Chemical Geology 551 (2020) 119759 https://doi.org/10.1016/j.chemgeo.2020.119759

Seasonal effects of water temperature and dissolved oxygen on isoGDGT proxy （TEX_{86}） in a Mediterranean oligotrophic lake.

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Abstract

To appraise the application of isoprenoid glycerol dialkyl glycerol tetraethers (isoGDGTs) as paleoclimate proxies in small lakes we investigated the effect of seasonal variability in temperature and dissolved oxygen concentration (DO) on the GDGT contents and its proxy in the water column of an oligotrophic karst lake in the Catalan pre-Pyrenees (Lake Montcortés). From October 2013 to November 2014, we collected suspended particulate matter (SPM) monthly at three depths and retrieved the sediment from a trap located at 20 m below the lake surface. The GDGT contents in the SPM and sediment trap presented a marked seasonal variation, showing the highest values in summer and autumn. In addition, the isoprenoidal GDGT proxy TEX_{86} in SPM and sediment trap showed a marked seasonal variability which matched the temperatures of the upper water column and fit the published global trend between TEX_{86} and mean annual lake surface temperature (LST). However, in the hypolimnion where oxygen was depleted for most of the study period, we found that TEX_{86} co-varied with DO. This further confirms previous claims with seasonal field data that the sedimentary TEX_{86} LST signal may be confounded by DO conditions. Consequently, the application of TEX_{86} to estimate LST should be carefully appraised in environments with depleted DO conditions.

Keywords: Temperature reconstruction, Dissolved oxygen, IsoGDGT proxy, Mediterranean area

1. Introduction

The distributions of glycerol dialkyl glycerol tetraethers (GDGTs) in sediments are used as a proxy measurement to infer past variations in climatic and environmental parameters (Schouten et al., 2013). These lipids are found ubiquitously in the environment and can be grouped into two classes of compounds: isoprenoid GDGTs (isoGDGTs) and branched GDGTs (brGDGTs). IsoGDGTs are found typically in marine and lacustrine settings (Karner et al., 2001; Wakeham et al., 2003; Sinninghe-Damsté et al., 2009; He et al., 2012), but also in soils (Weijers et al., 2006; Peterse et al., 2015; Dang et al., 2016; Wang et al., 2017), peats (Huguet et al., 2015; Naafs et al., 2018) and dust (Fietz et al., 2013; Weijers et al., 2014), characterized by two biphytane carbon skeletons with a varying number of cyclopentane moieties (Fig. S1), and exhibit sn-2,3 stereochemistry (Pearson and Ingalls, 2013). So far, compounds with 0 to 8 cyclopentane moieties have been identified, though isoGDGTs with more than 4 cyclopentane moieties have only been found in extreme settings such as hot springs and cultures of extremophilic Archaea (Schouten et al., 2013). IsoGDGTs are considered to be produced by phyla of Archaea, which are abundant in aquatic and terrestrial habitats, playing an important role in global biogeochemical cycles (Jarrell et al., 2011).

In general, water temperature appears to be the primary control on the sedimentary distributions of GDGTs. This finding led to the development of isoGDGT-derived proxies, such as TEX_{86}, which has been applied to estimate past sea surface temperature (SST) and lake surface temperature (LST) (Schouten et al., 2002; Kim et al., 2008; Powers et al., 2010). Although TEX_{86} was initially developed for the marine environment, the occurrence of Thaumarchaeota in lacustrine environments led to the development of global and regional TEX_{86} lake calibrations (Keough et al., 2003; Blaga et al., 2009; Powers et al., 2010; Yao et al., 2019). To estimate past SST, the sedimentary values of TEX_{86} were initially correlated with sea sub/surface temperatures worldwide (0–200 m) (Schouten et al., 2002; Kim et al., 2010; Tierney and Tingley, 2015). Such an approach has been applied in many climate reconstructions from the tropics to the poles also in lakes (Pearson et al., 2011). However, some studies questioned the general applicability of global TEX_{86} calibrations. The incubation experiments indicate that water temperature is indeed the major controlling factor for the membrane distribution of marine Crenarchaeota and confirm that the TEX_{86} proxy depends on a physiological response to regulate membrane fluidity (Wuchter et al., 2004, 2005). In cold water settings the relationship between core top TEX_{86} values and overlaying satellite SST is non-linear below 5°C, which prompted the definition of modified indices for settings with SSTs below 5°C (Kim et al. 2008, 2010), or using alternative isoGDGTs with hydroxyl groups (Fietz et al., 2013; Huguet et al., 2013, 2017; Lü et al., 2015). Furthermore, Yang et al. (2018) suggested that the hydroxylated GDGTs (OH-GDGTs) with 1 to 2 hydroxyl groups on the alkyl chain of the classic isoGDGTs exhibits a significant negative correlation with SST > 25 °C, suggesting that it has the potential to be used to reconstruct SST when the application of $U^{K}_{37}{}'$ was limited in tropical seas. Baxter et al. (2019) appraised that the distribution of lacustrine glycerol monoalkyl glycerol tetraethers (the brGMGTI) is correlated with MAAT based on a study in a set of East African lakes, which may also have potential to be applied to reconstruct paleoclimate.

