



Sources of glycerol dialkyl glycerol tetraethers (GDGTs) in catchment soils, water column and sediments of Lake Rotsee (Switzerland) – Implications for the application of GDGT-based proxies for lakes



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ABSTRACT

We analysed glycerol dialkyl glycerol tetraether (GDGT) distributions in the water column, sediment and catchment soils of the Swiss Lake Rotsee to determine the sources of GDGTs in the lake sediment and to determine the implications for GDGT-based palaeoclimate proxies. The branched GDGT (brGDGT) distribution in the soils surrounding the lake showed significant heterogeneity, which may be partly explained by vegetation cover and soil moisture. One group of soils seems to provide the largest contribution of soil-derived GDGTs to the lake, or the distribution of GDGTs in these soils is affected by the relatively high soil moisture availability, creating lake-like conditions and GDGT distributions. Comparison of GDGT distributions in soils, water column and sediments indicated that brGDGTs and crenarchaeol in the sediment are partly soil derived, but that in situ production in the water column and/or sediment also takes place. Eutrophication seems to affect the distributions of brGDGTs by dilution of the supply of soil derived brGDGTs to the lake and by changing the degree of in situ production of brGDGTs in the water column. Furthermore, the eutrophic conditions in the lake promote methanogenic activity and subsequently cause a contribution of isoprenoid GDGTs (isoGDGTs) of methanogenic origin to the sediments. The aquatic production of GDGTs has implications for the reliability of GDGT-based proxy results. In particular, the application of the BIT and TEX₈₆ indices is hampered by the mixed sources of the GDGTs in the lake. In contrast, global lake-specific brGDGT-based temperature calibrations resulted in temperature estimates that resemble measured mean annual and summer air temperatures. CBT-derived pH values agreed well with measured soil and water column values. Our results demonstrate that understanding the source of GDGTs in lake sediments is important for the robust interpretation of palaeoclimate records obtained from downcore proxy applications.

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1. Introduction

Glycerol dialkyl glycerol tetraethers (GDGTs; Fig. A1) are found ubiquitously in the environment [see Schouten et al. (2013) for a review] and can be divided into two classes. One class, with *sn*2,3 stereochemistry and containing isoprenoid alkyl moieties (isoGDGTs), is produced by Thaumarchaeota (formerly Crenarchaeota) and Euryarchaeota (De Rosa and Gambacorta,

1988; Schouten et al., 2002) and comprises planktonic (Wuchter et al., 2005; Blaga et al., 2009), as well as methanogenic and methanotrophic species (Hinrichs et al., 2000; Blumenberg et al., 2004). The second class exhibits *sn*1,2 stereochemistry and comprises methyl branched alkyl chains with 0–2 cyclopentane moieties (brGDGTs) and is produced by soil bacteria, most likely *Acidobacteria* (Weijers et al., 2009; Peterse et al., 2010; Sinninghe Damsté et al., 2011).

GDGTs have a strong potential as palaeotemperature recorders in lakes, as the relative distribution of both isoGDGTs and brGDGTs is temperature dependent (Schouten et al., 2002; Weijers et al., 2007b; Niemann et al., 2012). The extent cyclic moieties in the isoGDGTs originating from Thaumarchaeota that thrive in ocean water relates to sea surface temperature, which can be quantified with the TEX₈₆ index (Schouten et al., 2002; Kim et al., 2010).

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Application of this index to several lakes has also generated realistic lake water temperatures (e.g. Tierney et al., 2010; Woltering et al., 2011; Berke et al., 2012; Blaga et al., 2013). However, the application to lakes does not always result in reliable temperature values, as an additional input of isoGDGTs produced by e.g. methanogenic archaea in the lake, or isoGDGTs originating from catchment soils supplied to the lake, may disturb or overprint the original lake temperature signal (e.g. Blaga et al., 2009; Powers et al., 2010; Castañeda and Schouten, 2011; Pearson et al., 2011; Sinninghe Damsté et al., 2012a). The predominance of methanogen derived isoGDGT sources in the eutrophic and oxygen depleted Swiss Lake Rotsee (Naeher et al., 2012; Naeher et al., this issue) hinders the generation of reliable TEX₈₆-based temperature reconstruction for the lake.

In soils, the degree of cyclisation and the number of methyl branches in brGDGTs can be used to infer the mean annual air temperature (MAAT) of the environment of the producers using the MBT–CBT index (Weijers et al., 2007b). In addition, the CBT index can be used to reconstruct the pH of the soil. The MBT–CBT index has resulted in palaeotemperature reconstruction for a variety of locations of different geological age (e.g. Weijers et al., 2007a; Peterse et al., 2011; Gao et al., 2012), including some lakes (Fawcett et al., 2011; Niemann et al., 2012). However, its application to lakes generally appears to be complicated by in situ production of brGDGTs in the water column and/or sediment (Sinninghe Damsté et al., 2009; Tierney and Russell, 2009). Recently, several lake-specific calibrations have been developed that have incorporated the potential aquatic contribution of brGDGTs and thereby enabled reconstruction of palaeotemperature records based on brGDGT distributions in lake sediments (Tierney et al., 2010; Pearson et al., 2011; Sun et al., 2011; Loomis et al., 2012), although the controls on aquatic brGDGT production remain far from being understood.

In addition, the branched and isoprenoid tetraether (BIT) index, a proxy for determining the relative input of soil derived organic matter (OM) to lakes and the marine environment (Hopmans et al., 2004), may be influenced by aquatic production of brGDGTs. Moreover, crenarchaeol is also produced in soil, which results in an overestimation of the actual aquatic OM contribution in settings with a high input of soil-derived crenarchaeol (e.g. Weijers et al., 2006; Fietz et al., 2011; Smith et al., 2012). Alternatively, Fietz et al. (2011) proposed the use of the absolute concentration of brGDGTs instead of the BIT index, and others have suggested the use of brGDGTs without the normalisation to crenarchaeol (Smith et al., 2012) to determine the input of soil OM to an aquatic system. For systems with a strong CH₄ cycle, where isoGDGTs are primarily derived from methanogenic archaea in the sediment, the BIT_{CH} index has been proposed (Naeher et al., 2012).

