



Seasonal changes in glycerol dialkyl glycerol tetraether concentrations and fluxes in a perialpine lake: Implications for the use of the TEX₈₆ and BIT proxies

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Abstract

To determine where and when glycerol dialkyl glycerol tetraether (GDGT) membrane lipids in lakes are produced, we collected descending particles in Lake Lucerne (Switzerland) using two sediment traps (at 42 and 72 m water depth) with a monthly resolution from January 2008 to late March 2009. Suspended particulate matter (SPM) was monthly filtered from the water column at three different depths. The potential application of GDGTs in palaeoenvironmental and palaeoclimatic reconstructions was investigated by comparing core lipids and their relative GDGT distribution, with lake water temperatures throughout the year. Fluxes of GDGTs and their concentrations in the water column vary according to a seasonal pattern, showing a similar trend in the SPM and sediment traps. Fluxes and concentrations of isoprenoid GDGTs increase with depth, maximum values being observed in the deeper part of the water column, indicating production of isoprenoid GDGTs by Thaumarchaeota in the deep (~50 m), aphotic zone of Lake Lucerne. The flux-weighted averages of the proxies TEX₈₆ (0.27) and BIT (0.03) based on the total extracted GDGTs are similar at both trap depths. A sediment core from the same location showed that in the first few centimetres of the core TEX₈₆ and BIT values of 0.29 and 0.07, respectively, are similar to those recorded for descending particles and SPM, indicating that the sedimentary TEX₈₆ records the annual mean temperature of deeper waters in Lake Lucerne. TEX₈₆ values are slightly higher below 20 cm in the core. This offset is interpreted to be caused by the present-day trophic state of the lake, which probably resulted in a deeper niche of the Thaumarchaeota. Branched GDGTs represent only a minor fraction of the total GDGTs in the lake and their origin remains unclear. Our data reveal that GDGTs in lakes have a large potential for palaeoclimatic studies but indicate that knowledge of the system is important for accurate interpretation.

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1. INTRODUCTION

Lake sediments provide an important archive for reconstructing past climates in continental interiors (e.g. Meyers, 1997). Recently the organic proxies TEX₈₆ (TetraEther index of 86 carbon atoms) (Powers et al., 2004), MBT/CBT (Methylation index/Cyclization index of Branched Tetraethers) (Weijers et al., 2007) and BIT (Branched and Isoprenoid Tetraether) (Hopmans et al., 2004) proxies were developed. These proxies are currently increasingly used to reconstruct lake water and related continental air temperatures as well as the input of soil organic material to the lake (e.g. Powers et al., 2005; Tierney and Russell, 2009; Tierney et al., 2010a,b) and variations in rainfall (Verschuren et al., 2009).

The TEX₈₆ palaeothermometer, that is based on membrane lipids derived from aquatic Thaumarchaeota, an abundant group of prokaryotes formerly falling in the Crenarchaeota (Spang et al., 2010), was initially proposed as an organic geochemical proxy for sea surface temperatures (Schouten et al., 2002). Thaumarchaeota are ubiquitously distributed in the ocean and produce glycerol dialkyl glycerol tetraethers (GDGT), membrane lipids with a variety of cyclopentane moieties (from 0 to 4), as well as crenarchaeol, a specific GDGT with four cyclopentane moieties and one cyclohexane moiety (Sinninghe Damsté et al., 2002). Mesocosm studies (Wuchter et al., 2004) showed that the increase of cyclopentane moieties in the thaumarchaeotal GDGTs is an adaptation to temperature change as previously observed in their (hyper)thermophilic relatives (Gliozzi et al., 1983). Analysis of a suite of over 300 marine surface sediments revealed that the TEX₈₆ ratio, as defined by Schouten et al. (2002), correlates linearly with annual mean sea surface temperature (Kim et al., 2008).

The presence of thaumarchaeotal GDGTs in lake surface sediments (Powers et al., 2004; Escala et al., 2007; Sinninghe Damsté et al., 2009) confirmed the widespread occurrence of Thaumarchaeota in freshwater aquatic environments previously assessed by molecular ecological studies (Keough et al., 2003). Therefore, application of the TEX₈₆ was extended to freshwater systems with an initial lacustrine calibration of TEX₈₆ (Powers et al., 2004) that closely resembled the marine calibration. This calibration was improved when surface sediments from 47 European lakes (Blaga et al., 2009) and 46 globally distributed lakes (Powers et al., 2010) were analyzed for their GDGT content. These studies also constrained the applicability of TEX₈₆ to lakes where the production of isoprenoidal GDGTs is mainly attributed to aquatic Thaumarchaeota and not to other sources (e.g. methanogenic Archaea, or influx of isoprenoid GDGTs from soils). Lake palaeotemperatures were reconstructed using the TEX₈₆ proxy from sediment cores from tropical Lake Malawi and Lake Tanganyika (Powers et al., 2005; Tierney et al., 2008, 2010a; Woltering et al., 2010). Recently, Sinninghe Damsté et al. (2009) determined the provenance and distribution of isoprenoid GDGTs in suspended particulate matter and descending particles from the water column and in sediments of a small crater lake (Lake Challa) at the border of Kenya and Tanzania. The sediment trap time series re-

vealed that crenarchaeol and related isoprenoid GDGTs were predominantly produced in January and February, following the local prominent short rain season. The TEX₈₆-inferred temperature derived from sedimenting particles corresponded well with lake surface-water temperature at the time of largest crenarchaeol flux. However, in situ production of isoprenoid GDGTs in deeper waters or surface sediment influenced the isoprenoid GDGT distribution and the sediments could thus not be used for TEX₈₆ palaeothermometry. Soils also contain isoprenoid GDGTs (Weijers et al., 2006) and transport of soil organic matter into a lake may affect the in situ produced GDGT distribution. A high input of allochthonous isoprenoid GDGTs may, therefore, also hamper the straightforward application of TEX₈₆ in lakes (Blaga et al., 2009).

In addition to isoprenoid GDGTs, also branched GDGTs were found in soils (Weijers et al., 2006), often in large relative abundances (>90%). This group of GDGTs is produced by an as yet unknown group of anaerobic soil bacteria, possibly belonging to the group of acidobacteria (Weijers et al., 2009; Sinninghe Damsté et al., 2011). Their abundance, relative to that of isoprenoid GDGTs in aquatic systems, was quantified using the Branched versus Isoprenoid Tetraether (BIT) index (Hopmans et al., 2004). This index can be applied as a means to determine the relative changes in input of soil organic matter (OM) in aquatic systems (Hopmans et al., 2004; Blaga et al., 2009). Sinninghe Damsté et al. (2009) noted that in Lake Challa the main flux of branched GDGTs to the sediment during the short rainy season was most probably derived from eroded catchment soils and delivered through surface runoff. Verschuren et al. (2009) reconstructed variations in rainfall over the past 25,000 years using a high-resolution BIT record from the sediment of this lake. However, Tierney and Russell (2009) showed for an Indonesian lake that in situ production of branched GDGTs in the water column or in the sediment cannot be excluded. Subsequent studies that focused on the concentrations of branched GDGTs in the water column and sediments from lakes in East Africa (Tierney et al., 2010b), Switzerland (Bechtel et al., 2010), New Zealand (Zink et al., 2010), Europe and South America (Blaga et al., 2010) suggest that in situ branched GDGTs may constitute an important part of the total pool of branched GDGTs.