In continental settings, the application of TEX_{86} has been argued to be constrained to large lakes on the basis that Thaumarcheota in small lakes may not be present in sufficient abundance to produce detectable amounts of isoGDGTs (Powers et al., 2010). In addition, inputs of allochthonous organic matter containing isoGDGTs (non-aquatic Thaumarchaeota) to lakes and the sediments containing isoGDGTs derived from methanotrophs may potentially hamper the straightforward application of TEX_{86} (Blaga et al., 2009; Pearson et al., 2011; Naeher et al., 2012, 2014). Nevertheless, some studies have showed that TEX_{86}-based temperature in SPM corresponded well with *in situ* water temperature (Huguet et al., 2007a; Loomis et al., 2011).

An investigation demonstrated that DO concentration in two marine ammonia-oxidizing Thaumarchaeota cultures was an important driver of TEX_{86} values: reduced levels of DO resulted in higher TEX_{86} values (Qin et al., 2015). Another study shows that DO content, rather than temperature, exercised a primary control on TEX_{86} values (Zhang et al., 2016). Moreover, in cultures, TEX_{86} correlated negatively with ammonia oxidation rate, resulting in warmer TEX_{86} values at slower oxidation rates and colder values at faster oxidation rates (Hurley et al., 2016).

The successful interpretation of the isoGDGT proxies also relies on the determination of the depth of production and the spatiotemporal variations in the distributions and fluxes of isoGDGTs in the water column, and how all these affect the aforementioned parameters to estimate LST or SST (Blaga et al., 2011; Woltering et al., 2012). The analysis of isoGDGT production in the water column throughout the annual cycle is needed (Kumar et al., 2019). In order to further appraise the application of isoGDGT proxies, particularly in small lake basins, we have investigated their seasonal and vertical variability in the water column of Lake Montcortés (Fig. 1). We are seeking to establish if there is seasonality in the production and fluxes of isoGDGTs in the lake water column and sediment trap, and whether water temperature and aerobic conditions influence the sedimentary values of the proxies.

2. Methodology

2.1 Study area

The oligotrophic Lake Montcortés (42°19'50" N, 0°59'46" E, 1027 m a.s.l.), located in the Catalan pre-Pyrenean Range, is one of the deepest karstic lakes (about 30 m) in the Iberian Peninsula (Camps et al., 1976; Alonso, 1998) (Fig.1). The lake is roughly circular with a diameter between 400-500 m. The water column is stratified for most of the year and episodes of mixing during the winter have also been documented (Modamio et al., 1988; Trapote et al., 2018). During stratification, pH values ranged from 8.7 in surface water to 7.1 in the anoxic hypolimnion but with the average of 7.8 during the mixing period (Trapote et al., 2018). Relatively high surface/depth ratio and steep margins provide favourable environments for deposition and preservation of finely laminated facies (Corella et al., 2011). For the study period, meteorological data was obtained from a station located in the town of La Pobla de Segur (585 m a.s.l.), which is 10 km away in graphical distance from the lake. The wind velocity shows higher values from March to September but lower values from October to February. The monthly accumulated rainfall amount shows the lowest value in March (<30mm) and the highest in August (~150 mm) and annual average air temperature is 12.8 °C, with the maximum and minimum mean temperatures of 23.3 (July) and 2.9 °C (January), respectively (Trapote et al., 2018) (Fig.2). The lake is recharged by precipitation, via ephemeral creeks and groundwater flows, while it loses water mainly by evaporation or through a temporal outlet in the northern end of the basin (Camps et al., 1976). The main vegetation formations in the lake catchment are evergreen and deciduous oak forests, conifer forests and littoral vegetation (Mercadé at el., 2013).