Despite the increasing number of lake-specific calibrations, in order to further improve the applicability and reliability of GDGT-based proxies in lakes, it is important to better understand the sources of the GDGTs in these systems. This study aimed to evaluate the sources (soil, aquatic, sedimentary) of GDGTs stored in the sedimentary archive of Lake Rotsee, Switzerland, covering the period between ca. 1860 and the present. The conditions in the lake have been altered by eutrophication since the mid-19th century (Stadelmann, 1980; Naeher et al., 2012), which has resulted in enhanced methanogenesis and methane cycling (Naeher et al., this issue). This influences largely the concentration and distribution of GDGTs in the lake (Naeher et al., this issue) and makes it an excellent site for determining the influence of environmental change on the sources of GDGTs in the lake and assessing the implications for the application of GDGT-based proxies for estimating soil OM supply, soil pH and local air temperature.

2. Material and methods

2.1. Study site and sample collection

The small (0.46 km²) prealpine, monomictic and eutrophic Lake Rotsee (Fig. 1; hydrographical and limnological parameters summarised by Naeher et al., 2012) has a stable stratified water column with a strong chemocline between ca. 6 and 10 m depth and an anoxic hypolimnion for most of the year (Schubert et al., 2010). Since the mid-19th century, it has been subjected to eutrophication, especially because of excessive sewage and related nutrient supply (Stadelmann, 1980). The eutrophication history of the last ca. 150 yr has been described by Naeher et al. (2012).

At the maximum depth of 16 m, a 56 cm sediment core was recovered with a gravity corer in October 2009 (N 47°4.251 E 8°18.955, WGS84; Fig. 1). The sedimentation rate had been determined as ca. 0.38 cm yr⁻¹ (Naeher et al., 2012), so the core covered ca. 150 yr. It was sliced in continuous 1 cm intervals and frozen at –20 °C until analysis.

Particulate organic matter (POM) in the water column above the core location (Fig. 1) was sampled via in situ filtration (2–13 l) with a McLane filtration system (WTS-142) and GFF filters (retention of particles down to 0.7 µm) at 9, 10, 11 and 13 m (within and below the chemocline) in October 2004. Another POM sample at 4 m was obtained in October 2012. CTD (conductivity-temperature-depth) profiles showed that the chemocline was at ca. 8–10 m during the sampling campaigns. The filters were freeze dried prior to analysis. The samples from 2004, which had been used for microbial investigation (Schubert et al., 2010), were also used for GDGT analysis.

Surface soil samples (0–10 cm) were taken at seven locations with different vegetation type in the catchment in June 2012 (S1–S7; Fig. 1). The samples were mainly Cambisols, but wetland soils (Gleysols) were found in the northeast catchment (FAP, 1988). Samples were covered by deciduous trees (S1: N 47°4.121 E 8°18.913), deciduous trees, ferns and shrubs (S2: N 47°4.175 E 8°19.022; S5: N 47°4.142 E 8°18.622), reeds (S3: N 47°4.659 E 8°19.782), grassland (S6: N 47°3.864 E 8°17.990; S7: N 47°3.794 E 8°17.941) and grassland in direct neighbourhood with reeds (S4: N 47°4.287 E 8°18.884). At each site, soils were sampled in triplicate and mixed to account for heterogeneity. The soil samples were freeze-dried and sieved (1 mm) to remove pebbles and larger plant material, then ground and homogenised. For determination of soil pH, soil and nanopure water (10:25; w/w) were well mixed, allowed to settle for 30 min, followed by measurement of the pH in the water phase with a Metrohm 713 pH meter.

Instrumentally measured MAAT in Lucerne ranged between 7 and 11 °C over the last 130 yr (Fig. 5, Table 1; www.meteoschweiz.admin.ch/web/en/climate/climate_today.html).

2.2. GDGT analysis

Sediment and soil samples were extracted successively by ultrasonication with mixtures of MeOH and dichloromethane (DCM) as reported by Naeher et al. (2012). Half of each filter (POM samples) was Soxhlet extracted with DCM/MeOH (7:3, v/v) for 24 h. Aliquots of total lipid extracts (TLEs) from sediment, soil and POM samples were analysed for GDGTs. A synthetic C₄₆ GDGT standard (Huguet et al., 2006) was added to each extract for quantification.

Each lake sediment TLE was directly dissolved in hexane/isopropanol (99:1, v/v) and filtered through a 0.45 µm PTFE filter prior to high performance liquid chromatography (HPLC) as reported by Bechtel et al. (2010). Soil and water column TLEs were separated over a 5% water deactivated silica column using hexane/DCM

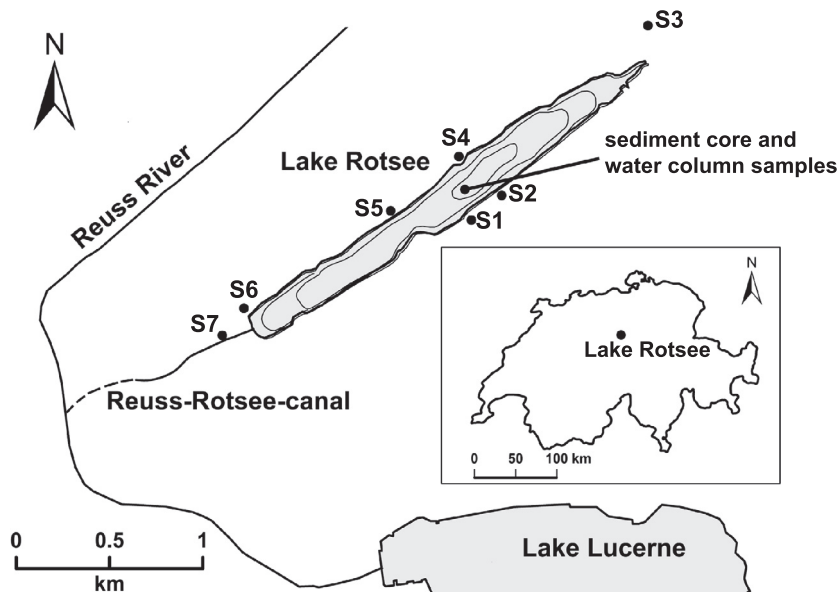


Fig. 1. Map with Lake Rotsee, the Reuss River and its connection with the lake by the Reuss–Rotsee-canal (partly below ground level, dashed line) and the northwest corner of Lake Lucerne. Insert map shows the location of the lake within Switzerland. The sampling stations of the sediment core and water column particulate organic matter (POM) are shown together with the locations of the seven soil samples (S1–S7).