Here we present the results of an integrated seasonal study, in which we quantified GDGTs in SPM, descending particles and surface sediments, to shed further light on the application of GDGTs as proxies for reconstructing palaeoclimatic and palaeoenvironmental changes in lakes. Lake Lucerne Chrüztrichter Basin was selected for this study based on the initial identification of high isoprenoidal GDGT concentrations and limited input of soil-derived GDGTs in surface sediments compared to the other studied basins (Blaga et al., 2009) and the potential of this lake as a recorder of regional climate since the last glacial maximum (Schnellmann et al., 2006). The lake was sampled at a monthly resolution, using in situ lake-water filtration of surface and deeper waters, and sediment traps deployed at two depths. In this way we determined when and where the different GDGTs are produced, transported through the

water column, and ultimately buried in the sediment. The assessment of spatial and temporal variability proved to be important for evaluating the proxy potential of the GDGTs.

2. MATERIALS AND METHODS

2.1. Setting

Lake Lucerne is an oligotrophic lake at the border of the Alps (434 m above sea level, 113 km² surface area, 104 m mean depth, 3.4 years residence time) situated in Central Switzerland. As an oligomictic lake a complete overturn occurs on average every 6 years. The lake has seven subbasins, separated by subaquatic sills formed by glacial bedrock-erosion and moraine deposits. The five subbasins that form a chain from the main inflow to the outflow (Lake Uri, Treib Basin, Gersau Basin, Vitznau Basin and Chrüztrichter Basin) (Fig. 1) are fed by four major alpine rivers: Reuss, Muota, Engelberger Aa and Sarner Aa, which drain a large part of the limestone and granite bedrock dominated catchment (2124 km²) and at the same time provide ~80% of the lake's total water supply (109 m³/s) (Schnellmann et al., 2002). The study site (Fig. 1) is located at the edge of the Chrüztrichter Basin that is characterized by a complex bathymetry as a result of its geomorphologic evolution, which was influenced by the nearby front of the alpine naps and two major confluencing alpine glaciers. The sediment trap was positioned at each deployment within a narrow area on the moraine-built sill separating the Chrüztrichter Basin from the Vitznau Basin in water depths between 80

and 90 m. The sediment core was taken in the same area at a water depth of ~90 m. Limnological parameters (temperature, oxygen, conductivity, pH profiles) were measured each time the sediment traps were deployed and recovered at the sampling site using a Conductivity–Temperature–Depth recorder (Seabird CTD SBE-19).

2.2. Sample collection

Sinking particulate organic matter was collected with a monthly resolution during a 14-month period, starting in January 2008 and ending in March 2009. In March 2008 the sediment trap was recovered later than usual and not immediately re-deployed, to avoid too short a sampling interval. For this reason the sediment trap deployment was continued until end of March 2009 thus completing a full annual cycle. Eight open cylinder sediment-traps (height 101 cm, ϕ 18.8 cm) were deployed every first week of the month, with four cylinder traps at 42 m water depth and four cylinder traps at 72 m. The traps were not poisoned but the relatively short time (i.e. 4 weeks at maximum) between deployments is thought to prevent substantial alteration of the organic matter during storage in the trap. Three thermistors (Minilog, Vemco, Canada) were attached to the mooring at water depths of 30, 42 and 72 m and logged water temperatures at 10 min intervals, to study the temperature regime of Lake Lucerne.

After the sediment traps were recovered the overlying water layer was drained and samples were centrifuged at 6500 rpm for 20 min (Centrikon centrifuge ϕ 25 cm; Kontron Instruments, Switzerland). The centrifuged particles

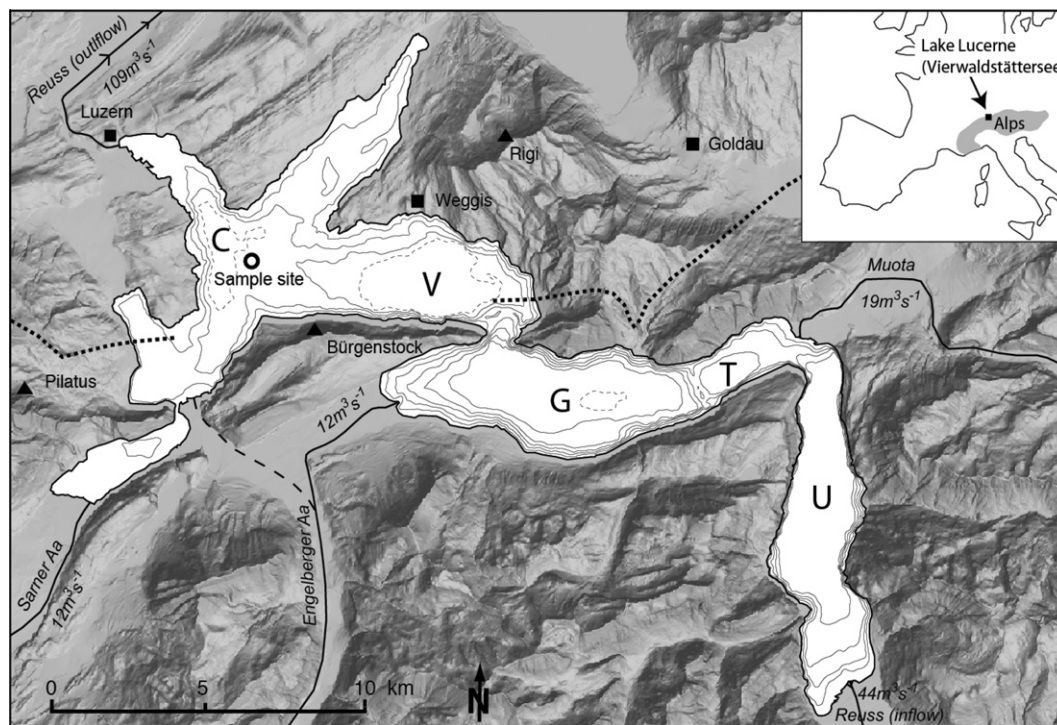


Fig. 1. Location of the sampling site in Lake Lucerne. Capital letters indicate names of sub-basins: C = Chrüztrichter, V = Vitznau, G = Gersau, T = Treib and U = Uri Basins. Major rivers are indicated.

were subsequently kept at -20°C and freeze-dried after returning to the home laboratory. Particulate matter was weighed after freeze-drying to calculate particle fluxes ($\text{g m}^{-2} \text{d}^{-1}$).

Water was filtered through a $0.7 \mu\text{m}$ ashed glass fibre filter (GFF) (ϕ 142 mm) using an in situ pump (McLane WTS-LV08) close to the sediment trap site. Samples were taken at 2, 42 and 72 m depth in the water column at the same days when the sediment traps were recovered and redeployed. The in situ pump filtered between 25 and 175 L, depending on when the capacity of the filter was reached.

A gravity core (111 cm long) was taken from the same site in November 2009. Using marker horizons, a cross correlation of this core with core 4WS00-4P (Schnellmann et al., 2006), taken in close vicinity was made, indicating that the new core covers the last ~ 1200 years of sediment deposition.

2.3. Sample preparation

A small aliquot of each sediment trap sample and several down-core sediment samples was treated with a solution of HCl (0.5 N, and 6 N, respectively) to remove any authigenic carbonate and further analyzed for total organic carbon (TOC) content using a C, N and S Fisons NA 1500 elemental analyzer (EA).

A known aliquot of the freeze-dried material collected in the traps was extracted three times using an accelerated solvent extractor (ASE; DIONEX2000), with a solvent mixture of dichloromethane (DCM)/methanol (MeOH) 9:1 (vol/vol) at a temperature of 100°C and a pressure of 7.6×10^6 Pa for 5 min. The total extracts were rotary evaporated under vacuum and separated over an activated Al_2O_3 column, using hexane/DCM 9:1 (vol/vol) to obtain the apolar fraction and DCM/MeOH 1:1 (vol/vol) for the polar fraction containing the GDGTs. The later fraction was dried under a continuous flow of N_2 , ultrasonically dissolved in a mixture of hexane/2-propanol 99:1 (vol/vol) at a concentration of 2 mg/ml and filtered through a $0.45 \mu\text{m}$ PTFE filter (ϕ 4 mm) prior to HPLC/APCI-MS analysis.

