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Bacterial GDGTs in Holocene sediments and catchment soils of a high-alpine lake: application of the MBT/CBT-paleothermometer

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Abstract

A novel proxy for continental mean annual air temperature (MAAT) and soil-pH, the MBT/CBT-paleothermometer, is based on the temperature (T) and pH-dependent distribution of specific bacterial membrane lipids (branched glycerol dialkyl glycerol tetraethers – GDGTs) in soil organic matter. Here, we tested the applicability of the MBT/CBT-paleothermometer to sediments from Lake Cadagno, a small high-alpine lake in southern Switzerland with a small catchment of 2.4 km^2. We analysed the distribution of bacterial GDGTs in catchment soils and in a radiocarbon-dated sediment core from the centre of the lake, covering the entire Holocene. The composition of bacterial GDGTs in soils are almost identical to that in the lake's surface sediments, indicating a common origin of the lipids. Consequently, their transfer from the soils into the sediment record is undisturbed, apparently without any significant alteration of their distribution through in situ production or early diagenesis of branched GDGTs. The MBT/CBT-inferred MAAT-estimates from soils and surface sediments are in good agreement with instrumental values for the Lake Cadagno region (~0.5 °C). Moreover, downcore MBT/CBT-derived MAAT-estimates match in timing and magnitude other proxy-based T-reconstructions from nearby locations for the last two millennia. Major climate anomalies recorded by the MBT/CBT-paleothermometer are, for instance, the Little Ice Age (~14th to 19th century) and the Medieval Warm Period (~10th to 14th century). Together, our observations confirm the applicability of the MBT/CBT-paleothermometer to Lake Cadagno sediments. Consistent with other T-records from both the Alps and from the subpolar NE-Atlantic, our lacustrine paleotemperature record indicates Holocene MAAT-variations with an apparent cyclicity of ~2 kyr. The good temporal match of the warm periods determined for the S-Alpine region with NW-European winter precipitation strength implies a strong and far-reaching influence of the North Atlantic Oscillation on continental European Holocene T-variations.

1 Introduction

The assessment of climate variations in Earth's history is of paramount importance for our comprehension of recent and future climate variability. Instrumental climate data or historical records are, if at all, available for only the last few hundred years. Alternatively, geological archives containing climate-sensitive proxy indicators are used to reconstruct paleo-climate. Temperature (T) is one of the master variables governing climate change and, as a consequence, large efforts have been made to reconstruct its variations in the past (IPCC, 2007). However, despite the successful reconstruction of pronounced T-changes during Earth's history (e.g. glacial-interglacial cycles) using proxy-indicators in marine and terrestrial climate archives (e.g. sediments, ice cores and speleothems), well-constrained T-reconstructions for the Holocene, particularly from the continents, are comparably rare (Battarbee and Binney, 2008). This is partly caused by the fact that the Holocene is considered a rather stable time period with only subtle fluctuations in T (IPCC, 2007) that are difficult to resolve. Consequently, the exact amplitude (Mann et al., 2009) as well as the geographical extent of Holocene T-variations (Davis et al., 2003; Renssen et al., 2009) remain uncertain. Holocene paleo-T records from the Swiss Alps, for instance, suggest that the central European/Alpine Holocene climate displayed distinct but not well-constrained climate transitions such as the Medieval Warm Period (MWP, ~1000–600 calendar years before present (i.e. before 1950) –cal. yr BP) and the Little Ice Age (LIA, ~600–150 cal. yr BP) (Heiri et al., 2004; Mangini et al., 2005, 2007; Larocque-Tobler et al., 2009, 2010b). Particularly for the early Holocene prior to 2 cal. kyr BP, estimates of absolute values for T-anomalies vary by several °C when comparing the available records. A second reason for our knowledge gap on continental Holocene T-variations is that paleoclimatological research traditionally focused on marine sediments. Typically, these records span very long time periods, but are rarely suitable to resolve sub-millennial time scales. As a consequence, lake sediments have become one of the prime targets for continental climate reconstructions (e.g. within the framework of the International Continental

Drilling Project – ICDP). Similar to marine sediments, lacustrine sediment records can span long time periods, yet with much higher sedimentation rates. Thus, they allow establishing proxy-based records with a comparably high temporal resolution. However, lacustrine application of classical marine T-proxies are often problematic. The stable O-isotope composition of skeletal and non-skeletal deposits, for example, does not only reflects environmental T, but also depends on the hydrology of the lake system (Leng and Marshall, 2004). Similarly, pollen and skeletal remains have an undoubted potential for indicating climatic and T-shifts, but floral and faunal community-structure-based T-reconstructions can be compromised by ecological and migratory effects (Seppä and Bennett, 2003; Larocque-Tobler, 2010). A promising complement/alternative to the set of existing proxy indicators for lake sediments are lipid biomarkers (Castañeda and Schouten, 2011). Microorganisms can modify the composition of their cellular-membrane lipids to adapt membrane functionality to specific environmental parameters such as T and pH (Hazel and Eugene Williams, 1990). This phenomenon provides the basis for reliable biomarker-paleothermometry. Well-established, lipid-based proxy indicators for sea surface temperature (SST) reconstructions, for instance, are the so-called TEX_{86} (Schouten et al., 2002) and U_{37}^{k}-indices (Brassell et al., 1986), but their application in lacustrine environments can be challenging. The relevant thaumarchaeotal glycerol dialkyl glycerol tetraethers (GDGTs) used for the TEX_{86}-index, as well as specific algal alkenones that are applied in the U_{37}^{k}-index are not ubiquitous in lakes (Zink et al., 2001; Blaga et al., 2009; Toney et al., 2010; Powers et al., 2010). Also, the admixture of GDGTs from soil- and sedimentary archaea can compromise the use of the TEX_{86}-paleothermometer in lacustrine systems (Weijers et al., 2006b; Sinninghe Damsté et al., 2009; Tierney and Russell, 2009). The origin of GDGTs in sediments can be traced with the BIT-index, which relates branched tetraethers to crenarchaeol, assuming that these compounds are of soil and aquatic origin, respectively (Hopmans et al., 2004; Weijers et al., 2006b). A viable alternative to proxy-indicators that are based on lipids produced in the water column, might be to use T-sensitive lipids that are produced in catchment soils only, and that are ultimately deposited and preserved within the lake sediments. A promising suite of lipids, which could fulfil these requirements are three series of bacterial GDGTs, consisting of three structural isomers, with increasing degrees of methyl branching (Sinninghe Damsté et al., 2000; Weijers et al., 2006a) (structures of series I, II and III, respectively; Fig. A1). Based on the analysis of globally distributed soil samples, Weijers and colleagues (2007a) developed transfer functions that relate the degree of the GDGT methylation (expressed in the methylation index – MBT) and cyclisation (expressed in the cyclisation ratio – CBT) to mean annual air temperature (MAAT) and to soil pH:

$$\mathrm{MBT} = \frac{\mathrm{I}abc}{\mathrm{I}abc + \mathrm{II}abc + \mathrm{III}abc} \tag{1}$$

$$\mathrm{CBT} = -\log\frac{\mathrm{I}b + \mathrm{II}b}{\mathrm{I}a + \mathrm{II}a} \tag{2}$$

$$\mathrm{pH} = -\frac{\mathrm{CBT} - 3.33}{0.38} \tag{3}$$

$$\mathrm{MAAT} = \frac{\mathrm{MBT} - 0.187\mathrm{CBT} - 0.122}{0.02} \tag{4}$$

Until now, only a few attempts have been made to apply the GDGT-based proxies to lacustrine sediment records. All studies so far, which have mostly been performed with surface sediments, revealed that branched GDGTs occur ubiquitously in lake sediments and often represent the most abundant sedimentary GDGTs (Sinninghe Damsté et al., 2009; Tierney and Russell, 2009; Tyler et al., 2010; Blaga et al., 2010; Bechtel et al., 2010; Tierney et al., 2010; Loomis et al., 2011; Pearson et al., 2011). However, when using the transfer function proposed by Weijers and colleagues (2007a), which was developed for soils, calculated MBT/CBT-indices translated into absolute MAAT-values that seemed to systematically underestimate the actual MAAT. We are only at the beginning of understanding the exact biogochemical mechanisms (e.g. in situ production) that can lead to such offsets, and it seems that local or ecosystem-based calibrations of the GDGT-paleothermometer are crucial for its successful application (Zink et al., 2010; Tierney et al., 2010; Pearson et al., 2011).