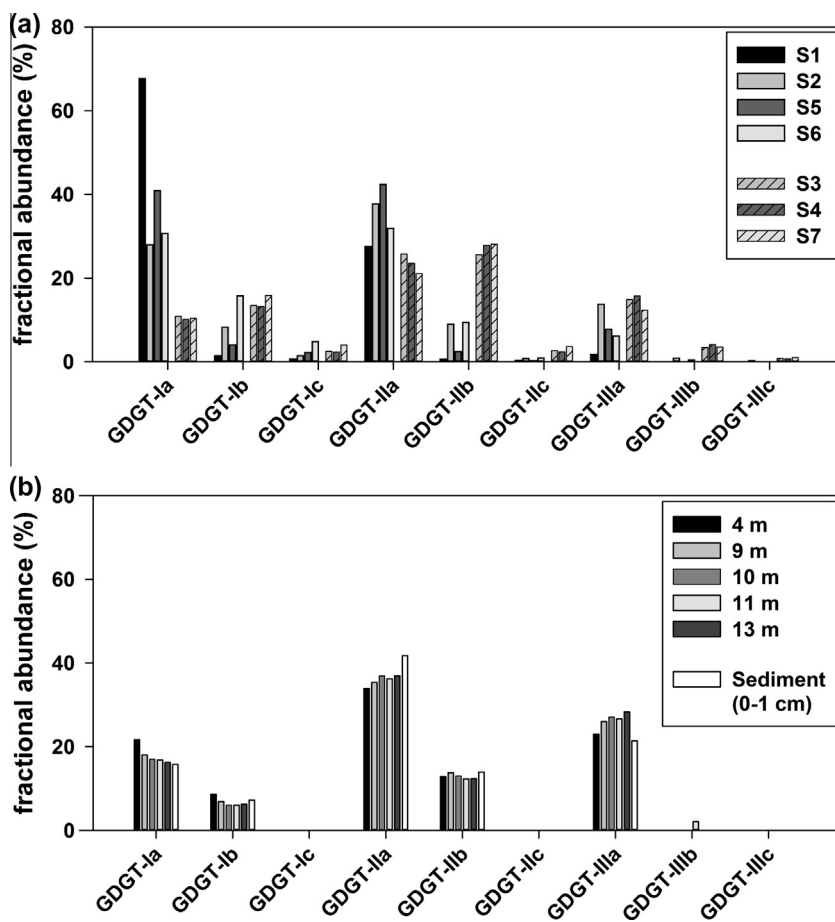


Fig. 2. Fractional abundance of branched GDGTs in (a) soil samples around the lake (S1–S7) and (b) water column (4 m, 9 m, 10 m, 11 m, 13 m) and surface sediment (0–1 cm). Soils grouped by dominant vegetation cover and similarity in GDGT distributions (see text for details). S1, S2, S5, S6, first soil group (left); S3, S4, S7, second soil cluster (right). Cren. regio. Crenarchaeol regio isomer.

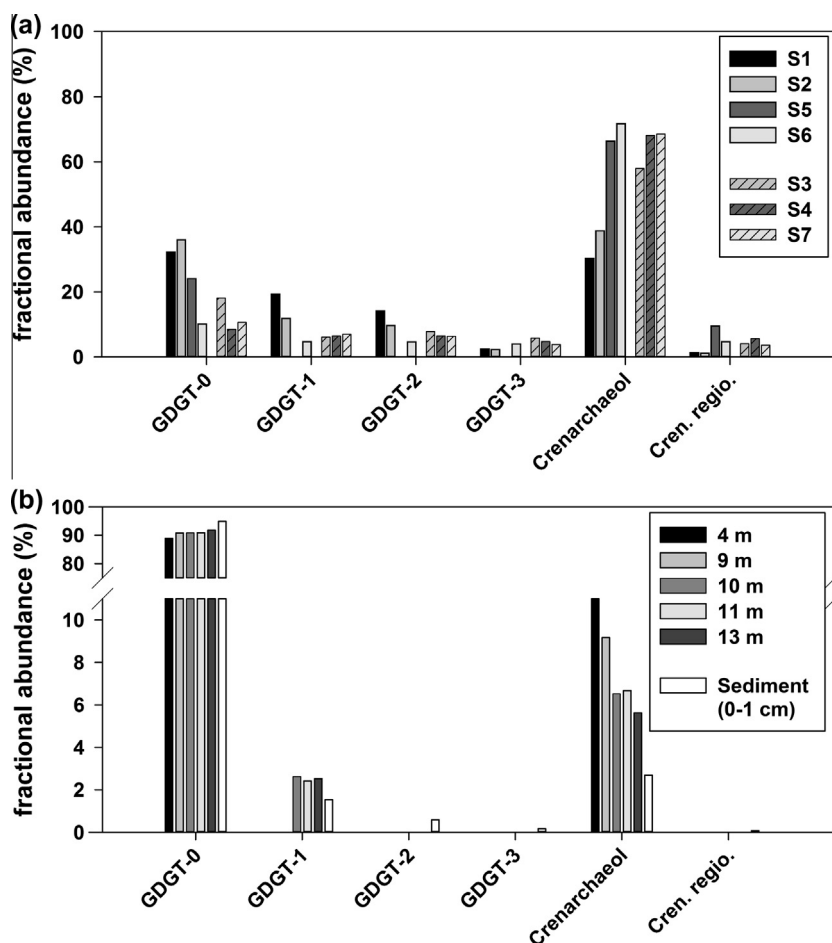


Fig. 3. Fractional abundance of isoprenoid GDGTs in (a) soil samples around the lake (S1–S7), (b) water column (4 m, 9 m, 10 m, 11 m, 13 m) and surface sediment (0–1 cm). Soils grouped by dominant vegetation cover and similarities in GDGT distributions (see text for details). S1, S2, S5, S6: first soil group (left); S3, S4, S7: second soil group (right). Cren. regio. Crenarchaeol regio isomer.