The GFF filters were freeze dried and ultrasonically extracted with MeOH, DCM/MeOH (1:1, vol/vol) and DCM, each three times. The total lipid extracts from the different extraction steps were combined after rotary evaporation and separated over an activated Al_2O_3 column similar to the extracts of the sedimenting particles.

The top 5 cm of the core was sampled continuously into 1 cm slices, and with a 10 cm resolution in the deeper section of the core. Extracts were obtained using ASE extraction in a similar way as described for the sediment trap material.

2.4. HPLC analysis

Polar fractions from both sediment traps and water filtrates were analysed using high performance liquid chromatography. GDGTs extracted with the ASE method were analyzed using HPLC/APCI-MS (Agilent 1100 series/Hewlett Packard 1100 MSD), equipped with an auto-injector and Chemstation chromatography manager software according to a modified procedure from Hopmans et al.

(2000) and Schouten et al. (2007). The separation was achieved in normal phase on an Alltech Prevail Cyano column (150×2.1 mm; $3 \mu\text{m}$). Injection volume was $10 \mu\text{l}$. An eluent consisting of hexane/propanol 99:1 (vol/vol) was used for 5 min to elute the GDGTs isocratically. The flow rate was set at 0.2 ml/min. Analysis was performed in single ion monitoring mode scanning the $[\text{M}+\text{H}]^+$ ions of isoprenoid and branched GDGTs (1302, 1300, 1298, 1296, 1292, 1050, 1036 and 1020). After evaluation of the mass chromatograms, peaks that were at least one order of magnitude greater than the background noise were integrated (Schouten et al., 2007). GDGTs were quantified by integration of the peak areas. Absolute amounts of GDGTs injected on column were calculated by adding a known amount of C_{46} internal GDGT standard (Huguet et al., 2006). The reproducibility of TEX_{86} using SIM-MS detection was 0.0043 (Schouten et al., 2007).

TEX_{86} and BIT indices were calculated according to the following equations by Schouten et al. (2002) and Hopmans et al. (2004):

$$\text{TEX}_{86} = \frac{\text{GDGT II} + \text{GDGT III} + \text{CREN isomer}}{\text{GDGT I} + \text{GDGT II} + \text{GDGT III} + \text{CREN isomer}}, \quad (1)$$

$$\text{BIT} = \frac{\text{GDGT V} + \text{GDGT VI} + \text{GDGT VII}}{\text{CREN} + \text{GDGT V} + \text{GDGT VI} + \text{GDGT VII}}, \quad (2)$$

where CREN, CREN isomer and I–VII refer to GDGT structures (see Blaga et al., 2009).

3. RESULTS

3.1. Temperature pattern of the water column

Water temperature of Lake Lucerne varied between January 2008 and March 2009 from 4.9 to 21.8°C , as a function of season and depth (Fig. 2). The lake did not freeze during the winter, and in both the winter of 2008 and 2009 complete water-column mixing occurred as revealed by homothermic conditions of 5.9°C over the entire water column. Surface waters started to warm up early April 2008. In May 2008 the onset of stratification is observed, with a temperature gradient starting to develop from the surface. Stable stratification, with an epilimnion comprising the upper 15 m, was complete by June. Subsequently, the mixed layer gradually deepened reaching a depth of 20–25 m by the end of October 2008. Early December 2008 the water column showed the first signs of mixing and in January 2009 a homogeneous temperature of 5.9°C was again measured.

3.2. Particle fluxes

The temporal variation of the particulate mass flux determined from the trap deployed at 42 and 72 m is shown in Fig. 3. For the duration of the study, average sediment fluxes were $0.8 (\pm 0.5)$ and $1.0 (\pm 0.5) \text{g m}^{-2} \text{day}^{-1}$, for the shallow and the deep trap, respectively. At both depths the flux of sinking particulate matter starts to increase in

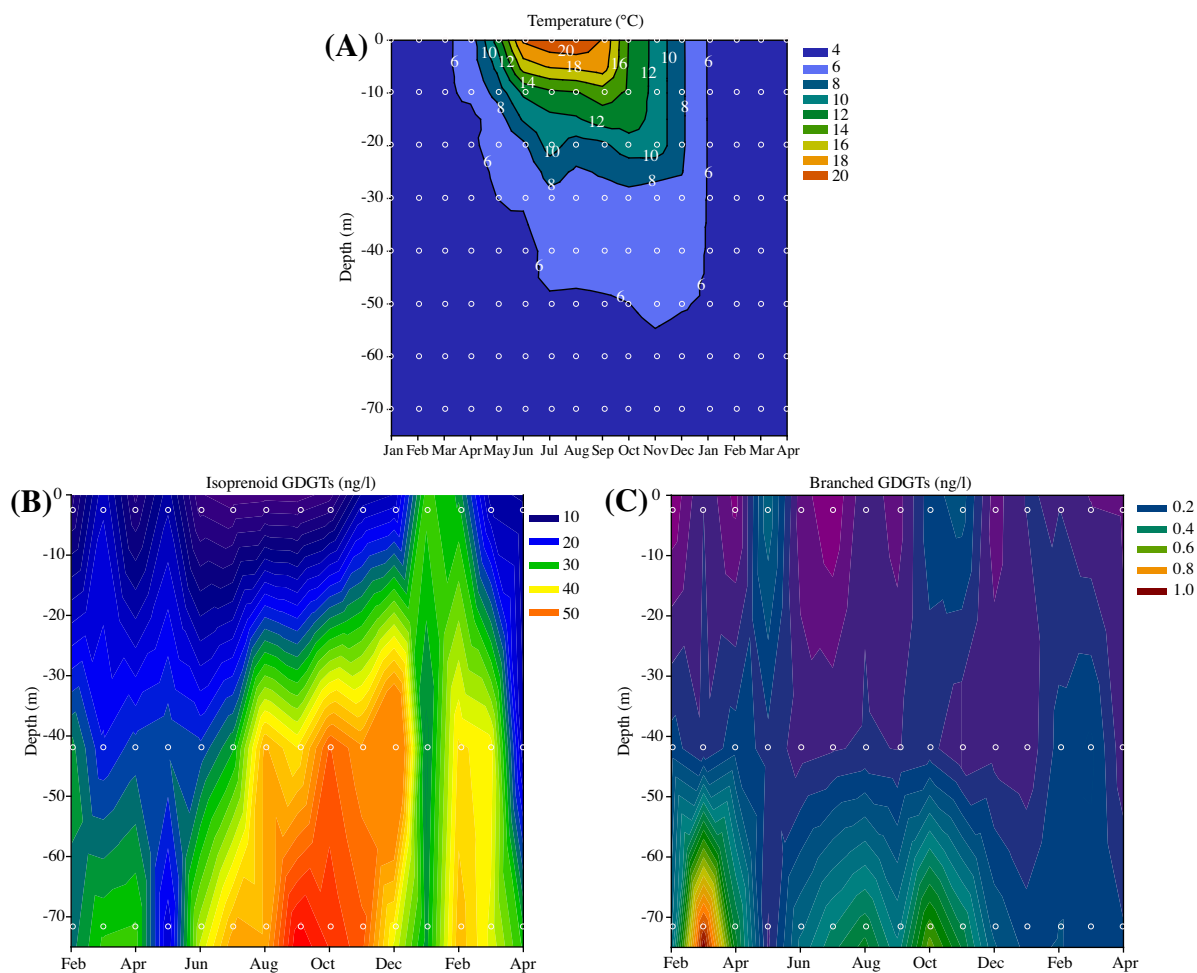


Fig. 2. Contour plots of (A) in situ water temperature measured at different depths during the study period; (B) concentrations of isoprenoid GDGTs in SPM, and (C) concentrations of branched GDGTs in SPM. Sampling grids are indicated with open white circles.