The main goal of this study is to expand the existing data set of lacustrine MBT/CBT-records in order to (i) ground-truth the applicability of the MBT/CBT-paleothermometer in sediments and catchment soils of a high-alpine lacustrine setting and to (ii) establish a Holocene temperature- and soil pH-record for the Swiss Alps. As a study area, we selected a small, high-alpine lake (Lake Cadagno, Switzerland) with a small, well-defined catchment and with a high potential for the preservation of sedimentary organic matter (OM). Our MBT/CBT-derived time-series of MAAT- and soil pH-sediment records for the Lake Cadagno catchment compares well with instrumental and independent proxy data, indicating subtle but significant Holocene climatic shifts in the Alpine realm and Europe.

2 Material and methods

2.1 Site description

Lake Cadagno is a relatively small (surface area 0.26 km^2, maximum depth 21 m), Alpine lake located at 1921 m above sea level (a.s.l.) in the Piora Valley in the south-central part of Switzerland (Fig. 1). Its high-Alpine setting results in a low MAAT of ~0.5 °C (see below). The small catchment area of ~2.4 km^2 (estimates from digital elevation model, Swisstopo) is defined by the almost crater-like setting of Lake Cadagno: a mountain range frames the lake from W to NE, and a moraine separates it from Lake Ritom's catchment in the south and the Piora Valley to the east. The hydrologic balance is controlled by the inflow of water from several small creeks and through subaquatic groundwater inflow from dolomite/gypsum bedrock, and the outflow to Lake Ritom in the SW. Due to the steep topography north of the lake, snow avalanches reach the lake shore on a frequent basis. Most of Lake Cadagno's catchment area is covered by alpine grassland, and to a lesser degree by conifer and blueberry shrubs, or swamps.

The more gentle slopes in the vicinity of the lake are used as cattle pasture. The constant supply of solute-rich (e.g. SO_4^{2-}) groundwater from subaquatic springs has lead to water column stabilisation and, ultimately, to meromixis with a permanent but seasonally dynamic chemocline between 9 and 14 m water depth (Del Don et al., 2001). The lake's monimolimnion is anoxic and characterised by high sulfide concentrations (up to 1 mM) derived from microbial sulfate reduction (Hanselmann and Hutter, 1998).

2.2 Sampling

Lake-sediment cores and soil samples were collected during two sampling campaigns in September 2009 and May 2010, respectively. For sediment coring, a platform was anchored at the deepest part of the lake (Fig. 1, Table 1) and two ~9.5 m long composite piston cores were recovered using an UWITEC percussion piston-coring system. Upon recovery, piston cores were sectioned into 1 m pieces. In addition, a short (1 m) gravity core was retrieved at the same location for the recovery of undisturbed surface sediments. The first composite core was dedicated to stratigraphic and dating analyses, and the second core was used for organic geochemical analyses. Immediately after coring, the core for organic geochemical analysis was cut longitudinally into halves. One core-half was then sub-sampled for lipid analyses (see Sect. 2.3) and the other one was used for lithological description and photo documentation. For lipid analysis, sediment intervals of 5 (gravity-) and 10 cm (piston cores) length were continuously sub-sampled throughout the core sections, and stored frozen (–20 °C) in pre-cleaned glass jars until further treatment in the home laboratory. The core for stratigraphic and dating analysis was opened after return to the home laboratory. Similar to the core used for organic geochemical analysis, we photo-documented and described the sedimentology as well as sampled wood particles and terrestrial macrofossils at distinct sediment depths for ^{14}C-AMS measurements (Sect. 2.6). Soil samples were collected from several locations within the lake's catchment area (Fig. 1, Table 1), using a small shovel (bulk surface soils) or a hand-operated soil corer. Each soil profile was subdivided into vertical horizons of 15 cm before sub-sampling. Just as sediments, soil samples were frozen in pre-cleaned glass jars until further treatment.

2.3 Lipid analysis

Prior to lipid extraction, sediment and soil samples were freeze-dried, and sub-samples were homogenised. Total lipid extracts (TLEs) were obtained by accelerated solvent extraction (ASE, DIONEX 200) from about 3–5 g freeze-dried sediments or ∼10 g of freeze-dried soil, as specified previously (Weijers et al., 2007a). 0.1 µg of the C_{46}-GDGT internal standard (Huguet et al., 2006) was added to the TLE before concentration under a gentle stream of N_2 to about 1 ml. Elemental sulfur in the TLE was then removed by treatment with activated Cu. The TLE was subsequently separated over an activated Al_2O_3 column using (i) ethyl acetate and (ii) dichloromethane:methanol (95:5, v/v) as solvents, yielding (i) a neutral and (ii) a polar fraction, respectively. The polar fraction (containing the GDGTs) was dried under N_2, re-dissolved in hexane:isopropanol (99:1, v/v), filtered through a 0.45 µg PTFE syringe filter and condensed to a total concentration of ∼2 mg of dried polar fraction per ml hexane:isopropanol mixture. GDGTs were analysed by high performance liquid chromatography/atmospheric pressure chemical ionisation mass-spectrometry (HPLC/APCI-MS) in single ion monitoring mode according to the analytical setup and instrument specifications described by Schouten et al. (2007). Peak areas of $(M+H)^+$-ions of GDGTs were determined by manual integration using the HP Chemstation software package. MBT- and CBT-indices, as well as corresponding MAAT- and pH-values were calculated according to Eqs. (1)–(4). Reproducibility (based on duplicate sample analyses and repeated integration) was 0.002 for the MBT- and 0.01 for the CBT-index, translating to an analytical error of ca. ±0.1 °C for MAAT and ±0.1 pH units. Together with the branched GDGTs, we also measured crenarchaeol to determine BIT-values as described previously (Hopmans et al., 2004). Analyses were carried out at the NIOZ organic geochemical laboratory (Texel, the Netherlands).

2.4 Environmental parameters

Modern MAAT at Lake Cadagno was assessed using instrumental data series for nearby locations published in the MeteoSwiss database (http://meteoschweiz.admin.ch/web/de/klima/klima_schweiz/tabellen.html). At Piotta, which is located in the valley just below Lake Cadagno (4.5 km distance; 990 m a.s.l.), MAAT is 7.2 °C (mean data 1961–1990). Relatively close-by and at lower altitudes are the long-term meteorological observatories (MeteoSwiss) in Lugano (273 m a.s.l., MAAT = 11.6 °C, mean data 1961–1990) and Locarno (366 m a.s.l., MAAT = 11.5 °C, mean data 1961–1990). The lapse rate in the area is hence 0.6 to 0.7 °C 100 m^{-1}, which calculates to a MAAT of ~1 °C at an elevation of 1921 m a.s.l., the altitude of Lake Cadagno. Based on similar records, MAAT was previously estimated for the Lake Cadagno area to be 0 °C (Schürmann et al., 2002), so that we assume here an average MAAT of 0.5 °C. Soil pH (pH = 4–7) was determined by measuring the pH in a soil/H_2O mixture (5 g of dried homogenized soil per 12.5 ml DI) using a Mettler Toledo Seven Multi pH probe.