Lake Montcortés contains one of the longest continuous varved records with a well-established varve chronology (Corella et al., 2012). Montcortés varves occur in a typical karst lake that is located on carbonate rocks, which provides excellent archives of climate and environmental changes because of high sedimentation rates (Corella et al., 2012; Trapote et al., 2018). Due to the long-lasting period with anoxic bottom, it is beneficial for conservation of organic matters (Vegas-Vilarrúbia et al., 2018). Water column mixing events took place in January, and hypoxia (≤2 mg L^{-1}) began in April, anoxia (0 mg L^{-1}) retained from June until December and the highest and lowest mass flux in the sediment trap was recorded in October 2013 and February 2014 (Trapote et al., 2018).

2.2 Sample collection

A sediment trap was deployed at 20 m depth within the lake (about 5 m above the lake bottom) to collect settling particulate matter, and was retrieved monthly from October 2013 to November 2014. Trapped material was filtered through pre-combusted and weighted glass fibre filters (GFF, pore size of 0.7 µm), freeze-dried and weighted. The mass flux in the sediment trap was calculated based on the material weight and duration of sampling days. Approximately in parallel time wise to the trap deployment from September 2013 to November 2014, the SPM in 40 L water was collected every month at three different depths: surface (0.5 m below the surface water level), metalimnion (between 5 and 17 m), and hypolimnion (~20 m). Vertical profiles of water column parameters (T, DO) were obtained monthly using a multi-parameter water quality probe sonde (Hydrolab DS5), the same day when the sediment traps were retrieved, which usually took place one day earlier than the water SPM sampling (Trapote et al. 2018). A few hours after collecting them, water samples for GDGT analyses were filtered in the laboratory using pre-combusted GFF, and which were subsequently freeze dried and stored frozen until analysis. Soil samples in the lake catchment were also collected on a monthly basis in three different sites with either littoral grassland, oak forests and dry grassland vegetation cover (see details in Cao et al. (2018)). For each soil type, three replicates were collected after removing leaf litter. The soils were placed in a pre-combusted aluminium tray, wrapped with aluminium foil and sealed in plastic bags. Five short sediment cores close to the deepest part in the lake were also retrieved in February 2013 using a Uwitec core sampler, from which the top 2 cm were cut and used as surface sediment in this study. Once in the laboratory, the soils and sediments were frozen, freeze-dried and ground to a fine powder.

2.3 Lipid extract and instrumental analysis

GDGT internal standard (abbreviated as GR) (Réthoré et al., 2007) was added to each GFF (containing filtered SPM or sediment trap particles) before they were extracted (×3) with 50 mL (20 mL×1, 15 mL×2) of dichloromethane and methanol (3:1, v/v) by ultrasonic solvent extraction. After adding an amount of GR standard, 2-8g of soil and 1g of sediment samples from the surface of the sediment cores were extracted following the same procedure as the filters but using 30 mL and 10 mL of solvent mixture, respectively. After centrifugation (2000 rpm for 5 minutes), the supernatants from each sample were combined and dried in a rotary evaporator.

The methods of column chromatography for separating and purifying the liquids were adapted from Huang et al. (1999) and Schouten et al. (2002), using Pasteur pipettes (previously combusted at 450 °C) containing 0.7 g of aminopropyl silica and 0.5 g of anhydrous Na_2SO_4. The columns were conditioned with 3 mL of dichloromethane:isopropanol (2:1, v/v), and the extracts were eluted with 6 mL of dichloromethane:isopropanol (2:1, v/v; F1 or neutral fraction) and 8 mL diethyl ether:acetic acid (96:4, v/v; F2 or acid fraction). The F1 fraction was further separated into non-polar (F1-1; *n*-alkanes), slightly polar (F1-2) and polar fractions (F1-3; GDGTs) using a silica column and eluted with 5 mL of hexane, 4 mL of dichloromethane and 6 mL of dichloromethane:methanol (95:5, v/v).