(9:1, v/v) and DCM/MeOH (1:1, v/v) to provide an apolar and a polar fraction, respectively. The polar fraction, containing the GDGTs, was dried under N_2 , re-dissolved in hexane/isopropanol (99:1, v/v), and filtered over a $0.45 \mu m$ PTFE filter prior to analysis using an Agilent 1260 Infinity series HPLC–atmospheric chemical pressure ionization mass spectrometry (HPLC–APCI–MS) instrument equipped with a Grace Prevail Cyano column ($150 mm \times 2.1 mm$; $3 \mu m$). The GDGTs were eluted isocratically with 90% A and 10% B for 5 min and then with a linear gradient to 18% B for 34 min at $0.2 ml min^{-1}$, where A = hexane and B = hexane/isopropanol (9:1, v/v). Injection volume was $10 \mu l$ and single ion monitoring of $[M+H]^+$ was used to detect GDGTs. The analytical reproducibility of GDGT analysis was within 15% based on duplicate measurements. The analytical variation in the GDGT based index values (MBT, CBT, BIT) was < 0.01 .

3. Results and discussion

3.1. Distribution and abundance of GDGTs

3.1.1. Soils

Soils from seven locations (Fig. 1) were analysed to resolve heterogeneity in GDGT distribution within the catchment and to determine a terrestrial GDGT end member. The soil brGDGTs were more abundant (60–98% of all GDGTs) than isoGDGTs, in line with

previous observations (e.g. Weijers et al., 2006). The average brGDGT and isoGDGT concentrations were $40 \pm 22 \mu g g^{-1}$ TOC and $8 \pm 7 \mu g g^{-1}$ TOC, respectively (data not shown).

The distribution of brGDGTs in the soils was heterogeneous (Figs. 2a and 4; Table 1). However, we could identify two distinct groups on the basis of brGDGT distributions (Fig. 2a). The first (S1, S2, S5, S6) was dominated by GDGT-Ia and GDGT-IIa, whereas the second (S3, S4, S7) was characterised by similar amounts of GDGT-IIa and GDGT-IIb, followed by GDGT-IIIa, GDGT-IIb and GDGT-Ia, with a relatively higher content of brGDGTs with one or more rings. The two groups could be explained partly by differences in the vegetation cover: The first group is dominated by deciduous trees, ferns and shrubs, whereas the second comprises reed and grassland dominated soils. The results indicate that vegetation and soil type may influence the conditions for, or composition of, bacterial communities in the soils, consistent with observations of Weijers et al. (2011). However, sample S6 is from a grassland covered soil, but falls within the first group, indicating that there must be additional factors besides vegetation cover and soil type that determine the GDGT composition in soils.

Crenarchaeol was the predominant isoGDGT in most soils, followed by GDGT-0 as the second most abundant (Fig. 3a). Only in soils S1 and S2 did GDGT-0 and crenarchaeol occur in similar amount. In contrast to the brGDGTs, the differences in fractional abundance of isoGDGTs between both groups was relatively small (Fig. 3a).