2.5 Independent proxies

To groundtruth the MBT/CBT-derived climate reconstructions, we compared our data with climate reconstructions based on independent climate proxies. In order to avoid biasing effects that may arise from geographical variations, we focused on regional data sets. These are based on O-isotope derived *T*-reconstructions from stalagmites in the Spannagel Cave, central Alps (Mangini et al., 2005, 2007) and *T*-dependent chironomid population dynamics in Lake Silvaplana (Larocque-Tobler et al., 2010a), as well as Lake Egelsee (Larocque-Tobler et al., 2010b; Larocque-Tobler, 2010) in the central and northern Alps, respectively. In addition, we present our *T*-record in the context of larger/hemispherical-scale climate variations through comparison with Holocene sea-surface *T*-variations in the NE-Atlantic (Thornalley et al., 2009) and with reconstructions of the North Atlantic Oscillation (NAO) from NW-Europe (Nesje et al., 2001). Whenever possible, we used original data available at the World Data Center for

Paleoclimatology (www.ncdc.noaa.gov/paleo/recons.html) and harmonised the temporal resolution to match our data.

2.6 Core chronology

A sediment core chronology was developed using eight AMS radiocarbon ages derived from wood and terrestrial macrofossils (Table 2), providing age points that are unaffected by the hard water dating error (Deevey et al., 1954). Analyses were carried out at the AMS-^{14}C laboratory at the ETH Zurich, Switzerland. The radiocarbon ages were converted to calendar years before 1950 (cal. yr BP) using the online calibration software OxCal 4.1 (https://c14.arch.ox.ac.uk/oxcal/OxCal.html) (Bronk Ramsey, 2009) and the Intcal09 calibration curve (Reimer et al., 2009). Dated sample material that was collected from slump-deposits was not considered for age-depth modelling (see below). The core used for organic-geochemical sampling was dated through accurate stratigraphic correlation with the AMS ^{14}C-dated master core using more than 50 tie points. All sediment depths are reported in metre depth of the core dedicated for stratigraphic and dating analysis.

3 Results

3.1 Sedimentological units and age-depth model

A detailed discussion of the lithologies and depositional units and their paleoenvironmental significance, as well as details on the age-depth modelling, will be provided elsewhere (Wirth et al., 2011). Briefly, the Lake Cadagno sediments consist of regular, laminated background sediments, intercalated with flood layers and slump deposits, the latter of which were sometimes extensive with a thickness of up to 71 cm (Fig. 2). Slump deposits in the composite section represent mobilised, mixed and re-deposited sediments from shallower parts of the lake that were transported to the deepest lake area. Hence, they provide sediments out of chronological sequence with the over- and underlying sediments (see Table 2) and were, therefore, not considered for age-depth modelling and paleoclimate reconstructions. As their bases are likely non-erosive in the deepest basin, their removal should not create hiatuses, and thus make the sediment succession continuous. Figure 2 depicts the age depth model based on calibrated ^{14}C-AMS ages and using sediment depths that were corrected for slump deposits. Ages between single dating points were interpolated using a cubic spline. The composite core dedicated to organic-geochemical analyses was correlated to the second composite core that was taken in parallel for sedimentological and chronological analyses. The composite sections were continuous, except for two gaps between 3.26 to 3.64 and 6.36 to 6.71 m sediment depth, which translates into temporal hiatuses between 3050 to 3375 and 5020 to 5813 cal. yr BP (Figs. 4a and 6).

3.2 GDGT distribution in sediments and soils

All sediment and soil samples contained branched GDGTs. Generally, branched GDGTs without cyclopentyl moieties (Series a; see Fig. A1 for a structural representation) were most abundant, followed by compounds with one or two cyclopentyl moieties (Series b and c, respectively) (Fig. 3). The composition of GDGTs in most soil samples ($n = 11$, i.e. all samples collected from positions 2, 3, 5–7 and 9; Fig. 1), was almost identical to lake surface sediments, directly indicating a common origin of GDGTs. MBT values ranged between 0.18 to 0.39, with an average of 0.28 ± 0.08 standard deviation (S_D), and CBT-values between 0.28 and 1.41 (average = 0.85 ± 0.41 S_D). Variations in the MBT or CBT ratios did not seem to be associated with soil type, nor could significant trends be discerned within vertical soil profiles (data not shown). Soils from sampling Sites 2 and 3 were taken from a meadow, Site 5 corresponds to the river bed of a creek, Sites 6 and 7 represent soils from the upper edge of a snow avalanche with admixture of eroded soil and Site 9 samples represent a wet/swampy soil. Only soils from sampling Sites 4 ($n = 4$) and 8 ($n = 2$), which were taken from a meadow (similar to sampling position 2 and 3) – in the following referred to as "irregular" soils – showed a considerably different GDGT abundance pattern when compared to lake sediments and the "regular" soils: these particular soils contained relatively high amounts of GDGT Ia and low amounts of compounds IIb and IIIa (Fig. 3). The "irregular" soils displayed average MBT values of $0.54 \pm 0.08\ S_D$ and average CBT values of $1.19 \pm 0.22\ S_D$, with maximum values of 0.66 and 1.40, and minimum values of 0.42 and 0.80 for MBT and CBT, respectively. Whereas the MBT/CBT-ratios in surface sediments and "regular" soils translate (using the Weijers et al., 2007a global soil calibration) to reasonably low MAAT values of 1.47 (Fig. 4a and e) and 0.1 °C ± 1.2, respectively (i.e. within the range of instrumental measurements of ~0.5 °C), MBT/CBT-derived MAAT estimates based on the "irregular" soil samples were, with 9.7 °C ± 4.1 S_D, significantly higher (f-test, $p < 0.05$). CBT-based pH estimates from both "regular" and "irregular" soils slightly overestimated, but were within the range of measured pH-values (Fig. 5). In order to address the possibility of contaminating effects of the irregular soil sites through cattle pasturing, we also analysed 2 samples of cow faeces, but these were found to contain only trace amounts of the target GDGTs (data not shown).

In the lake sediments, the matrix of the samples was very complex, probably as a result of the high content of organic carbon. In about 15 % of the lake-sediment analyses, this led to high background levels during HPLC, which compromised sufficient chromatographic resolution. Thus, GDGT distributions could not be determined adequately in these samples, and, as a consequence, they were not considered for paleoclimate reconstructions (resulting in a few ~200 yr gaps in the climate records; Figs. 4a, e and 6). The distribution of GDGTs varied with depth in the sediment core. MBT and CBT values ranged from 0.18 to 0.30 and 0.37 to 0.88, respectively, with average values of $0.26 \pm 0.02\ S_D$ (MBT) and $0.73 \pm 0.08\ S_D$ (CBT) ($n = 50$). Variations in the MBT/CBT-derived MAAT estimates seemed to follow a ~2 kyr cycle (see section, Fig. 4a). Crenarchaeol was present in all investigated sediment and soil samples. However, in contrast to MBT/CBT-indices, BIT-ratios did not show any systematic variation with sediment depth (data not shown) and were generally high, averaging at

0.97 (±0.04 S_D). Only the 4 samples below 9 m depth (i.e. older than 10.4 cal. kyr BP) showed slightly lower BIT values of 0.77 to 0.88.