For GDGT analysis, fraction F1-3 was dried and redissolved in 200-600 µL hexane:isopropanol (99:1, v/v) and filtered through a 0.45 µm polytetrafluoroethylene filter. An aliquot of 5 to 20 µL was injected in an Agilent Time-of-Flight (TOF) mass spectrometer with an atmospheric pressure chemical ionization (APCI) interface set in positive mode. Following the methods in Escala et al. (2007) and Huguet et al. (2013), the extracts were eluted through a Tracer Excel CN column (Teknokroma; 20 cm length, 0.4 cm diameter and 3 µm particle size) equipped with a pre-column filter and a guard column. The mobile phase consisted of n-hexane:isopropanol (98.5%:1.5%) and was eluted at a flow of 0.6 mL/min. The proportion of isopropanol was held at 1.5% for 4 minutes and increased gradually to 5% during 11 minutes, then increased to 10% for another 1 minute, and remained at this proportion for another 4 minutes, to be finally decreased back to 1.5% during 1 minute and held at 1.5% for 9 minutes until the end of the run. The parameters of the APCI interface were set as follows to generate positive ion spectra: corona discharge 3 µA, vaporizer temperature 400 °C, sheath gas pressure 49 mTorr, auxiliary gas (N_2) pressure 5 mTorr and capillary temperature 200 °C. GDGTs were detected in selected ion monitoring (SIM) mode at the following m/z (Schouten et al., 2007): 1302, 1300, 1298, 1296, 1292, 1050, 1048, 1046, 1036, 1034, 1032, 1022, 1020, 1018 and the synthetic tetraether lipid (GR) at 1208 m/z (Fig. S1).

2.4 Calculation of TEX_{86}-related temperatures

The TEX_{86} as defined by Schouten et al. (2002):

$$TEX_{86} = \frac{[GDGT-2]+[GDGT-3]+[GDGT-4']}{[GDGT-1]+[GDGT-2]+[GDGT-3]+[GDGT-4']} \quad (eq.\ 1)$$

Here, GDGT-4 and GDGT-4' are crenarchaeol and crenarchaeol' in Fig.S1, respectively. LST estimates were calculated using the lacustrine calibration by Powers et al. (2010):

$$LST = -14.0 + 55.2 \times TEX_{86} \quad (eq.\ 2)$$

We calculated $TEX_{86(w)}$ as a combined index from SPM samples at three depths in the water column. The equation (*eq.*3) presented as follows:

$$TEX_{86(w)} = ([TEX_{86}]_{0m} + [TEX_{86}]_{5-12m} + [TEX_{86}]_{20-22m})/3 \quad (eq.\ 3)$$

3. Results

3.1 Seasonal changes in environmental variables

There was a marked difference in the temperature range between the coldest and hottest month, with a mean annual air temperature of 20.9 °C during the study period. The mean annual rainfall was Montcortés 793 mm (Cao et al., 2019). In the study period, surface water temperature ranged from 5.4 °C to 22.2 °C; the water temperature in the metalimnion from 4.8 °C to 20.2 °C and the water temperature in the hypolimnion from 3.5 °C to 6.9 °C in Lake Montcortés (Fig.2). Dissolved oxygen showed maximum concentrations (14–17 mg L^{-1}) between 7m and 10 m in the euphotic metalimnion from May to September around the thermocline; in contrast, near the lake bottom water transitioned from fully anaerobic to aerobic (Trapote et al., 2018).

3.2 Archaeal lipid abundance and distribution in the water column

SPM isoGDGT abundance in the water column showed significant seasonality at all depths, with similar trends and concentration ranges, but decreasing with depths (Fig.3). The lowest isoGDGT concentrations occurred from January to

April/May, whereas the highest were in May/June to August/November. From April to August the isoGDGT concentrations in the SPM decreased with depth (generally when concentrations were overall the highest in the study period), while concentrations were similar or increased with depth at other times. Regarding to concentration ranges, in the epilimnion they varied from 0.1 ng L^{-1} (February 2014) to 2.2 ng L^{-1} (November 2014) with the mean value of 0.75±0.63 ng L^{-1}, while in the metalimnion from 0.1 ng L^{-1} in April to 2.2 ng L^{-1} in August 2014 with a mean value of 0.64±0.55 ng L^{-1}. In the bottom waters, the lowest value was 0.1 ng L^{-1} in April while the highest 1.1 ng L^{-1} in September with the mean value of 0.48±0.27 ng L^{-1}. These concentration ranges are similar to those reported for other type of European lakes like Lake Brienz and Lake Lugano in Switzerland (Bechtel et al., 2010), but were lower than isoGDGT concentrations in other sites, like Indrepollen Lake in Norway (Zhang et al., 2016). The flux of isoGDGTs in the trap showed the maximum (0.99 $\mu g \cdot m^{-2} \cdot day^{-1}$) in December 2013, and the minimum (0.03 $\mu g \cdot m^{-2} \cdot day^{-1}$) in February 2014 with the mean of 0.50±0.29 $\mu g \cdot m^{-2} \cdot day^{-1}$ (Fig.3). The isoGDGTs abundance in surface sediment (0-2cm) was 7.3 µg/g TOC (Table 2).