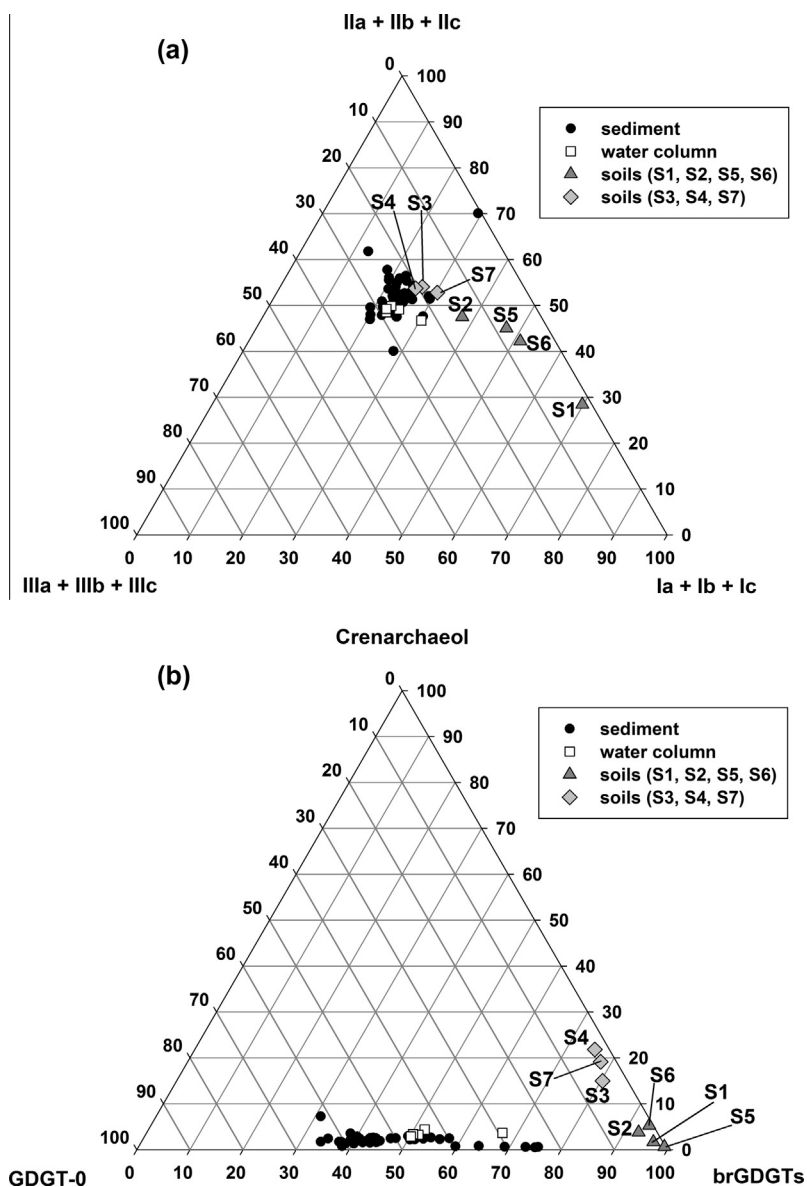


Fig. 4. Ternary diagrams with relative contribution of sum of (a) GDGT-I, GDGT-II and GDGT-III (each as the sum of the respective brGDGTs with and without cyclopentane moieties) and (b) crenarchaeol, GDGT-0 and the sum of all brGDGTs in the water column, sediment and soils. Soil samples S1–S7 are indicated. The different symbols for soils show the division into two clusters.

3.1.2. Water column and sediment

Total brGDGTs and isoGDGTs in the water column occurred in similar concentration ($1\text{--}3\ \mu\text{g g}^{-1}$ POC) and decreased with water depth, whereas the concentration in the surface sediment was different (28 and $49\ \mu\text{g g}^{-1}$ TOC, respectively). The decrease in GDGT concentration with water depth suggests that they primarily originate from soil input and/or are produced in the upper part of the water column, in agreement with previous observations (e.g. Bechtel et al., 2010; Schouten et al., 2012). However, degradation is another factor influencing the water column profiles of GDGTs.

The relative distributions of brGDGTs and isoGDGTs in the water column were more similar to those in the sediment than in the catchment soils (Figs. 2–4). The water column was dominated by brGDGTs without cyclopentane moieties (GDGT-IIIa > GDGT-IIa > GDGT-Ia). In most samples, GDGT-Ic, GDGT-IIc, GDGT-IIIb and GDGT-IIIc were below the detection limit (Fig. 2b), in contrast to the surrounding soils. GDGT-0 was the predominant isoGDGT (> 91%) in the water column and sediment, followed by

crenarchaeol. Its predominance suggests that it must be produced in situ in the water column and/or sediment. GDGT-2, GDGT-3 and the regio isomer of crenarchaeol were below detection limit in the water column, and were only found in detectable amounts in the sediment (Fig. 3b), indicating a mainly sedimentary origin for these compounds.

3.2. Sources of GDGTs in the lake

3.2.1. brGDGTs

The brGDGT distributions in the water column and sediment were more similar (Fig. 4a) to those in the second soil cluster (S3, S4, S7) than to those in the first soil cluster (S1, S2, S5, S6). This may indicate that the supply of soil-derived brGDGTs entering the lake system is greater from soils of the second soil group compared with the other areas. A second possibility is that differential transport led to differences in brGDGT distributions, as observed for other biomarkers due to selective partitioning to different grain

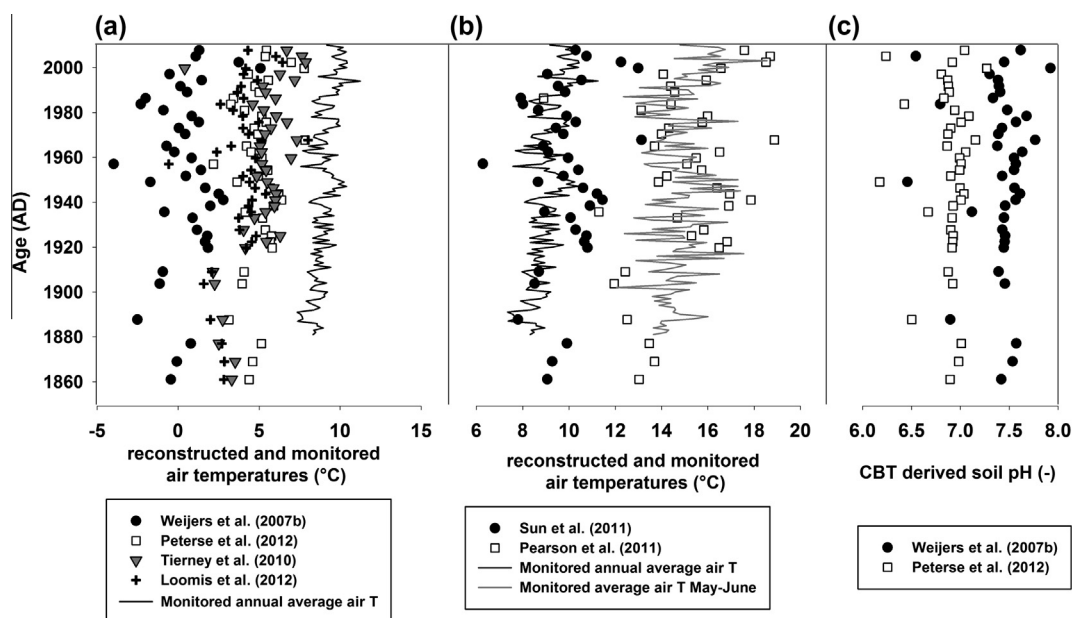


Fig. 5. Profiles of parameters derived from GDGTs in the sediment vs. age (AD): (a) MAAT calculated according to calibrations of Weijers et al. (2007b), Peterse et al. (2012), Tierney et al. (2010) and Loomis et al. (2012). For comparison with the derived MAAT values, annual average air temperature monitoring data from Lucerne are shown (data from MeteoSwiss climap-net, 1881–2010, http://www.meteoschweiz.admin.ch/web/en/climate/climate_today.html). The most recent warming trend in the monitoring data is not visible because of the temperature scale used for the x-axis. (b) Similar to (a), MAATs based on the calibration of Sun et al. (2011) for pH < 8.5 are shown together with the same annual average air temperature monitoring data from Lucerne. Reconstructed air temperature based on the calibration of Pearson et al. (2011) is compared with monitored average air temperature during May and June. (c) CBT derived soil pH values calculated according to Weijers et al. (2007b) and Peterse et al. (2012).

sizes of soil particles (Keil et al., 1998). Alternatively, brGDGTs are also produced in situ in the lake with a pattern more comparable to that of the second soil group, including reed covered soils. These soils might be poorly oxygenated due to a high moisture content, thereby mimicking the wet anaerobic conditions in the lake.