4 Discussion

4.1 Origin of GDGTs in lake Cadagno sediments

The MBT/CBT-indices are based on the distribution of branched GDGTs of presumably soil-bacterial origin (Weijers et al., 2007a), probably Acidobacteria (Weijers et al., 2009; Sinninghe Damsté et al., 2011). Consequently, the successful application of the MBT/CBT-paleothermometer to lake sediments requires an unbiased transfer of the soil GDGT-signature into the lacustrine record. An important factor, which has likely contributed to the discordance between estimated and actual T observed in previous studies, is the in situ production of the relevant GDGTs within the lake system. Admixed to the soil-derived compounds, autochthonous GDGTs would obviously change the primary, soil-derived GDGT-signal (Sinninghe Damsté et al., 2009; Tierney and Russell, 2009; Blaga et al., 2010; Tierney et al., 2010). As for Lake Cadagno, we found that most soils and the surface sediments showed almost identical GDGT-patterns, which by itself argues for a common origin of these compounds and rules out alteration of the primary GDGT-signal by in situ production. Only compounds IIb and, to a lesser degree, Ib display more pronounced discrepancies when comparing lake sediments and "regular" soils. Yet, their influence on MAAT estimates is relatively small (see Eqs. 1 and 4). The application of the MBT/CBT-paleothermometer in lakes with elevated fluxes of in situ produced branched GDGTs is problematic and requires, if possible at all, a correction for authigenic production of the target compounds. This aspect has been addressed in recent studies by developing alternative calibrations based on the distribution of branched GDGTs in modern (surface) lake sediments and not in soils (Zink et al., 2010; Tierney et al., 2010; Pearson et al., 2011). However, when applied to Lake Cadagno surface sediments, these translate to unreasonably high values, overestimating instrumental MAAT by ~6 (Tierney et al., 2010) to 9 °C (Zink et al., 2010), which provides additional indication that the distributions of branched GDGTs in Lake Cadagno's sediments is not markedly influenced by in situ production.

Also, post-depositional alteration of branched GDGTs during (early) diagenesis may have a biasing effect on the sedimentary GDGT signatures, an aspect that has not been investigated for bacterial GDGTs in limnic environments. Yet, research on alkenones and archaeal GDGTs could show a rapid decrease in concentration of these compounds, particularly during oxic conditions, which typically also led to alteration in the lipid patterns (Hoefs et al., 1998; Sinninghe Damsté et al., 2002; Schouten et al., 2004; Huguet et al., 2009; Zabeti et al., 2010). Again, the congruent GDGT distribution in soils versus surface sediments at Lake Cadagno argues for a common origin of the lipids and against any substantial influence due to early diagenesis.

It remains unclear as to why in situ production (or early diagenesis) may have a strong biasing effect on the distribution of bacterial GDGTs in other lake systems, while it appears to be of lesser importance for Lake Cadagno. More analyses are required to investigate possible mechanisms/pathways that may compromise the soil-derived GDGT signals in greater detail. To date, we can only speculate that the particular environmental conditions in Lake Cadagno's water column and sediments prevent the diagenetic alteration or the in situ production of branched GDGTs. It is, in particular, the high sulfide concentration that distinguishes Lake Cadagno from other meromictic lakes where indications for in situ production of bacterial GDGTs were found (Sinninghe Damsté et al., 2009; Bechtel et al., 2010), so that this might prevent growth of bacteria synthesising the branched GDGTs. Moreover, euxinia is less conducive to the degradation of organic matter (Canfield et al., 2005), and was found to lead to enhanced preservation of (chemically similar) archaeal GDGTs (Sinninghe Damsté et al., 2002; Schouten et al., 2004; Huguet et al., 2009). If relevant, a sulfide-dependent biogeochemcial control on in situ production and/or decomposition of bacterial GDGTs would have been active throughout the Holocene, because we found pigments derived from anoxigenic phototrophs in all sediment samples (unpubl. data). In addition to its peculiar limno-biogeochemistry, Lake Cadagno is characterised by a relatively small surface area, so that the flux of allochthonous organic matter to the sediments probably by far exceeds autochthonous production. Indeed, consistently high BIT-values throughout the sedimentary sequence indicate a dominant soil-origin of sedimentary organic matter (Hopmans et al., 2004; Weijers et al., 2006b). As a consequence, if in situ production of branched GDGTs occurs at all in Lake Cadagno, its potential impact on the sediment GDGT pool would be minor (i.e. overprinted by the high flux of soil-derived GDGTs).

As suggested by the "irregular-soil" biomarker data, in situ production of bacterial GDGTs and diagenetic alteration effects are apparently not the only factors with the potential to compromise MAAT estimates. Soil from two sampling locations (Sites 4 and 8, Fig. 1) yielded CBT/MBT-ratios that appeared "irregular" in that they translated into unrealistic (i.e. too high) MAAT values. We were not able find these signatures anywhere in the sedimentary record so that we are confident that the "irregular" soils are not common in the Lake Cadagno catchment. Further investigations are, however, needed to assign particular soil properties/conditions to such "irregular" GDGT-signals, and we do not know whether similar features may have been responsible for erratic MAAT estimates in other catchments/previous studies. If abundant, such "irregular" soils clearly have the potential to influence MAAT estimates. Yet, as for Lake Cadagno, the admixture of GDGTs from these soils seems to be of minor importance, and provided the evidence discussed above, we conclude that Lake Cadgno's sediments represent an excellent archive to be used for MBT/CBT-paleothermometry using the global soil calibration.

4.2 MBT/CBT-based MAAT estimates and comparison to instrumental data and independent proxy records

For Lake Cadagno, we could show that branched GDGTs of soil origin are transferred by erosion to the sediment record where the primary GDGT signatures remain preserved, without substantial alteration by in situ GDGT production and/or early diagenesis. Therefore, it seems appropriate to calculate MAAT values using the global soil calibration (Weijers et al., 2007a). According to Eqs. (1)–(4), the composition of branched GDGTs in the lake sediment translate into paleo MAAT-estimates as depicted in Fig. 4a and e. The MAAT-record indicates that temperature variations over the Holocene epoch were relatively subtle with minima and maxima of about −1.4 and 2.4 °C, respectively (average = 0 °C ± 0.8 S_D), which, considering the modern MAAT of ∼0.5 °C (SwissMeteo), appears reasonable. However, while we have provided circumstantial evidence that the environmental conditions at Lake Cadagno lead to well preserved soil-derived GDGT-signals in the lake's sedimentary matrix, further validation of our GDGT-record is necessary to estimate its suitability for paleoclimate reconstructions, particularly with respect to the absolute magnitude of T-fluctuations. Groundtruthing a novel paleoclimate proxy using realistic instrumental data is of paramount importance for assessing the quality of proxy-based climate records. Yet, for our record, such calibration efforts are hampered by the fact that instrumental data (MeteoSwiss) are only available for the last ∼150 yr. Also, the relatively low temporal resolution of our proxy record prevents an in-depth comparison of measured versus proxy data. Thus, for the most part of our data set, we used an alternative, less direct approach for groundtruthing by comparing our estimates to other, independent proxy records.

4.2.1 The late Holocene after 2 cal. kyr BP

The climate of the last 2 millennia received considerable scientific attention. Consequently, several proxy-based climate reconstructions ranging from regional to hemispherical scales are available in the literature, and, in general, consensus exists with respect to magnitude and amplitude of major climate shifts. The MBT/CBT-ratio from the youngest sediment slab translates to a MAAT-value of 1.5 °C for the Lake Cadagno region for the time period ∼1930–present. This value is very similar to the extrapolated instrumental average of 0.9 °C (MeteoSwiss) for the Lake Cadagno region for the same time period. Absolute T-values are often compared to a long-term average, which typically represents the time period 1961–1990 (IPCC, 2007). During the 2nd half of the 20th century, increasing deviations from this average (∼0.5 °C) where found, culminating in an extrapolated absolute MAAT-value of 2.2 °C for the Lake Cadagno region in 2010 (MeteoSwiss). Our most recent T-estimate thus seems to include, and consequently reflects, the ongoing T-increase during the 20th century. Reaffirmingly, 20th century increases in T have been recorded by independent proxy records from central Alpine locations: for instance, shifts in the community structure of chironomids at Lake Silvaplana (Fig. 4g) (Larocque-Tobler et al., 2010a) indicate a T-increase of 0.6 °C from the 1930's until present. These observations also agree well with tree ring based T-reconstructions for central Europe (Büntgen et al., 2011), and an estimated 0.5 °C global increase in surface temperature on land since the 1960's (IPCC, 2007).