The composition of isoGDGTs (GDGT-0, 1, 2, 3 and 4 (crenarchaeol), 4' (regio-isomer crenarchaeol)) in the aquatic environments was largely different from that in soils that was dominated by GDGT-0 and crenarchaeol, accounting for 40% of the total isoGDGTs, respectively (Fig.4). All SPM, sediment trap and surface sediment samples were dominated by GDGT-0 (with the relative abundance >70%), followed by GDGT-1 (~10%), GDGT-2 and GDGT-4. GDGT-3 and GDGT-4' were generally minor compounds in the lake environment (Fig.4). The distribution of isoGDGTs in the surface sediment was highly correlated with that from the SPM and sediment trap in the water column at different depths (R^2>0.99, p<0.001). Furthermore, the GDGT-2/GDGT-3 ratio of SPM increases with depth, but decreases at sediment trap and surface sedimen.

3.3 TEX_{86} values

TEX_{86} values were calculated based on the distribution of isoGDGTs in the surface sediments and the overlying water column. TEX_{86} values in the SPM showed a similar seasonal variation at the three different depths investigated, ranging from 0.35 (December) to 0.65 (May) with a mean value of 0.46±0.02 for the epilimnion water, from 0.35 (January) to 0.60 (November) with a mean value of 0.48±0.02 for the metalimnion water, and from 0.33 (February) to 0.61 (September) with a mean value of 0.46±0.02 for the hypolimnion water (Table 1). In the sediment trap, TEX_{86} values of settling particulates varied from 0.39 (February) to 0.63 (April), with a mean value of 0.51±0.02 that is consistent with TEX_{86} values in surface sediments (0.54±0.01). TEX_{86} values of soils were within 0.66 and 0.77, and therefore generally higher than lacustrine TEX_{86} values, and their temporal trend during the study period showed no seasonality (Table 2).

4.1 Potential sources of isoGDGTs in the lake surface sediments

The highest concentration and flux of isoGDGTs in the SPM and settling matter in Lake Montcortés occurred from April to September, corresponding to a bloom of phytoplankton dominated by diatoms (more than 75% of the total assemblage) (Trapote et al., 2018). Thaumarchaeota are purported to be ammonia-oxidizers (Murray et al., 1998; Herfort et al., 2007). Seasonal changes in isoGDGT abundance have been previously related to the release of ammonium generated by the decay of the phytoplankton biomass (e.g. Blaga et al., 2011). Consequently, the enhanced fluxes and concentrations of isoGDGTs in the water column during the year could be related to the occurrence of the phytoplankton bloom (Fig.3a). This would be consistent with the observation that isoGDGTs concentration correlate generally with the concentration of chlorophyll in sediments (Fietz et al., 2011). In addition, the vertical fluxes of phytoplanktonic particulate material could contribute to the increase of isoGDGTs in the SPM (Fig. 2a).

Arguably, surface runoff could have brought allochthonous GDGTs from the surrounding soils into the lake and deposited them in the sediment through water column. The maximun mass flux corresponded to the highest precipitation during August, 2014, which suggests that the precipitation may also increase the surface runoff and the tranportation of isoGDGTs from land to the lake water. Nevertheless, we find no conclusive evidence if such a process occurred as the mass flux and isoGDGT flux in the sediment trap was not linearly correlated with precipitation (Fig.2a, 3a). Furtherly, the isoGDGT abundance in soils is much lower than the surface sediments, which also suggests that the iGDGTs in the study lake could be primarily derived from autochthonous sources. IsoGDGTs in the SPM of the water column may be affected by the surrounding soils that only exert minor impact on those in the surface sediments (Qian et al., 2019).