The fractional abundance of GDGT-IIIa was lower in both soil groups than in the water column and sediment (Fig. 2a and b). Consequently, GDGT-IIIa in the sediment must have an additional source, likely in situ production. Indeed, this compound has been shown to significantly alter the soil-derived GDGT-signal in several other lakes (Sinninghe Damsté et al., 2009; Tierney and Russell, 2009; Tierney et al., 2010). Minor amounts of GDGT-IIa might also originate from in situ production, as indicated by its slightly lower abundance in both soil groups compared with the lake.

Despite the in situ production of brGDGTs in the lake, the strong similarity between the sedimentary profiles of detrital elements (Fe, K and Ti) and the concentration of brGDGTs, as well as the ratio of brGDGTs/isoGDGTs, has been interpreted as a soil-derived origin for the brGDGTs in the sediments of the lake (Naeher et al., 2012). The downcore records showed a decreasing trend from the 1850s to around 1920 and remained constantly low since then (Naeher et al., 2012). The covariance between the records indicates an increase in aquatic and/or sedimentary OM production as a result of lake eutrophication, which started in the mid-19th century and diluted the relative contribution of soil derived brGDGTs and detrital elements stored in the sediment (Naeher et al., 2012).

3.2.2. isoGDGTs

The presence of crenarchaeol and other isoGDGTs in both the soils and the lake suggests that the isoGDGTs in the sediment are not only derived from Thaumarchaeota (NH_4^+ oxidising archaea) in the water column (Naeher et al., 2012), but also from soil Thaumarchaeota living in the soils surrounding the lake, corroborating previous findings (Blaga et al., 2009; Pitcher et al., 2011; Niemann

et al., 2012; Sinninghe Damsté et al., 2012b). The high relative abundance of crenarchaeol in soils of the second group (S3, S4 and S7) vs. the other soils, water column and sediment (Fig. 4b) may indicate that the largest contribution of soil-derived crenarchaeol to the lake is supplied by soils of the second cluster. However, the BIT values of these soils were typically < 0.7, whereas the BIT index is > 0.9 in the water column and sediment (Table 1). This implies that the sediment likely receives both soil-derived crenarchaeol and aquatically produced brGDGTs, and confirms the idea that the BIT index is not adequate for determining the soil OM in this lake, as previously suggested (Naeher et al., 2012).

The ratio of GDGT-0/crenarchaeol has been proposed to detect a contribution of isoGDGTs produced by methanogens (Blaga et al., 2009). Whereas the values of this ratio were ≤ 1 in the soils, we found 8–16-fold higher values in the water column and up to 77-fold higher values in the sediment (Table 1; Naeher et al., this issue). Together with the enriched ^{13}C signature of the biphytanes released from the isoGDGTs after ether cleavage (see Naeher et al., this issue) this indicates a substantial contribution of methanogenic isoGDGTs to the lake sediment. The increase in GDGT-0/crenarchaeol values down the water column indicates an increasing contribution of methanogenic isoGDGTs with depth, thereby diluting the planktonic (non-methanogenic) contribution, as well as that from the soil-derived isoGDGTs. Additionally, resuspension of GDGT-0 from the sediments may also contribute to the higher GDGT-0/crenarchaeol values in the lower water column. However, the fully oxygenated conditions in the surface water argue against a purely methanogenic origin of the isoGDGTs. Therefore, at least for the upper water column, the diagnostic value of the GDGT-0/crenarchaeol ratio (with a value of 8 at 4 m) needs to be reconsidered to make it suitable for tracing methanogenic biomass.

GDGTs 1–4 are considered to originate from methanotrophs or Thaumarchaeota, with methanogens possibly not being an important source (Pancost et al., 2001; Blumenberg et al., 2004; Schouten

Table 1
GDGT-0/crenarchaeol, BIT index, MBT, MBT' and CBT indices and derived soil pH and MAAT values from soil, water column particulate organic material (POM) and surface sediment samples (units in brackets).

Sample	GDGT-0/ crenarchaeol (-)	BIT (-)	MBT (-)	MBT' (-)	CBT (-)	MAAT (°C)	MAAT (°C)	Average summer air T (°C)	Soil pH (-)	Soil pH (-)	Soil pH (-)
		Hopmans et al. (2004)	Weijers et al. (2007b)	Peterse et al. (2012)	Weijers et al. (2007b)	Weijers et al. (2007b)	Peterse et al. (2012)	Pearson et al. (2011)	Weijers et al. (2007b)	Peterse et al. (2012)	Measured
Soil S1	1.1	0.98	0.70	0.70	1.67	13.2	13.0		4.4	4.6	3.8
Soil S2	0.9	0.95	0.38	0.38	0.58	7.3	9.3		7.2	6.8	6.4
Soil S5	0.4	0.99	0.47	0.47	1.11	7.1	9.1		5.8	5.7	5.3
Soil S6	0.1	0.92	0.51	0.51	0.40	15.8	14.5		7.7	7.1	6.4
Soil S3	0.3	0.73	0.27	0.28	-0.03	7.6	9.7		8.8	8.0	7.3
Soil S4	0.1	0.63	0.26	0.27	-0.09	7.6	9.7		9.0	8.1	7.3
Soil S7	0.2	0.64	0.30	0.32	-0.15	10.4	11.5		9.2	8.2	7.2
Water - 4 m	8.0	0.94	0.30	0.30	0.41	5.2	7.9	20.4	7.7	7.1	
Water - 9 m	9.9	0.90	0.25	0.25	0.41	2.5	6.2	16.7	7.7	7.1	
Water - 10 m	13.9	0.93	0.23	0.23	0.45	1.2	5.4	15.1	7.6	7.0	
Water - 11 m	13.6	0.92	0.23	0.23	0.46	1.0	5.4	15.2	7.6	7.0	
Water - 13 m	16.3	0.93	0.22	0.22	0.46	0.9	5.2	15.1	7.6	7.0	
Surface sediment (0–1 cm)	35.3	0.94	0.23	0.23	0.43	1.3	5.5	17.6	7.6	7.0	