Prior to the 20th century, our data series indicates a MAAT minimum (up to 1 °C colder than during the reference period) at about 300 cal. yr BP (i.e. from ∼480 to 175 yr BP), which agrees in timing and amplitude with the Spannagel Cave and Lake Silvaplana records. However, these records indicate an intermediate T-high around 450 cal. yr BP (Fig. 4f and g), which is not apparent in our record, possibly due to our rather low sampling resolution. The observed cold event coincides with the Little Ice Age (LIA) (IPCC, 2007). The LIA has been first described in the context of glacier fluctuations in the Sierra Nevada, USA (Matthes, 1939) and appears to be a common climate anomaly in the Northern Hemisphere (Fig. 4h) (Moberg et al., 2005). Prior to the LIA, the MBT/CBT-ratios suggest that the climate at Lake Cadagno was considerably warmer than during the LIA. In timing, this warm period matches the so-called Medieval Warm Period (MWP), sometimes also referred to as the Medieval Climate Anomaly, a major northern hemispherical climate oscillation (Mann et al., 2009). Our record, as well as the proxy data from Lake Silvaplana and the Spannangel cave indicate MWP temperatures similar to the present-day values (i.e. ∼0.5 °C higher than during the reference period 1960–1990).

The rather far-reaching geographical extension of proxy evidence for the MWP and LIA suggests that these climate anomalies are driven by larger-scale phenomena. The exact mechanisms/processes that lead to the observed T-fluctuations are still uncertain, but growing evidence suggest the close coupling between shifting atmospheric circulation patterns and mean annual surface temperatures on land (Lamb, 1965; Trouet et al., 2009; Graham et al., 2010). Notably, Trouet and co-workers (2009) found that during the MWP, the North Atlantic Oscillation index (NAOI) was dominantly positive, while it weakened during the LIA (Fig. 4i). A positive NAOI reflects a higher-than-average atmospheric pressure difference between the subtropical Atlantic and the polar low-pressure regime (Barnston and Livezey, 1987), and is associated with strong Westerlies and enhanced heat and moisture transport towards the mid-latitudes of the northern hemisphere (Hurrell, 1995). As a result, the W-European climate, particularly during wintertime, becomes rather mild and humid (Nesje et al., 2001; Jones et al., 2003; Luterbacher et al., 2004).

4.2.2 The middle and early Holocene prior to 2 kyr BP

Our MBT/CBT-record (Fig. 4a) shows a good agreement with recently published T-records from the N-Alpine Lake Egelsee (Larocque-Tobler et al., 2010b; Larocque-Tobler, 2010) (Fig. 4b) and sea-surface temperature (SST) records from the sub-polar NE-Atlantic (Thornalley et al., 2009) (Fig. 4c), at least back until 8 cal. kyr BP. However, the records seem to be slightly phase-shifted. The chironomid-based T-record (Fig. 4b), for instance, indicates a relatively warm period at 3.3 cal. kyr BP, whereas our and the SST record for the NE-Atlantic (Fig. 4c) indicate that this event occurred slightly earlier. We attribute these apparent temporal offsets to inaccuracies of the applied age-depth models. In general, our GDGT-based paleo-T record seems to be consistent with other independent proxy records throughout most of the past 12 kyr, at least with respect to the rough timing and sequence of climate undulations.

Our paleo T-record indicates periods of elevated T that, with the exception of the early Holocene (before 8 cal. kyr BP) and the present-day MAAT-high, seem to display an apparent cyclicity of ~2 kyr. We do not have any data for the time period between 5020 and 5813 cal. yr BP (as well as for some shorter periods <250 yr; Fig. 4a, e) so that it remains speculative whether the MAAT-high at 5 cal. kyr BP evolved directly after the MAAT-low at ca. 6 cal. kyr BP. Nevertheless, our MAAT-estimates compare well with other quantitative or qualitative T-records from terrestrial and marine archives located on the NW-hemisphere, for example from the northern Alps (Larocque-Tobler et al., 2010b; Larocque-Tobler, 2010) (Fig. 4b), the NE-Atlantic (Fig. 4c) (Thornalley et al., 2009) and the Sargasso Sea (Keigwin, 1996). From the central Alps, the Spannagel Cave record (Mangini et al., 2007) and, albeit to a lesser degree, a record from Lake Hinterburgsee (Heiri et al., 2003) match reasonably well with our data. Concertedly, this provides evidence for significant T-oscillations at a frequency of ~2 kyr throughout the Holocene (i.e. major warm phases at 1, 3, 5, 7, 9 and 11 cal. kyr BP). Only the 9 cal. kyr BP warm event indicated by the independent records, as well as the so-called 8.2 kyr event, a brief cold spell of a few hundred years, which has been found in many proxy records (Alley and Agustsdottir, 2005, and references therein), are not represented in our MBT/CBT T-record. The rather broad, temporal resolution and/or the hiatus from ~8.3 to ~8.7 cal. kyr BP could be responsible for the absence of the 8.2 kyr event in our record. However, at this point, we are unable to explain why the MBT/CBT-paleothermometer did not record the warm phase at 9 cal. kyr BP.

Similar to the MWP and the LIA, at least some of the warm phases detected in our record were probably of considerable geographical extension and not only restricted to W-Europe. For example, broader-scale implications of the temperature fluctuations recorded in the Cadagno core for the continental/hemispherical climate are suggested by the good match of our data (back until 8 cal. kyr BP) with a record of winter precipitation in SW-Norway (Fig. 4d) (Nesje et al., 2001). Elevated winter precipitation in NW-Europe is linked to comparably mild temperatures and strong westerly winds, and is thus a qualitative indicator for the strength of the NAO (Nesje et al., 2000; Reichert et al., 2001). Accordingly, the NAO was strong during the warm phases at about 3, 5 and 7 kyr BP. Together with the findings of a dominantly positive NAOI during the MWP (Trouet et al., 2009), this indicates a generally strong and far-reaching influence of the NAO on Holocene T-variations beyond W-Europe.

4.3 Paleo soil-pH

Our CBT-based pH-estimates of soil-pH (including the "irregular" soils) are only slightly higher than in situ measured pH (Fig. 5). Also, the pH-estimate from surface sediments (pH = 6.9) agrees well with the average in CBT-based soil pH estimates (average pH = 6.8). This again indicates a predominant soil origin for the sedimentary branched GDGTs. At present, pH is ca. 8.5 in the surface waters decreasing through the chemocline to about 7.2 in the monimolimnion. Water column pH is thus generally higher than soil-pH from the watershed of the lake. As Lake Cadagno is recharged with carbonate-rich water from sub-aquatic springs (Del Don et al., 2001), the pH of the lake (bottom) water is well buffered, and it appears unlikely that the buffering capacity of the lake has changed over the last millennia. As a consequence, we assume that changes in sedimentary CBT ratios are due to changes in the pH of the catchment soils and not in the lake water column.

