20 μg/g TOC for most of the last 150 yr. During the productivity maxima, *Methanosaeta* spp. apparently increased up to at least ca. 9.2×10^8 cells g^{-1} dry sediment at 17–21 cm (1953–1964) and 1.8×10^9 cells g^{-1} dry sediment at 33–34 cm (1918–1921). From these estimates, it was assumed that the proportion of *Methanosaeta* spp. to all Archaea in surface sediment has remained constant at 91% for the last 150 yr.

The extent to which the supply of archaeal lipids within the sediment core compensated for degradation losses remained; however, constrained. GDGTs and archaeol are considered to be relatively recalcitrant (Pease et al., 1998). The linear decrease in the ratio of archaeol and GDGT-0 with depth (Fig. A8) indicates that archaeol is more rapidly degraded than GDGT-0, suggesting slow degradation of GDGT-0 in Rotsee sediment.

Based on the results, the average cell content of GDGTs was estimated on the basis of values from the literature, with 1–3 fg intact GDGTs (iGDGTs) $cell^{-1}$ (Sinninghe Damsté et al., 2002; Wuchter, 2006; Huguet et al., 2010). IGDGTs consist of core GDGTs (cGDGTs) and polar head groups. In sediments, polar head groups are decomposed within days to weeks (Harvey et al., 1986; Lipp et al., 2008). A cell density in the surface sediment of 4.6×10^8 cells g^{-1} sediment (Falz et al., 1999) and 1–3 fg intact GDGTs, together with the correlation between iGDGTs and cGDGTs (Huguet et al., 2010) leads to cGDGT concentration between 1.6 and 4.9 μg/g sediment. This range is of the same order of magnitude as the measured concentration of the sum of isoGDGTs (2.0 μg/g sediment). In the other direction, a theoretical iGDGTs/cell value for Rotsee sediment can be estimated, with a cell density of 4.6×10^8 cells g^{-1} sediment and 2.0 μg/g sediment isoGDGTs, leading to an average value of ca. 2.2 fg i-GDGTs/cell for Rotsee Archaea.

4. Summary and conclusions

Rotsee has been shown to be an ideal site for studying an anthropogenically altered ecosystem due to eutrophication. A multi-proxy approach, using lipid biomarkers and trace metals with a high temporal resolution of 4 yr, made it possible to reconstruct

short term changes in the physical, chemical and biological status. A direct impact of higher sewage and nutrient input on the increase in productivity and OM accumulation was observed, which led predominantly to a radiation in diatoms, primary producers and methanogens between about 1918 and 1921 and all microorganism groups and macrophytes between about 1958 and 1972. A higher abundance of bacteria and NH_4^+ oxidising Archaea was likely related to the construction of a mechanical sewage treatment plant in 1933. The decrease in OM accumulation in the lake since the end of the 1960s resulted from the construction of an interceptor sewer between 1967 and 1969. Furthermore, the decrease in fossil OM/biodegraded oil related biomarkers (C_{27} Ts/Tm and C_{27} hopanoids, long chain odd *n*-alkanes) is a clear indication for the achievement by the sewage treatment plant construction in 1974. The $\delta^{15}N$ of bulk OM, in contrast to coprostanol and epicholestanol, traced the eutrophication and recovery during the past 150 yrs.

Based on the correlation of trace metals (Fe, Ti, K) with br/iso GDGTs, terrestrial input could be reconstructed. We propose an altered BIT index, BIT_{CH}, as the sum of all brGDGTs/the sum of all isoGDGTs, the ratio better reflecting the balance between all aquatic Archaea, including those related to the methane cycle, and soil-derived brGDGTs than the original BIT index.

The impact of eutrophication on microbial assemblage changes could be traced. Also based on previous microbial studies, the sources of certain biomarkers could be partly identified down to the species level. The $C_{18:2(9,12)}$, $C_{18:3(5,9,12)}$ and $C_{20:5(5,8,11,14,17)}$ FAs likely originated mainly from the diatoms *C. radiosa* and/or *A. formosa*. The $C_{25:2}$ HBI originated from mixed sources and a clear source distinction between diatom species was not possible. *S. parvus* could be the main source of dinosterol and 24-methylcholesterol. The abundance of methanogenic Archaea and the cellular membrane lipid content (GDGTs) could be estimated.

Although microbial biomass reconstruction based on lipid biomarkers is often limited due to the non-specificity of lipids and their lability with respect to degradation, the use of high resolution multi-proxy records can improve the distinction of biomarker sources. Biomarker analysis can trace short term, and eutrophication related, ecosystem and microbial community changes.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orggeochem.2012.05.014. These data include Google maps of the most important areas described in this article.

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