early spring, reaching a first maximum in June. In July and August the particle flux decreases but a second, less pronounced peak is observed in September at both depths. After that, fluxes generally decrease towards the winter (Fig. 3). The lower trap shows two additional maxima: the first in April 2008, the second at the end of the study in March 2009, both not observed in the mass-fluxes of the upper trap. During the annual cycle mass flux values range between 0.31 and $1.9 \text{ g m}^{-2} \text{ day}^{-1}$ in the sediment trap deployed at shallow depth and between 0.27 and $1.8 \text{ g m}^{-2} \text{ day}^{-1}$ for the deeper trap. The TOC content of the trapped particles varies from 3.8 to 8.8% . Particulate organic carbon fluxes generally mimic total particulate matter fluxes and vary between 0.04 and $0.18 \text{ g OC m}^{-2} \text{ day}^{-1}$ (Fig. 3). The ratio between organic carbon and total nitrogen ($C_{\text{org}}/N_{\text{tot}}$ ratio) of the descending particles is relatively constant (~ 7.1) through time for both trap depths.

3.3. GDGTs

3.3.1. GDGTs in the suspended particulate matter

The distribution of isoprenoid and branched GDGTs at three different depths in the water column revealed only min-

or differences (Fig. 4A). Crenarchaeol and GDGT-0 dominate at all depths, while the branched GDGTs represent only a minor fraction. In the suspended material collected at 42 m , GDGT-0 was slightly more abundant than at the other two depths [weighted average 38.4% of GDGT-0 at 42 m compared to 36.8% at 2 m and 35.1% at 72 m ; this difference is statistically significant for the material collected at 2 and 42 m ($P = <0.001$), but not for that at 42 and 72 m ($P = >0.210$). On the other hand branched GDGTs show a contrasting pattern, with slightly higher abundances in the surface waters (weighted average 1.3%) and at 72 m (1.2%) compared with the material from 42 m (0.5%). Also for the branched GDGTs a *t*-test was performed which shows that the difference between 2 and 42 m is not statistically significant ($P = 0.168$) while between 2 – 72 m and 42 – 72 m the difference is statistically significant ($P = <0.001$). Concentrations of SPM-associated isoprenoid GDGTs in Lake Lucerne vary between 0.6 and 58 ng/l , while summed branched GDGT concentrations vary between 0.04 and 1 ng/l . Concentrations of different GDGTs change through time and differ with sampling depth (Fig. 5, see also electronic annex). In the SPM from 72 m taken between June and December 2008 highest isoprenoid GDGT concentrations (35 – 60 ng/l) are

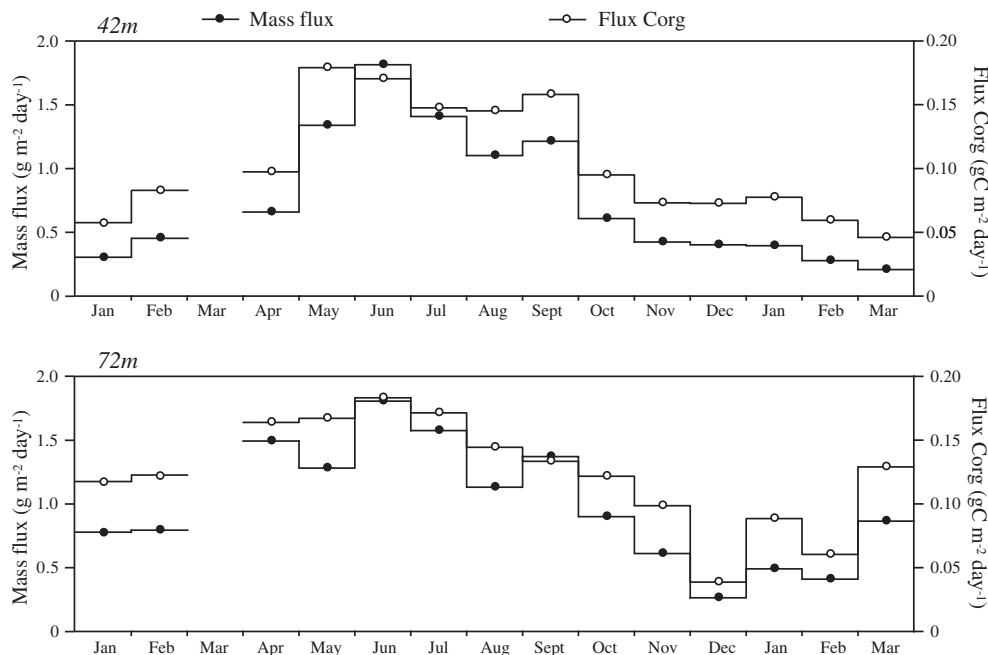


Fig. 3. Annual variation in mass flux of descending particles and organic carbon flux measured in sediment traps deployed at 42 and 72 m in Lake Lucerne.

observed, with maximum GDGT values in September 2008. Concentrations at 42 m are slightly lower, but not significantly different from the ones measured at 72 m, with maximum concentrations measured between August and December 2008 varying between 40 and 60 ng/l. In February and March 2009, a second GDGT maximum is observed at both 42 and 72 m. A different temporal evolution of GDGT concentrations is exhibited at the lake water surface compared with the other two depths. Isoprenoid GDGT concentrations at the surface are substantially lower than in the deeper waters, varying between 1 and 30 ng/l. In March and May 2008 two minor peaks are observed, while maximum concentrations were measured later in the year from November 2008 to March 2009 with the highest concentration in January 2009 at the time of the overturn of the water column (30 ng/l).

The low concentrations of branched GDGTs are also expressed by the low BIT index values, varying between 0.01 and 0.24 at 2 m, 0.005 and 0.02 at 42 m and 0.01 and 0.07 at 72 m water depth (Fig. 6, EA-1). The TEX_{86} varies between 0.24 and 0.34 at 2 m, 0.22 and 0.30 at 42 m and 0.26 and 0.36 at 72 m depth. The changes observed in BIT and TEX_{86} follow a seasonal pattern; highest BIT values are observed during summer (principally at shallow depth), maximum TEX_{86} values are observed during late summer to autumn at surface and in March at 72 m.

3.3.2. Distribution and fluxes of total GDGTs

The sediment trap study revealed nearly identical distribution for the GDGT in descending particles at different depths (Fig. 4B). The flux-weighted average distribution of GDGTs is dominated by crenarchaeol (48%), followed

by GDGT-0 (36%), with branched GDGTs representing only a minor component (Fig. 4B).

For the trap deployed at 42 m isoprenoid GDGT fluxes range between 0.08 and $0.4 \mu\text{g m}^{-2} \text{day}^{-1}$. In the deep trap fluxes are similar and vary between 0.1 and $0.4 \mu\text{g m}^{-2} \text{day}^{-1}$ (Fig. 7, EA-1). Throughout the time period studied, isoprenoid GDGT fluxes remained generally constant in the deep trap, whereas in the shallow trap all isoprenoid GDGT fluxes gradually increase over the year, culminating in a distinct maximum in November 2008. A clear minimum in all isoprenoid GDGT fluxes is observed during December 2008 at both depths. Branched GDGT fluxes are between 0.84 and $3.0 \text{ ng m}^{-2} \text{day}^{-1}$ in the shallow trap, whereas branched GDGT fluxes measured in the deep trap are between 0.87 and $11.7 \text{ ng m}^{-2} \text{day}^{-1}$ (Fig. 7). For branched GDGTs a distinct higher flux is observed for the deep trap in January and February 2008. Overall isoprenoid GDGTs make up 99% of the total GDGT flux while the branched GDGTs represent only a minor component.