The most prominent feature of the soil pH-record is a decrease from pH 7.8 to 6.8 in the early phase of the Holocene, at the end of the Younger Dryas (12–11 cal. kyr BP) (Fig. 6). During the subsequent 10 kyr until present, soil pH did not deviate strongly from its long-term average of pH 6.9, with the exception of an apparent pH-minimum (pH = 6.6) during the Bronze Age (∼4 kyr BP) and a subsequent pH-increase that peaked with a pH value of 7.0 at 1 kyr BP. A pH-decrease of about 1 pH unit between 12 and 10 cal. kyr BP has also been reported for a sediment record from central Africa (Weijers and et al., 2007b), and it was attributed to enhanced precipitation at the end of the Younger Dryas. Indeed, strong precipitation events may cause leaching of basic ions, which, in turn leads to soil acidification (Schaetzl and Anderson, 2005). Lake-level stand reconstructions from the Jura mountains indicate humid climate conditions throughout the early Holocene in W-Europe (Magny, 2004), which are also reflected in the flood record from Lake Cadagno, evidenced by a high (but variable) frequency of flooding events throughout the last 12 kyr (Wirth et al., 2011). Consequently, leaching of soils by enhanced precipitation seems to be a plausible explanation for the observed decrease in soil pH. The minor drop in reconstructed pH around 4 cal. kyr BP would then imply an even more humid climate during the Bronze Age. The pH minimum seems to be qualitatively consistent with low δ^{18}O-values from the Spannagel cave record (Mangini et al., 2007), as well as with a enhanced deposition frequency of flood layers in Lake Cadagno (Wirth et al., 2011), both of which independently suggest increased precipitation rates during this time period. However, the flood record by Wirth et al. (2011) indicates a particularly high frequency of flooding events during the Bronze Age, which stands out in the context of the last 10 kyr, and which is much higher than during the Younger Dryas. This suggests that the relationship between precipitation rates, soil leaching and soil pH is not always linear. To some extent, this may be related to the variations in the chemical composition and the buffering capacity of catchment soils, which can change in time with soil maturation (Schaetzl and Anderson, 2005). It has to be noted that in high alpine locations, glaciers were retreating at the end of the Younger Dryas (e.g. Ivy-Ochs et al., 2009). Accordingly, soils in the Lake Cadagno region were at that time in a very early development stage in which the buffering capacity typically is determined by a fast-leaching carbonate buffer (Schaetzl and Anderson, 2005). An elevated buffering capacity of a more matured soil in the Cadagno catchment during the Bronze Age may have prevented further soil acidification, because mature soils are primarily buffered by silicates, which are more resistant to soil leaching. The apparently variable response of paleo soil pH in the Lake Cadagno catchment to paleo-precipitation changes provides evidence that this parameter is a qualitative rather than a quantitative proxy for precipitation, and that it should consequently be used with caution.

5 Conclusions

We recovered an almost continuous Holocene sediment sequence from the meromictic, Swiss high-Alpine Lake Cadagno, providing a well-preserved archive for paleoclimate reconstructions. We could show that soil-derived, branched GDGTs are transferred and preserved in the sedimentary matrix, and that the primary distribution of these compounds remain unaffected by early diagenesis and/or dilution by in situ produced GDGTs. Both processes can ultimately affect the GDGT composition in the sediment and thus lead to biased MBT/CBT-based paleotemperature estimates. We putatively attribute the absence of these biasing effects to the euxinic/sulfidic conditions of bottom waters, preventing biosynthesis and/or decomposition of the relevant GDGTs. Also, the high import of soil-derived GDGTs is likely to overprint any in situ signature (if present at all). Our MBT/CBT-based record agrees well with instrumental data and with various other independent proxy-based paleoclimate reconstructions. The application of the MBT/CBT-paleothermometer to Lake Cadagno sediments thus provides a robust and quantitative measure for paleo-MAAT and soil pH-variations during the Holocene. The reconstructed temperature variations together with other proxy records indicate a broad geographical extension of surface temperature maxima in Europe that seem to be linked to a ~2000 yr cyclicity of the North Atlantic Oscillation. Our data set confirms that, compared to other periods of Earth history, the Holocene has generally been a climatically stable period. However, it displays subtle but resolvable temperature variations of a few °C in central Europe and the Alpine realm. While our dataset clearly shows that the links between climate humidity and soil pH are not linear, soil acidification at the end of the Younger Dryas may further attest to significant changes in climate at the beginning of the Holocene period, at least in the Cadagno region. The applicability of the MBT/CBT-paleothermometer to lakes with preservation conditions and sedimentation regimes other than those found in Lake Cadagno needs further testing, particularly with respect to environmental factors that control the in situ production or decomposition of bacterial GDGTs in the water column and/or sediments. Moreover, soils provide time-integrated geochemical signals, so that the time-scale captured by the GDGT-proxy is, to some extent, uncertain, and possibly markedly different from the time of sedimentation. This may complicate the temporal resolution and direct comparison to other paleo-proxies. Nevertheless, despite these constraints, it is encouraging with regards to future applications of GDGT measurements in paleoclimatological studies, that the MBT/CBT-paleothermometer has the potential to resolve subtle temperature changes of <1 °C, at least in lakes with specific environmental/preservation conditions.

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Table 1. Sediment and soil samples recovered from Lake Cadagno and its catchment area.

Sampling position	Lat (° N)	Long (° E)	Sample type	Profile depth (cm)	Sampling interval (cm)
1	46.5507	8.7139	lake sediments (short core)	surface – 96	5
			lake sediments (composite long core)	surface – 870	10
2	46.5491	8.7044	soil	surface	bulk
3	46.549	8.7044	soil (profile)	surface – 60	15
4	46.5506	8.7072	soil (profile)	surface – 60	15
5	46.5526	8.7145	creeksoil /sediment	surface	bulk
6	46.5523	8.7175	soil	surface	bulk
7	46.5523	8.7176	soil	surface – 96	bulk
8	46.547	8.7208	soil (profile)	surface – 30	15
9	46.5481	8.7129	soil (profile)	surface – 45	15

Table 2. Radiocarbon dates of terrestrial organic material collected from various sediment depths. All radiocarbon dates were converted to calendar years before 1950 (yr BP). Ages derived from sample material in slump deposits were not considered for age-depth modelling (ages denoted with asterisks).

Lab code	Composite depth (cm)	Sample material	^{14}C age (^{14}C yr. BP)	$\pm 1\sigma$	Callibrated age (yr. BP), 2σ-range
ETH-42351	102.5	terr. macrofossils	1255	60	1056–1295
ETH-39236	223	wood	2035	35	1898–2112
ETH-41051	337.5	terr. macrofossils	3015	35	3079–3338
ETH-39237	419.5	wood	3305	35	3452–3630
ETH-41052	652	wood	4595	35	5068–5460
ETH-39238	696	wood	5035	35	5663–5899*
ETH-41053	778.5	terr. macrofossils	8015	35	8765–9012*
ETH-42352	798	wood	6450	35	7291–7430
ETH-41054	871.5	wood	8055	35	8776–9079
ETH-39238	919.5	wood	9630	45	10776–11180