et al., 2013). However, the relatively high $\delta^{13}\text{C}$ values of acyclic (-35‰ to -32‰) biphytanes derived from GDGT-0 and GDGT-1, and monocyclic biphytanes (-31‰ to -30‰) derived from GDGTs-1 to -3, indicate an acetoclastic methanogenic origin of the compounds in the sediment (Naeher et al., this issue). Additional sources from surrounding soils cannot be excluded, where they are also present (Fig. 3a).

3.3. Implications for application of GDGT-based proxies

3.3.1. MBT–CBT palaeothermometer

The brGDGTs in the soils around the lake led to reconstructed MAAT between 7 and 16 °C using the original MBT–CBT proxy of Weijers et al. (2007b), and 9–15 °C when the recently recalibrated MBT'–CBT proxy of Peterse et al. (2012) was used (Table 1). Although the MAAT estimates are mostly within the calibration error of the proxy (± 5 °C; Weijers et al., 2007b; Peterse et al., 2012), the variability in reconstructed temperature is surprisingly high, particularly considering the close vicinity of the soils within the catchment. Part of the error in the global soil calibration might be attributed to soil heterogeneity (Weijers et al., 2007b). This is supported by our findings, which show a large scatter within a small region that experiences the same temperature conditions. The suggested potential influence of vegetation type on variation in the distribution of brGDGTs (Weijers et al., 2011; Peterse et al., 2012) cannot explain the large range of MAATs reconstructed from the soils around Lake Rotsee, as MAAT estimates within the different surface soil groups also show this variation in brGDGT distribution (Fig. 2a, Table 1). This indicates that there are additional environmental factors other than temperature and pH that influence the distribution of brGDGTs, possibly soil moisture, nutrient conditions, or soil type. Alternatively, in the case that the distribution of brGDGTs in a soil is determined by the microbial community composition rather than by membrane adjustment to environmental change, not all strains of brGDGT-producing bacteria may generate the same brGDGT pattern for the same temperature.

Despite the large scatter in MAAT estimates derived from the soils around the lake, the substantial and integrated input of soil to the lake still provides a promising base for the application of the MBT–CBT proxy in sediments. However, the application of both soil calibrations (Weijers et al., 2007b; Peterse et al., 2012) to water column POM and lake sediments resulted in an underestimation of monitored MAAT by up to 15 °C. Such an underestimation has been found for several other lakes, and might be attributed to the in situ production of brGDGTs, in particular, GDGT-IIIa, and to a lesser degree GDGT-IIa (Sinninghe Damsté et al., 2009; Tierney and Russell, 2009; Blaga et al., 2010; Tierney et al., 2010; Pearson et al., 2011).

Of the lake calibrations, we tested those developed for global use (Pearson et al., 2011; Sun et al., 2011). The calibrations for tropical African lakes (Tierney et al., 2010; Loomis et al., 2012) are based on climatic conditions that are very different than those at Lake Rotsee, and do indeed yield unrealistic estimates of MAAT (Fig. 5). In contrast, the calibration of Sun et al. (2011) for lakes with pH < 8.5, like Lake Rotsee, temperature estimates varied between 6 and 13 °C, which fits relatively well with the measured MAAT record (7–11 °C; Fig. 5). In contrast to all other calibrations, Pearson et al. (2011) used summer air temperature rather than MAAT to derive their transfer function. Indeed, the temperature values obtained using this latter calibration were higher (9–19 °C) than those derived from using the calibration of Sun et al. (2011), and do reflect the same range of temperature as the measured late spring/summer temperature data (avg. for May–June between 12 and 18 °C, Fig. 5, as well as being a good match for average temperature of 13–17 °C for April–September; data not shown). The derived air temperature values based on brGDGTs in

the water column also match these obtained for the surface sediment (Table 1). However, the measured average air temperature for June–August was higher than the brGDGT-derived temperature estimates based on the calibration of Pearson et al. (2011). This means that the reconstructed temperature values show a slight bias towards spring temperature. This might be due to the higher productivity in the lake in spring (e.g. Bloesch, 1974), leading to slightly lower temperature estimates than expected due to the higher in situ production of GDGTs in the lake at this time of the year.

Although the downcore variation in reconstructed temperature is greater than the variation in measured temperature, the values are still mostly within the calibration error of the proxies (± 2 – 5 °C). The scatter may potentially be introduced by temporal changes in the supply of brGDGTs from different sources, which may then influence the proxy record independent of temperature. Furthermore, eutrophication (nutrients) and the anoxic and euxinic conditions, as well as the strong methane cycle (e.g. Bloesch, 1974; Naeher et al., 2012; 2013; this issue) in the lake are other factors that may influence brGDGT-producing organisms in the lake, and could lead to changes in brGDGT distributions and thus a lower accuracy in the brGDGT-based temperature reconstruction. Despite the large spread in reconstructed MAAT for soils, eutrophication-driven changes in environmental conditions in the lake and partial in situ production of brGDGTs in the water column, the brGDGT-derived temperatures based on the global lake calibrations of Sun et al. (2011) and Pearson et al. (2011) accurately reflect measured mean annual and summer air temperatures at Lake Rotsee (Fig. 5), holding promise for the generation of a longer palaeotemperature record for this lake. However, the temperature variation within the Holocene, the only temporal unit covered by the sediments, is only 3–4 °C (Folland et al., 1990). This indicates that the sedimentary proxy record cannot be used to reconstruct short term changes within this epoch due to the large scatter in reconstructed GDGT-based temperature.