GDGT-0 is assumed to be produced by all major groups of Archaea except halophilic Archaea while GDGT-4 is mainly from Thaumarchaeota (Schouten et al., 2013). Thus, the ratio of GDGT-0/GDGT-4 is proposed to identify methanogen-derived isoGDGTs contributions: if this ratio is >2, it indicates a substantial methanogenic origin for GDGTs with anaerobic mineralisation processes (Blaga et al., 2009), as in Thaumarcheota this ratio between 0.2 and 2 is considered as temperature-dependent (Schouten et al., 2002). The GDGT-0/GDGT-4 ratio ranged from 0.2 to 4.4 in the catchment soils in Montcortés (Table 2). Whereas the ratios were between 13.0 and 16.7 in water column and sediment traps, and the mean was 21.8 in surface sediments, indicating that the abundant GDGT-0 could be produced *in situ* in the aquatic environment. Moreover, in the surface sediments of Lake Montcortés, the composition of Methanomicrobia and Bathyarchaeota occupied about 50% and 40% of the total Archaea based on 16S rDNA analysis, respectively (Compte-Port et al., 2017). Therefore, the isoGDGTs in the study lake can be mainly derived from Methanomicrobia and Bathyarchaeota. Methanogenic and methanotrophic archaea are believed to produce isoGDGTs in our volcanic lakes with a stratified anoxic bottom waters (Yao et al., 2019), which showed similar fractional abundance of isoGDGTs in our study lake. All the water column showed that GDGT-0 was the dominant compound, suggesting that other aerobic archaea communities than methanogenic Euryarchaeota can also contribute to isoGDGT production from the SPM and sediment trap in the water column at different depths (R^2>0.99, p<0.001).

4.2 Influence of temperature on TEX_{86}

Both pieces of evidence can be construed as a further indication that TEX_{86}-related isoGDGTs in the water column were predominantly derived from *in situ* production in the aquatic environments in our study. In fact, the average sediment TEX_{86} signal in Montcortés fits well in the global lake TEX_{86}-LST calibration (Powers et al., 2010; Tierney et al., 2010; Blaga et al., 2011) (Fig.5).

We collected SPM samples from the water column in the lake every month, *in situ* water temperatures in the lake cover a wide range from 5.4 °C to 22.2 °C (Fig. 2), which provides an opportunity to study how water temperature affects TEX_{86} values of SPM and the sediment traps in the water column. TEX_{86}-estimated temperatures (eq. 2) from the SPM at three depths in the water column of Lake Montcortés showed a remarkable similarity to each other and within the range of *in situ* CTD-measured temperatures (Fig. 2, 3). TEX_{86}-estimated temperatures ranged from 5.1 °C to 22.1 °C (mean 11.6±1.1 °C) at the surface water, from 5.3 °C to 19.1 °C (mean 12.7±0.9 °C) at the metalimnion and from 4.4 °C to 19.5 °C (mean

11.3±1.0 °C) at the deep water (Fig.3c). SPM at three depths of the water column confirms that TEX_{86} index reflects upper water temperatures compared with CTD-measured temperatures (Fig.2, 5.4~22.2 °C vs. 4.8~20.2 °C) with seasonal changes, which agreed with the observation in Lake Challa that Thaumarchaeota were present for isoGDGT production in the upper part of the water column and in Lake Kivu throughout the epipelagic waters (Sinninghe-Damsté et al., 2009; Llirós et al., 2010).

TEX_{86}-estimated temperatures from the SPM at all depths in the whole water column showed a marked seasonality which is close to the *in situ* CTD temperature in the metalimnion (Fig.3c, 3d). The minimum estimated TEX_{86} values at three depths occurred in different months, from December to February (Fig.3c). The average TEX_{86}-estimated temperature (11.9 °C) in the water column was lower than that in the sediment trap, indicating the other sources for isoGDGT productions that increase TEX_{86} values in the deep water. The estimated temperatures in the sediment trap and SPM in water column confirm that TEX_{86}-related Thaumarchaeota occur in the upper section of the water column and transported from the surface water to the sediment (Wakeham et al., 2003). The minimum (5.0 °C) and maximum (19.5 °C) of $TEX_{86(w)}$-temperatures were nearly the same as the measured metalimnion temperatures (4.8~20.2 °C).

While the minimum $TEX_{86(trap)}$-temperature (7.7 °C) was higher compared with the *in situ* minimal metalimnion temperature and the estimated TEX_{86} temperatures from the trap materials in winter (November-May) were generally higher than recorded CTD temperatures but colder in summer (June-October) (Fig.3d). Continuous presence of varves in Lake Montcortès shown by the sediment record of the last three millennia suggests that resuspension of bottom sediments can be excluded in a nearly meromictic lake (Corella et al., 2012; Vegas-Vilarrúbia et al., 2018). The increased GDGT-2/GDGT-3 ratio along depth is believed to reflect the deep-water Thaumarchaeota (Besseling et al., 2019).