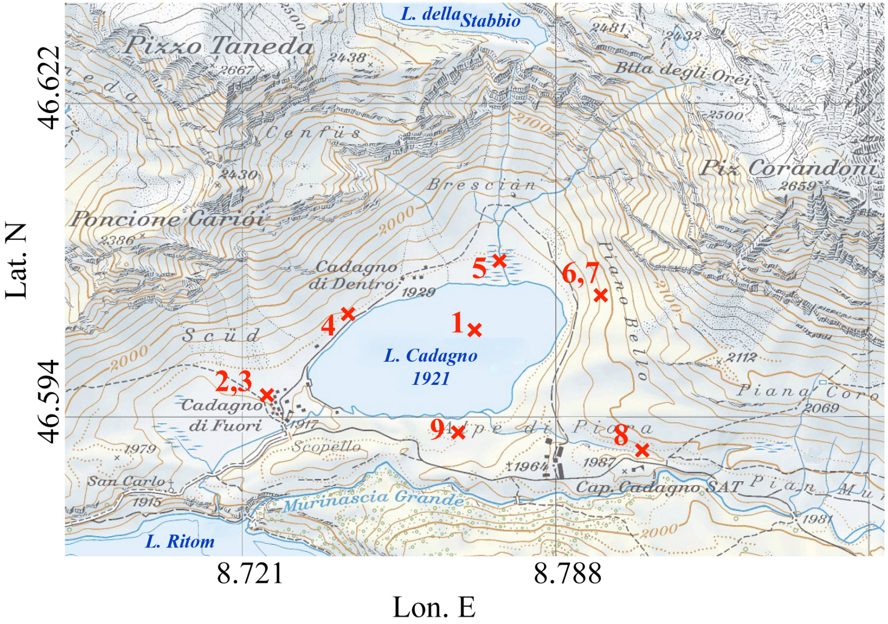

Fig. 1. Lake Cadagno and its crater-like shaped catchment area, including the smaller Lake della Stabio in the North. Sampling positions of sediment coring (Site 1) and soil collection (Sites 2–9) are indicated (modified from Swisstopo).

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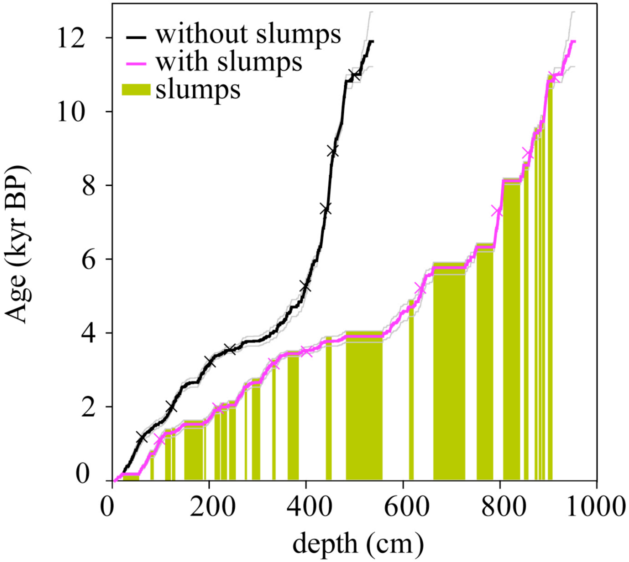

Fig. 2. Age-depth model for the Holocene sediment sequence developed from calibrated radiocarbon ages of terrestrial macrofossils and wood. Almost half of the recovered composite core consists of slump deposits intercalating regular sediments. The magenta curve shows the age-depth model including all deposits; for the black curve, slump deposits were excluded from the record. Vertical line sections on the depth-axis represent slump deposits (in green).

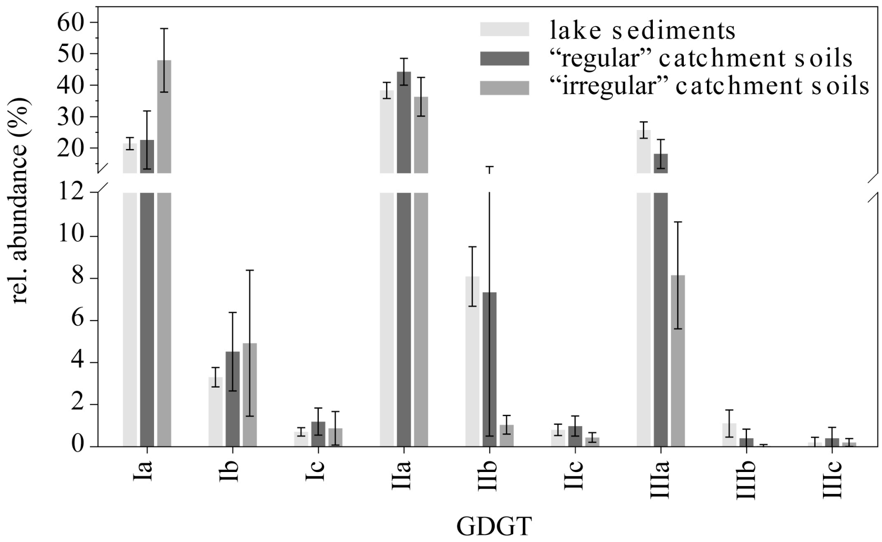

Fig. 3. Relative abundance of GDGTs comprised in the MBT/CBT ratios from lake sediments and soils. Series a GDGTs (i.e. without cyclopentane moieties) are most abundant, followed by Series b and c (see Fig. A1 for structural information). Based on the strong differences in GDGT abundance, we defined two soil types. The distribution of GDGTs in most soil samples (regular soils, $n = 11$) was very similar to the uppermost lake sediments. Only soils from sampling positions 4 ($n = 4$) and 8 ($n = 2$) (irregular soils) showed considerably different abundance patterns (i.e. rel. high amounts of compound Ia and low amounts of compounds IIb and IIIa). Soil profiles did not reveal recognisable trends in either MBT or CBT ratio with depth.

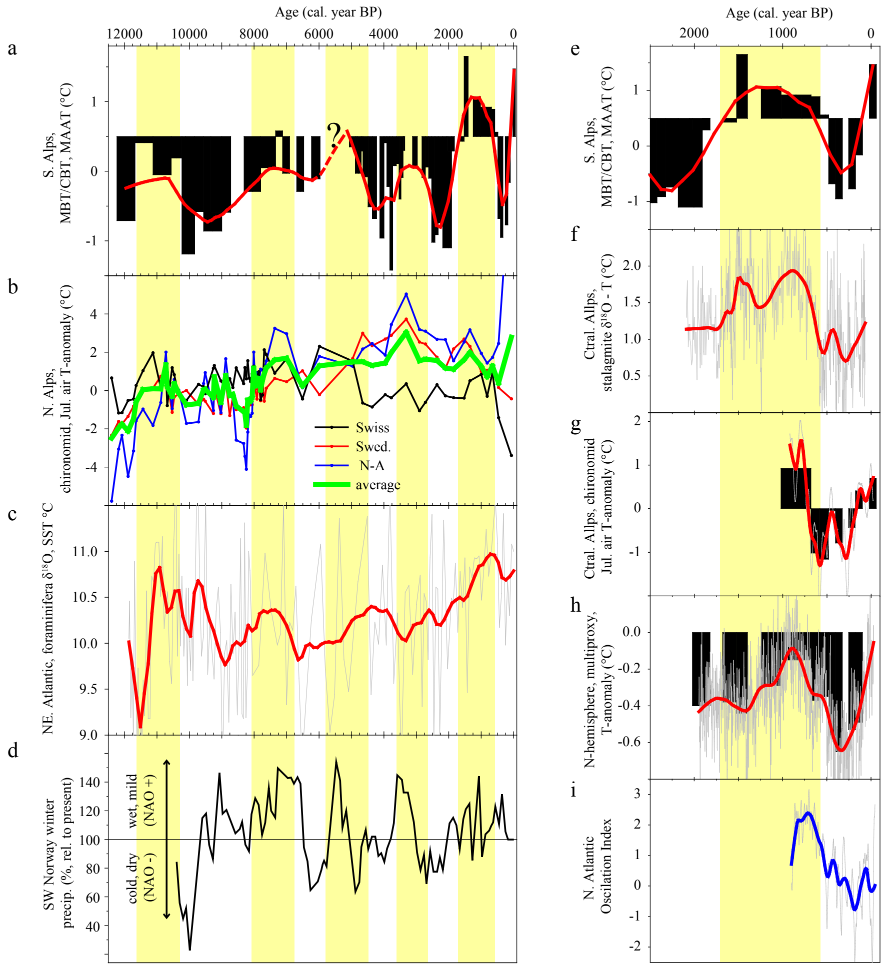

Fig. 4. Caption on next page.