The relatively low amounts of branched GDGTs are reflected by the low BIT values, which varied from 0.01 to 0.03 for the shallow trap and from 0.01 to 0.11 for the deep trap (Fig. 7, EA-1). The TEX_{86} values for the material collected in the upper sediment trap were on average 0.27 and almost identical values (average of 0.28) were observed for the deep trap.

3.3.3. GDGTs in sediments

Sixteen sediment intervals from a ~ 1.2 m long core were analyzed for their total GDGT distribution and content (Fig. 8, EA-1). A slight change in the GDGT distribution can be observed down core (Fig. 4C). For surface sediments the GDGT distributions are dominated by crenarchaeol

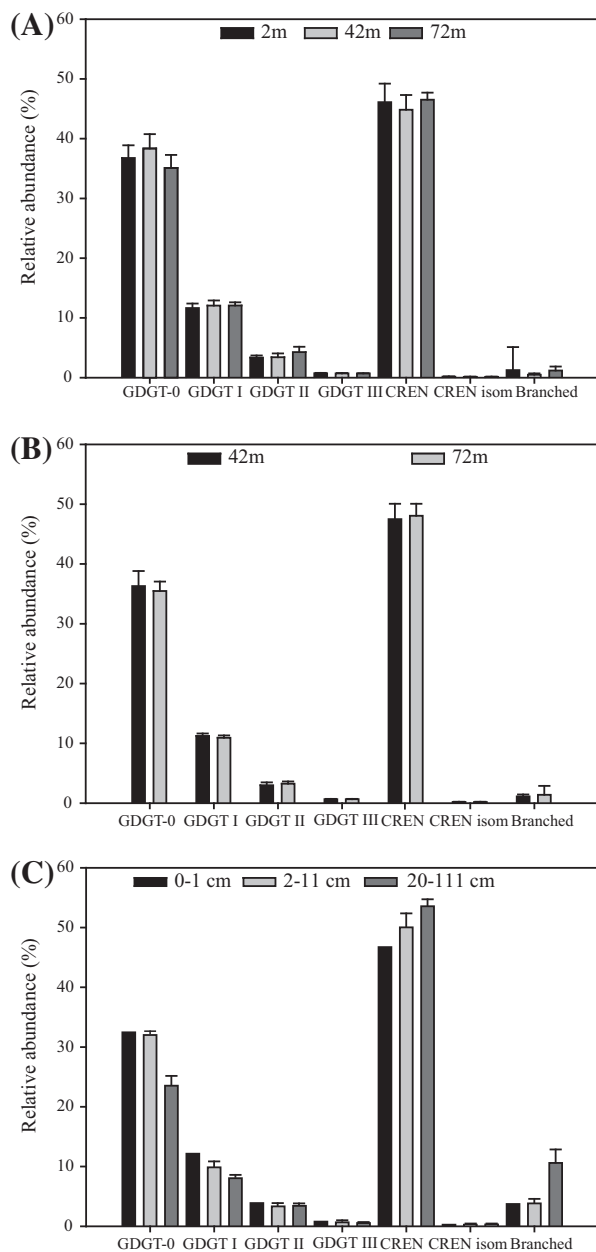


Fig. 4. GDGT distributions showing (A) concentration-weighted average for SPM at three depths, (B) flux-weighted average of total GDGTs for the two traps, and (C) average of specified sediment intervals. Error bars indicate the standard deviation of the average.

(47%) followed by GDGT-0 (33%), and with increasing depth lower relative abundances are recorded for GDGT-0 and higher for crenarchaeol. Sediments from the top 10 cm are characterized by high concentrations of summed isoprenoid GDGTs varying between 46.1 and 226 ng/g compared with the deeper part of the core where concentrations only reach 31 ng/g at maximum (Fig. 8). A similar down core shift towards lower abundances in the last 80 cm of the core can be observed for the branched GDGTs. Relatively low concentrations of branched GDGTs (0.3–4.1 ng/g in top 10 cm and 0.1–1.3 ng/g in the rest of the core) are observed in the

sediments, also revealed by the low BIT index ranging between 0.06 and 0.2 (Fig. 8). The values for TEX_{86} increase from an average of 0.29 in the top 10 cm to an average of 0.34 in the deeper part of the core.

4. DISCUSSION

4.1. Thaumarchaeotal GDGTs in Lake Lucerne

The distribution of isoprenoid GDGTs in SPM, descending particles, and the surface sediments of Lake Lucerne are almost identical (Fig. 4), indicating one dominant source for these components. This distribution, dominated by crenarchaeol, and to a lesser extent by GDGT-0, strongly suggests that the isoprenoid GDGTs are derived from Thaumarchaeota. These Archaea are so far the only organisms demonstrated to produce crenarchaeol (Sinninghe Damsté et al., 2002; Schouten et al., 2008; Pitcher et al., 2010, 2011).

Changes in the concentrations of isoprenoid GDGTs in the SPM reflect the dominant niches of the aquatic Thaumarchaeota over time and space. Isoprenoid GDGTs in the suspended organic matter generally have highest concentrations in the deepest part of the water column (Fig. 2B). The 14-month sediment trap study revealed a change from lower to higher biological activity over the annual cycle, as reflected by relatively high mass fluxes during summer (Fig. 3). Maximum isoprenoid GDGT fluxes occurred shortly after the peak in mass flux (Fig. 7). Concentrations of GDGTs were consistently lower in the surface waters, except for the winters 2008 and 2009 when the water column mixed and thaumarchaeotal cells were probably transported from deeper waters to the surface. This indicates that the main niche for Thaumarchaeota producing the isoprenoid GDGTs is the deeper part of the water column. Moreover, isoprenoid GDGTs are not transported to the sediment as part of the regular lake algal bloom and associated authigenic carbonate precipitation, but rather follow such blooms with a time lag. In the SPM measured in the deeper water column (both at 42 and 72 m), the isoprenoid GDGTs show increased concentrations during late summer and autumn (Figs. 2 and 5). Both production of isoprenoid GDGTs in the deeper part of the water column, and the observed seasonal changes are in good agreement with Thaumarchaeota being predominantly nitrifiers (Könneke et al., 2005; Wuchter et al., 2006; Pitcher et al., 2009a). As such they depend on the release of ammonium from the decomposition of particulate organic nitrogen produced by phytoplankton communities in the lake surface waters. Also in Lake Challa a high flux of isoprenoid GDGTs occurred shortly after a peak in the organic carbon flux (Sinninghe Damsté et al., 2009). In contrast to our study, however, crenarchaeol fluxes in Lake Challa remained much lower during the rest of the year. The slightly higher flux of isoprenoid GDGTs at 72 m compared to that at 42 m is probably due to a thriving community of Thaumarchaeota at mid-water depth (Fig. 2).