Our data support the need for and importance of lake calibrations that enable a wide applicability of brGDGT-based lake palaeothermometry. However, whether the brGDGT-based temperature proxy really gives valid results for individual lakes must be carefully checked.

3.3.2. CBT index

The instrumentally measured pH of the soils surrounding the lake varies from 3.8 to 7.3 (Table 1). The wide range is reflected in the distribution of brGDGTs in the soils, for which CBT-based pH values vary between 4.4 and 9.2, and 4.6 and 8.2 using the CBT index of Weijers et al. (2007b) and Peterse et al. (2012), respectively (Fig. 5). Soil pH values reconstructed with the calibration of Peterse et al. (2012) gave the best match with measured pH, although they generally overestimated actual pH values by a maximum 1.0 pH unit (Table 1). The reconstructed and measured soil pH values were higher for the soils of the second group (Table 1) than for the deciduous tree/fern/shrub covered soils. Indeed, the soil group with the highest soil pH had higher relative amounts of GDGT-Ib, GDGT-IIb, GDGT-IIc, GDGT-IIIb and GDGT-IIIC, supporting studies which report a greater degree of cyclisation at higher soil pH values, to maintain membrane permeability and fluidity under these conditions (Weijers et al., 2007b; Sinnighe Damsté et al., 2009; Peterse et al., 2010, 2012).

The CBT-based pH values for the POM and sediment (Fig. 5, Table 1) are comparable to the measured pH of the surface water (7.0–8.5; monitoring data, 1969–2010, Office for Environment and Energy, Canton of Lucerne, Switzerland), and at the same time fall within the range of measured and reconstructed soil pH values. This makes it difficult to determine to which source of brGDGTs the CBT-derived sediment pH can be related. The soil signal may

potentially be overprinted by the production of brGDGTs in the water column, although the concentration of brGDGTs in the POM of the water column is very low compared with that in the soils. This indicates that the majority of the pH signal is likely derived from the surrounding soils. However, like the brGDGT-based temperature proxies, the CBT index for the water column and sediment may record the average of mixed sources rather than soil pH alone.

4. Summary and conclusions

The surface soil around Lake Rotsee is dominated by brGDGTs vs. isoGDGTs, though the GDGTs are present in varying relative distributions. Soils of the first group contained relatively a high content of GDGT-Ia and GDGT-IIa, in contrast to soils of the second group, which contained similar amounts of GDGT-IIa, GDGT-IIb and crenarchaeol. Comparison of soil brGDGT distributions with those in POM and sediments indicated that the brGDGTs in Lake Rotsee are partly derived from the surrounding soils, but in situ production in the water column and/or sediment also occurs, and is also controlled by changes in eutrophication. Similarly, crenarchaeol in the sediment also seems to have a mixed soil and water column origin. Of the isoGDGTs, GDGT-0 is the most dominant isoGDGT in the water column and sediment. High GDGT-0/crenarchaeol values and high $\delta^{13}\text{C}$ values of isoprenoid alkyl chains indicate that the isoGDGTs originate mainly from methanogens in the sediment (see also Naeher et al., this issue).

Eutrophication seems to affect the distributions of brGDGTs by dilution of the supply of soil derived brGDGTs to the lake and by changing the degree of in situ production of brGDGTs in the water column. The aquatic production of GDGTs has implications for the application of GDGT-based proxies to the lake. The reliability of the BIT index suffers from input of soil-derived crenarchaeol and in situ production of brGDGTs in the lake (cf. Naeher et al., 2012), and the TEX_{86} index is hampered by the large contribution of methanogenic isoGDGTs. In contrast, global lake-specific brGDGT-temperature proxies reflect MAAT and summer temperatures that resemble the measured temperature record, but differ by up to 5 °C. Our data confirm the need of lake-specific calibrations that account for in situ production of GDGTs in lakes, and demonstrate the potential of GDGTs as indicators of past environmental change. However, their sources must be well constrained, as we also showed that mixed sources of the various GDGTs can yield misleading results for GDGT-based proxies. We recommend that future studies that apply GDGT-based proxies in lacustrine settings should include soil, water column and sediment samples to capture the full range of potential sources of the GDGTs in the sedimentary archive of the lake.

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Appendix A

See Fig. A1.

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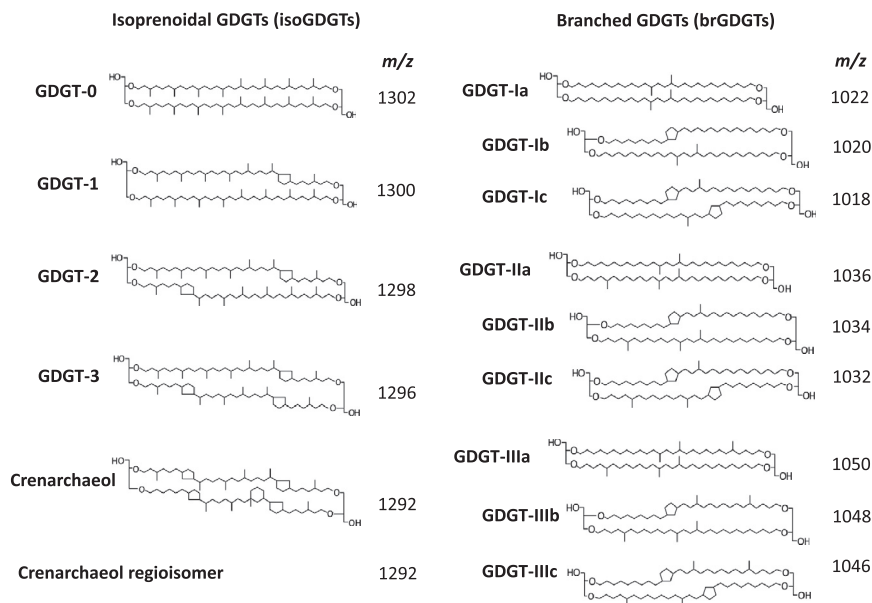


Fig. A1. Isoprenoid and branched GDGTs.

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