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Fig. 4. MBT/CBT-derived MAAT estimates for the Holocene epoch in comparison to independent proxy records. Temperature highs determined from the MBT/CBT-record are highlighted in yellow. **(a)** Lake Cadagno MBT/CBT-based paleotemperature. Bars represent raw data of MBT/CBT-paleothermometry (temporal resolution is indicated by bar width) and the red curve a low-pass filter (bisquare, 0.15). **(b)** July air-T anomaly at Lake Egelsee, northern Alps as estimated from chironomid communities using different transfer functions that were developed for Switzerland, Sweden and North America (Larocque-Tobler et al., 2010b; Larocque-Tobler, 2010; raw data courtesy by Isabelle Laroque-Tobler). **(c)** Sea surface temperatures of the sub-polar NE-Atlantic estimated from foraminiferal δ^{18}O-signatures (Thornalley et al., 2009). **(d)** Winter precipitation in W-Norway, indicating variations in the North Atlantic Oscillation (NAO). Redrawn and modified from Nesje et al. (2001). **(e)** Sectional enlargement of MBT/CBT-based MAAT estimates of the last 2500 yr in comparison to **(f)** temperature estimates for the central Alps based on δ^{18}O-variations of stalagmites (Mangini et al., 2005), **(g)** July air temperature anomaly in the central Alps estimated from chironomid assemblages (Larocque-Tobler et al., 2010a), **(h)** Northern Hemisphere temperature anomaly reconstructed from a multiproxy record (Moberg et al., 2005) and **(i)** NAOI estimated from a tree-ring–based drought reconstruction for Morocco and a speleothem-based precipitation proxy for Scotland (Trouet et al., 2009). Ages are presented as calendar years before 1950 (cal. yr BP). Raw data from panels **(c)** and **(f–i)** (grey lines) are available at the World Data Center for Paleoclimatology, Boulder, USA (http://ncdc.noaa.gov/paleo/recons.html). Raw data were harmonised by applying low-pass filters (bisquare, 0.075, panel **(c)**; bisquare 0.15, red and blue lines, **f**–**i**). Raw data of panels **(g)** and **(h)** were also averaged to match time intervals represented in our data (bars). MBT/CBT-based MAAT reconstructions show a very good match in timing and amplitude to independent T-estimates for the last 2 millennia (panels **f**–**h**). Most of the major T-anomalies recorded by the MBT/CBT-paleothermometer (1, 3, 5, 7 and 11 kyr BP) are also visible in chironomid-based T-estimates for the northern Alps (panel **b**) and sea surface temperatures of the NE-Atlantic (panel **c**). All temperature highs after ca. 8 cal. kyr BP agree well in timing to maxima in the NAO (panels **d** and **i**).

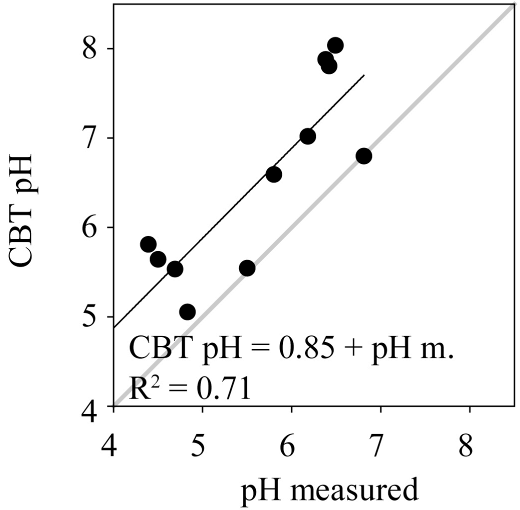

Fig. 5. pH measurements and CBT-based pH estimates in soils. Soil-pH measurements versus CBT-based pH estimates indicate that the estimated pH is slightly overrated but within the range of measured pH-values (a 1:1 relation is indicated by the grey line).

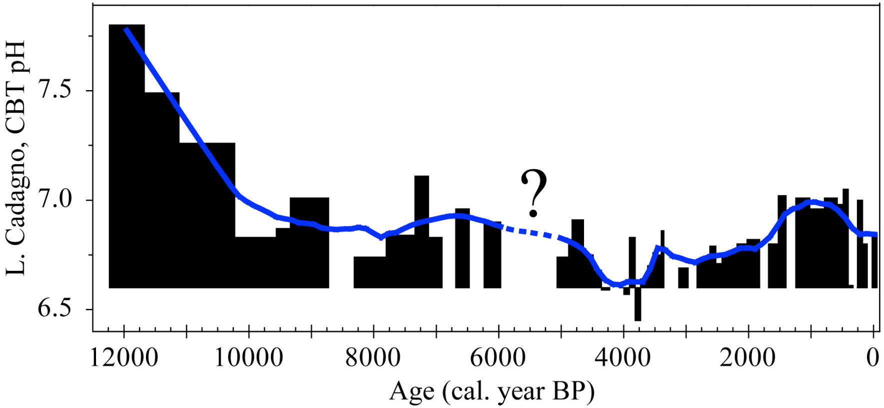

Fig. 6. Paleo-soil pH estimates based on CBT-ratios in the sediments of Lake Cadagno. Bars represent raw data (temporal resolution is indicated by the bar width) and the blue curve a low-pass filter (bisquare, 0.15). The CBT-based estimate indicate a decrease of about 1 pH unit during the early Holocene (ca. 12–9 cal. kyr BP).

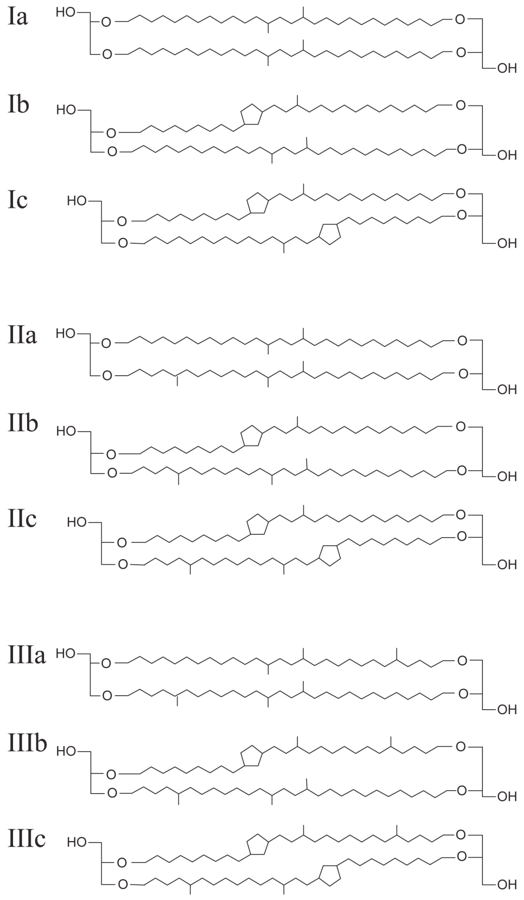

Fig. A1 Chemical structure of bacterial glycerol dialkyl glycerol tetraethers (GDGTs) comprised in the MBT/CBT-paleothermometer.