The sedimentary isoprenoid GDGTs do not reveal a substantial contribution of methanogens (producing predominantly GDGT-0) since relative GDGT-0 concentra-

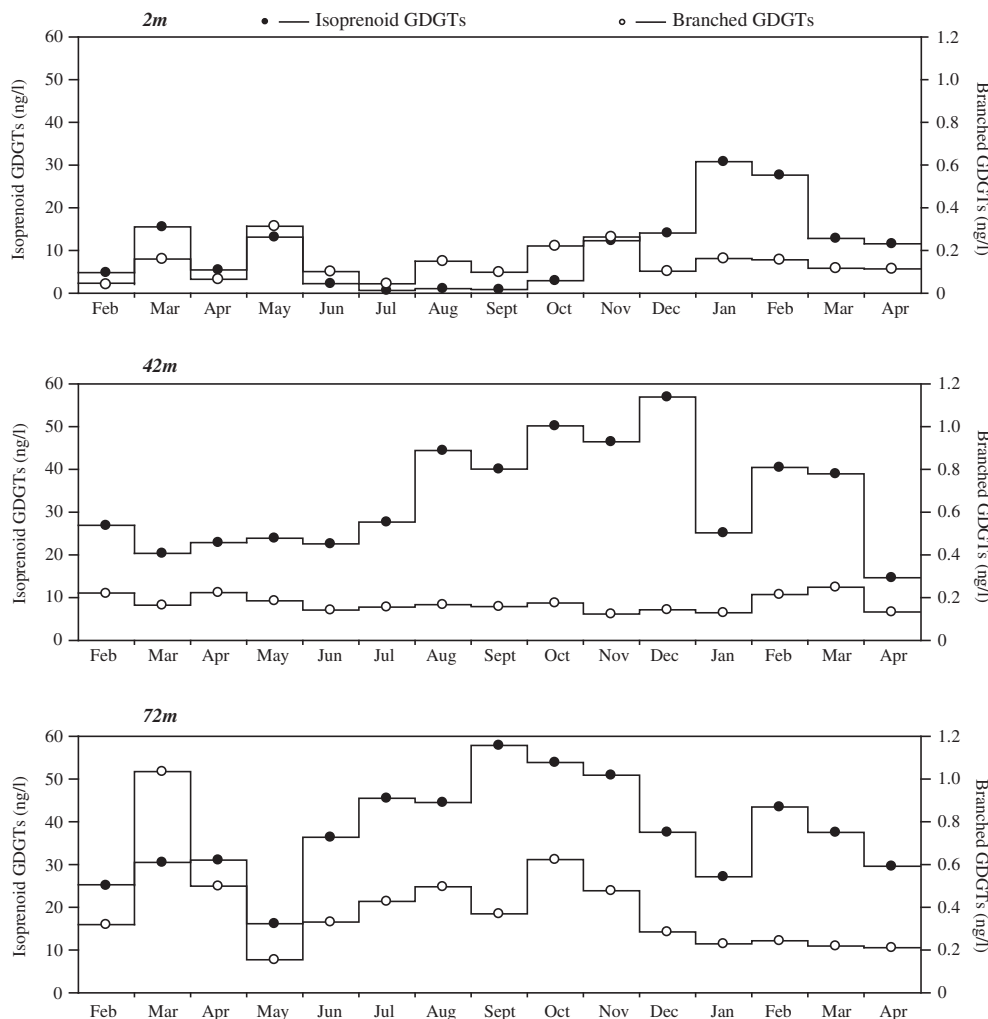


Fig. 5. Annual variation in concentrations of isoprenoid and branched GDGTs in SPM at 2, 42, and 72 m in Lake Lucerne.

tions decrease down-core (Fig. 4C). Substantial changes in the concentration of isoprenoid GDGTs down core are observed (Fig. 8). Although this may partially be due to diagenesis, it is more likely that this relates to changes in the lake eutrophic status during the last few decades.

Between 1955 and 2001, Lake Lucerne went through four periods of varying trophic state: an oligotrophic period before 1969; a period of accelerated eutrophication (1970–1977) with total phosphorus (TP) concentrations reaching 30 mg m^{-3} and nitrate–nitrogen (N-NO_3) concentrations of 500 mg m^{-3} ; a moderate mesotrophic period (1978–1988) when TP values decreased but N-NO_3 increased and a fourth period of growth limiting P concentration (1989–2001) with TP concentrations between 5 and 10 mg m^{-3} and N-NO_3 concentrations between 600 and 700 mg m^{-3} (Bürgi and Stadelmann, 2002). The transitions between the four periods are clearly revealed in the sediment core by the transition from greyish sediments with a lower TOC, to finely-laminated black coloured sediments with a higher TOC content (Fig. 8). Lake Lucerne is now P-limited as it was before the eutrophication period but the N concentration has tripled and consequently the

present-day oligotrophic conditions in the lake are different from former conditions. This present state has a strong impact on the species assemblages which differ from the previous ones. Due to the increase in nutrients the change in species composition was rapid, whereas during the re-oligotrophication the response was slower as it takes much longer for the original (i.e. before 1969) oligotrophic community to be re-established (Bürgi and Stadelmann, 2002). The present oligotrophic structure of the lake characterized by an oxygenated water column with relatively high N concentrations may be supporting a higher density of thaumarchaeotal cells compared to the microbial community that existed prior to 1969 in the lake.

A comparison of the GDGT concentration in the water column with the GDGT flux captured in the sediment traps shows that on average 20% of the SPM standing stock of GDGTs is exported annually to the sediment. The burial efficiency of the GDGTs can be calculated by comparing the flux in the sediment trap at 72 m, which is about 18 m above the lake floor, with the GDGT accumulation rate ($\text{GDGT}_{\text{acc. rate}}$) in the sediment. The burial efficiency (BE) was calculated according to:

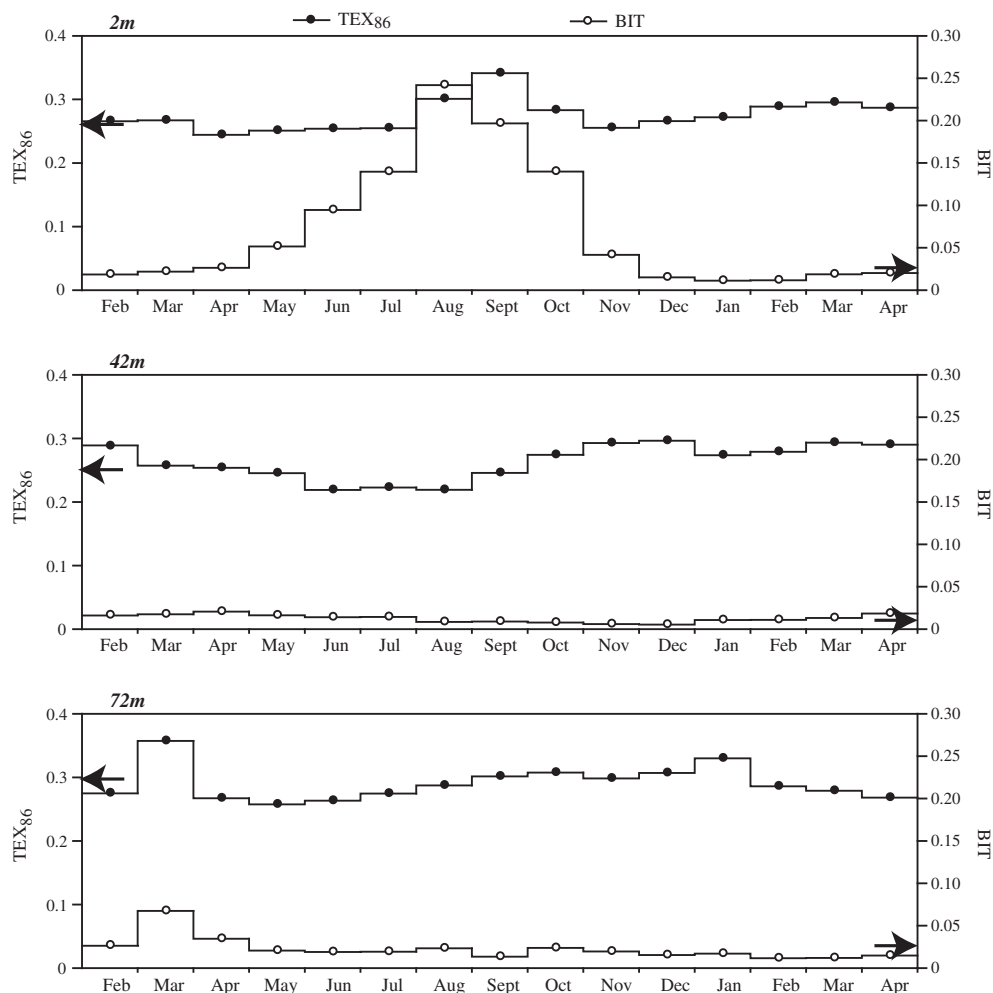


Fig. 6. Annual variation in TEX_{86} and BIT indices in SPM at 2, 42, and 72 m in Lake Lucerne. Arrows indicate the concentration-weighted average.

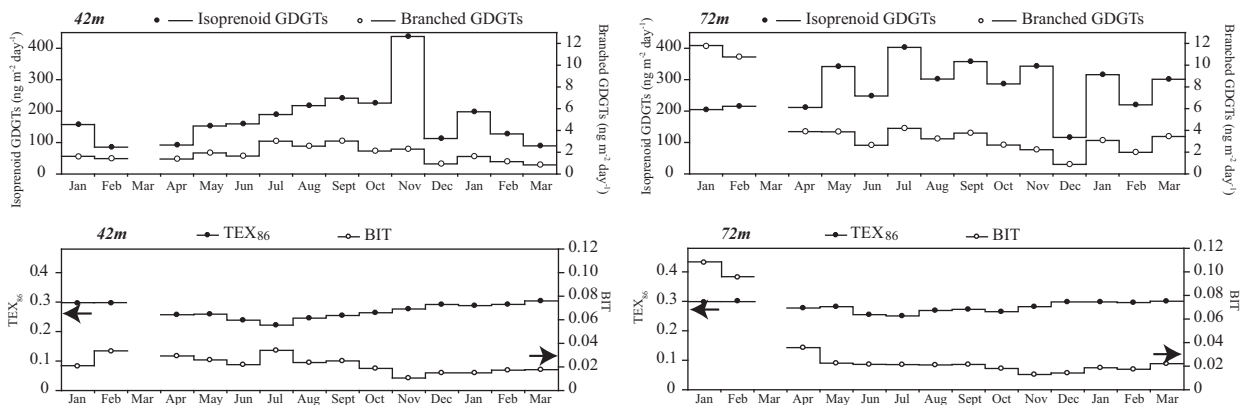


Fig. 7. Annual variations in fluxes of isoprenoid and branched GDGTs in descending particles at 42 and 72 m in Lake Lucerne (upper panels). Annual variation in TEX_{86} and BIT indices of total GDGTs present in descending particles at 42 and 72 m. Arrows indicate the flux-weighted average.

$$\text{BE} = \text{GDGT}_{\text{acc. rate}} / \text{Flux of GDGT} * 100\%. \quad (3)$$

Because the lake is presently restored to an oligotrophic state we compared present day GDGT fluxes with the GDGT accumulation rate before the lake became eutrophic.

Although we acknowledge that the current oligotrophic state is different from that before the eutrophication of the lake, with probably slightly different thaumarchaeotal production, it is not possible to compare fluxes to the GDGT

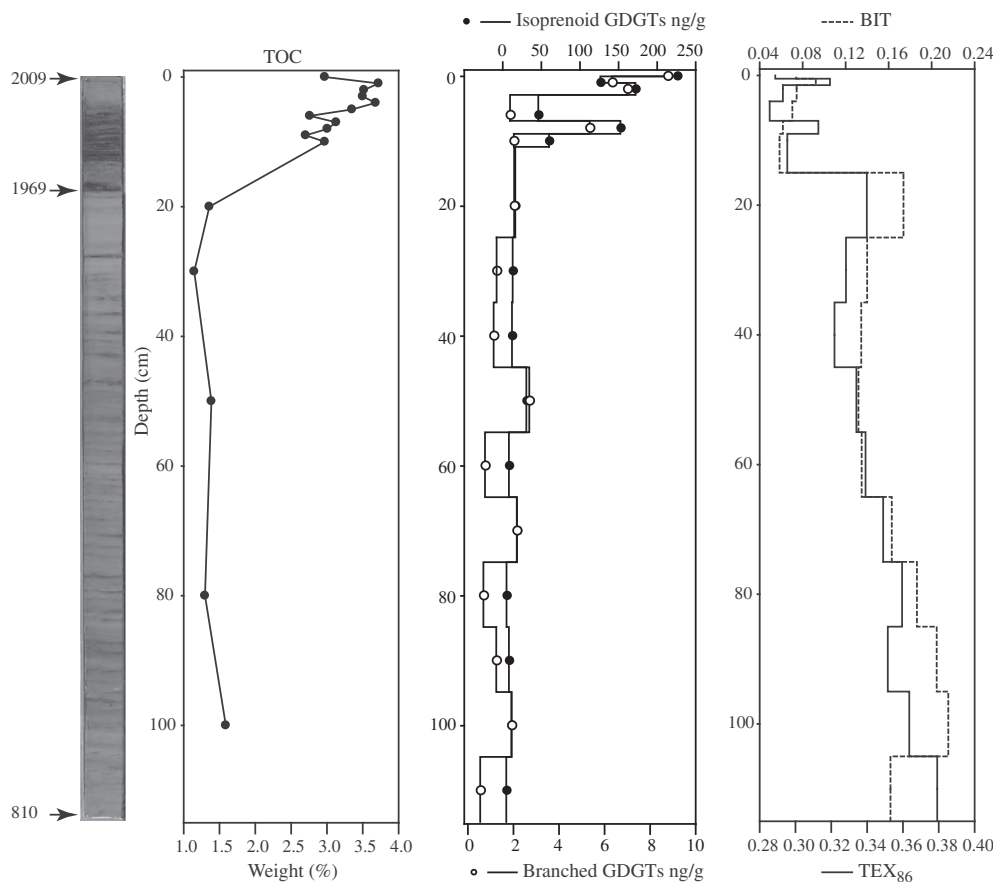


Fig. 8. Down-core profiles (0–100 cm) of TOC, concentrations of isoprenoid and branched GDGTs and TEX_{86} and BIT indices. The photograph at the left shows the core with the darker sediments at the top representing deposition of sediments enriched in TOC during the eutrophic phase of the lake (last 45 years of deposition).

accumulation rates at the top of the sediment because this would not include the ongoing sedimentary degradation. Moreover, bioturbation at the top of the sediment ad-mixes organic rich sediments and GDGTs originally deposited during the eutrophic state of the lake. The accordingly calculated average BE of the GDGTs is ca. 18%, which is similar to oxic marine sediments (Sinninghe Damsté et al., 2002). No appreciable differences are observed in BE between individual GDGTs.

4.2. Consequences for the interpretation of TEX_{86} in Lake Lucerne

TEX_{86} values for SPM are similar to those observed in the trapped particles, with a flux weighted average value of 0.27, and the average TEX_{86} value of the surface sediment of 0.29. This is consistent with the almost identical contributions of isoprenoid GDGTs in these different compartments (Fig. 4).

TEX_{86} values of ~ 0.28 translate into a relatively low water temperature of $\sim 2^\circ\text{C}$, if we apply the lake core top calibration of Powers et al. (2004, 2010). This temperature has a relatively large error since it is at the low end of the calibration curve (Powers et al., 2010) and as shown for

marine systems by Kim et al. (2008) the TEX_{86} calibration for temperatures $< 10^\circ\text{C}$ is non-linear. Mean annual lake surface temperatures for Lake Lucerne are $\sim 11^\circ\text{C}$ (Bühler and Ambühl, 2001) and during the study period fluctuated between 6 and 22°C (Fig. 2A). This suggests a large discrepancy between the TEX_{86} -inferred and actual temperature. However, our SPM data indicate that most of the Thaumarchaeota reside deeper in the water column below the thermocline (Fig. 2B). The temperature of the water at this depth fluctuates between 5 and 8°C over the year (Fig. 2A) and this is consistent (within the calibration error) with the TEX_{86} -inferred temperature. Consequently, these large changes in the temperature of the surface waters would not influence the TEX_{86} values in this lake system to a significant extent.

This is substantially different from what is typically seen in marine systems where TEX_{86} was found to reflect upper water temperature only, even though Thaumarchaeota occur throughout the water column (Wuchter et al., 2005), because grazing processes effectively only transfer particles from the surface ocean to the sediment and to a much lesser degree from deeper waters (see also Wakeham et al., 2003). However, the surface mixed layer in the ocean is at least 100 m thick, whereas in lakes it is much smaller. This prob-

ably explains why there can be such a large offset between TEX_{86} -inferred temperatures and mean surface lake temperatures.

The top few centimeters of the core collected from the study site show average TEX_{86} values of ca. 0.3, in line with the water column observations. However, below the interval characterized by elevated organic matter contents deposited during the time when the lake was eutrophic, TEX_{86} values are about 0.34 (Fig. 8), which corresponds, using the calibration by Powers et al. (2010), to a slightly higher average lake temperature of about 5 °C. Since lake temperatures before the 1970s were likely not higher (Bühner and Ambühl, 2001) than in the period of 1980 to today, the eutrophication phase of Lake Lucerne clearly influenced also the archaeal community in such a way that it affected the distribution of GDGTs and thus also TEX_{86} . It is conceivable that the reduced primary production before the eutrophication led to Thaumarchaeota residing, on average, in shallower waters and thus recording slightly higher TEX_{86} values. The GDGT distribution in the surface sediments is similar to that of sediments deposited during the eutrophic state of the lake (Fig. 4). This suggests that the archaeal community in the present-day re-oligotrophic state (with only P limitation but not the former multi-nutrient limitation) is still occupying the same niche as during the eutrophic state of the lake and, consequently is recording the same TEX_{86} values.

4.3. Branched GDGTs and BIT as potential recorders of soil organic matter input

Branched GDGTs represent only a small fraction of all GDGTs in the SPM, settling particles, and sediments. This is consistent with a previous study in which sediments from four basins of Lake Lucerne were analyzed for their GDGT distribution (Blaga et al., 2009), showing that the relative abundance of branched GDGTs was lowest in the Chrüztrichter Basin. This probably reflects the position of this basin relative to the main sites of river inflow (Fig. 1). Recent studies suggest that in situ production of branched GDGTs in marine sediments (Peterse et al., 2009) and in lake waters and sediments (Sinninghe Damsté et al., 2009; Tierney and Russell, 2009) cannot be excluded as a source in addition to input from soil erosion by run-off. The observed one to two orders of magnitude higher concentration of branched GDGTs in the deeper water SPM of Lake Challa suggested production in the water column (Sinninghe Damsté et al., 2009), whereas the higher branched GDGT concentration of Lake Towuti sediments compared to its tributaries and surrounding soils suggested either water column or in-sediment production (Tierney and Russell, 2009).

In Lake Lucerne the concentrations of branched GDGTs in the SPM at 0 and 42 m are somewhat lower compared to that at 72 m but this difference is only marginal. The maxima in branched GDGT concentrations at 72 m are not observed at the more shallow sampling depths (Figs. 2 and 5). This could be caused by deep water in situ production of branched GDGTs but also by resuspension events (the surface sediments contain higher relative amounts of branched GDGTs) or lateral advection of water

masses containing relatively higher amounts of branched GDGTs, possibly derived from incoming rivers transporting soil-derived GDGTs. The ratios of the major branched GDGTs show gradual changes through the year, although with a trend opposite (cf. Weijers et al., 2007) to what would be expected for local production (i.e. highest relative abundance of the least methylated branched GDGT VI during winter time).

Our results clearly show that the most common GDGTs are isoprenoidal, which is reflected also in the low BIT values. For SPM at 42 and 72 m the BIT values are low for the entire duration of the study (on average 0.02), while at the lake surface slightly increased values (on average 0.07) are observed. Higher values in the surface waters are recorded between May and October, coinciding with the lowest concentrations of isoprenoid GDGTs. The low crenarchaeol production in the surface waters is the most likely cause for the higher BIT values rather than in situ production of branched GDGTs in surface waters. Although these higher BIT values of surface water SPM were also recorded in the material recovered from the sediment traps, due to the low particle flux at the time, it had only a small impact on the flux-weighted average.

The BIT measured in the top few centimeters of the sediment core was slightly higher compared to the particulate organic matter and the material collected in the sediment traps. This suggests that sporadic events, not captured by our sampling period, may provide an additional source of branched GDGTs to the lake sediments, thus influencing the ratio between isoprenoid and branched GDGTs. Such events are more likely related to the sudden influx from soil-derived branched GDGTs than from in situ production. Further down-core, prior to the 1960s–1980s eutrophication period, higher BIT values are observed. At that time also the concentrations of isoprenoid GDGTs are relatively low, which could explain the higher BIT values, since the ratio is based on relative concentrations. In situ bacterial production of branched GDGTs in the lake is, however, also expected to be stimulated by the higher fluxes of organic matter at this time, increasing accumulation of branched GDGTs. The fact that the concentrations of branched GDGTs only increased marginally at this time and that the BIT was, consequently, much lower suggests that BIT values in the sediments are mainly controlled by the input of soil derived branched GDGTs.

5. CONCLUSIONS

Our study reveals both seasonal and vertical changes in concentrations and fluxes of isoprenoid and branched GDGT in Lake Lucerne over the course of an annual cycle. However, the distribution of GDGTs is remarkably constant over this time. In situ production of isoprenoid GDGT, by Group 1 Thaumarchaeota, takes place mainly in the deeper part of the water column and is likely influenced by seasonal variability in primary production from the upper layers. Branched GDGT membrane lipids are also present in the water column and sediments of Lake Lucerne but in significantly lower concentrations and fluxes. Comparing TEX_{86} values from the water column and the

surface sediment shows similar values, which implies that thaumarchaeotal GDGTs produced in lake water dominate the sedimentary GDGTs. Although the TEX₈₆ values show seasonal changes, they do not reflect recorded annual surface water temperature changes. The SPM data indicate that most of the Thaumarchaeota reside deeper in the water column. The temperature of the water at this depth fluctuates between 5 and 8 °C over the year and this is consistent (within the calibration error) with the TEX₈₆-inferred temperature. Down core, a change in TEX₈₆ values is observed that coincides with the change in trophic state of the lake (from eutrophic to oligotrophic), suggesting that the niche of the archaeal community, and consequently TEX₈₆ changed. During this eutrophication period the BIT was low due to enhanced production of crenarchaeol, indicating that the flux of branched GDGTs was not affected by the trophic state and also that the branched GDGTs in Lake Lucerne are primarily derived from soil erosion in the catchment of the lake. Overall, the results show that isoprenoid GDGTs can be used as lacustrine palaeothermometers but detailed knowledge on the niche of the Thaumarchaeota is required for a proper interpretation of lacustrine TEX₈₆ records. The observed subsurface niche of Thaumarchaeota in Lake Lucerne may also apply to other lakes and should be taken into account in future TEX₈₆ lake calibration studies.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.gca.2011.08.016](https://doi.org/10.1016/j.gca.2011.08.016).

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