Another issue that warrants explanation is the discrepancy in the TEX_{86}-estimated temperatures from settling particulates in the sediment trap with those in the SPM (Fig.3d). We have shown that allochthonous inputs are likely to be negligible in biasing the isoGDGT authochthonous signal. Alternatively, environmental factors other than temperature may exert an influence on GDGT distribution and drive the TEX_{86} signal. Thus, the seasonality in the water temperatures is also paralleled by changes in phytoplankton production in the lake, which might also depend on phytoplankton-derived resources, such as ammonium (Fietz et al., 2011), seasonal thermal stratification and DO variations in the lake. For example, high-nutrient/productivity sites may lead to cold TEX_{86} temperatures while lower ammonia oxidation rates may result in warm TEX_{86} temperatures (Huguet et al., 2007b; Lee et al., 2008). Thus, the colder TEX_{86} temperatures in summer might also be related to high nutrients in the lake. However, a study from Lake Malawi suggested that a second, deeper-dwelling Thaumarchaeotal population exists near the chemocline, which appears to produce isoGDGTs with much lower temperature signals than the surface-dwelling clade, but its imprint on sedimentary TEX_{86} is unknown (Meegan Kumar et al., 2019).

The good correspondence between $TEX_{86(w)}$-LST and $TEX_{86(trap)}$-LST indicates that both SPM and settling particles had the similar origins for isoGDGTs (Fig. 3d). There were positive relationships between lake surface temperature (LST) vs. $TEX_{86(w)}$ (R^2=0.47, p<0.05) and LST vs.$TEX_{86(trap)}$ (R^2=0.47, p<0.05) based on the calibration of Powers et al. (2010). $TEX_{86(trap)}$ value in April was higher compared to the samples collected in other months, which gives a warm bias of reconstructed temperatures. Without the sample from April, the correlations between $TEX_{86(trap)}$ and surface or metalimnion temperatures in the water column were more significant (R^2=0.61 and R^2=0.62, respectively, p<0.05). The factors that promoted the $TEX_{86(trap)}$-LST might be due to surrounding soil isoGDGT inputs that showed high TEX_{86} values. However, if true, the trend of $TEX_{86(trap)}$-LST towards higher values should have occurred primarily in rainstorm period. This observation also agreed with the phenomenon from high latitudinal North Pacific where a trend of underestimation of temperatures in shallow water depth sites but overestimation of SSTs in deep ocean sites was observed (Seki et al., 2014).

4.3 Influence of DO on TEX_{86}

During the study period, SPM TEX_{86}-temperatures overall mirror the upper water column temperatures, but there are discrepancies at different depths in Montcortés lake (Fig.3d). In fact, the relationships between SPM TEX_{86} and CTD temperatures in the whole water column are not distinctively linear (R^2=0.38, $p<0.05$, Fig.6a), and the data from the deepest interval (20-22 m, near the lake bottom) follow a different trend than those from the upper water column (i.e. at the deep chlorophyll maximum or above). If only the SPM TEX_{86} data are considered for the upper water column (surface intervals), their relationship with CTD measured temperatures is linear (R^2=0.59, $p<0.05$, Fig.6a; two outliers were removed with TEX_{86}>0.6; Fig.6a). We note that the same data do not show a correlation (R^2=0) with DO content in the water column at the same depth (Fig.6b). In contrast, SPM TEX_{86} data from the deepest interval showed a significant negative relationship with DO content (R^2=0.78, $p<0.05$; Fig.6d), with a higher regression coefficient than with water temperature (R^2=0.53, $p<0.05$) (Fig.6c), which suggests DO played an important role for TEX_{86}.

A negative relationship between TEX_{86} and DO content has been reported in laboratory cultures of marine Thaumarchaeota isolates (Hurley et al., 2016), and DO content was also claimed to have a primary role in controlling TEX_{86} values in SPM from a stratified Norwegian coastal lake (Zhang et al., 2016). In our study, TEX_{86} values from the deeper water column reflect contributions from the upper and the deeper water column, and both anaerobic and aerobic Archaea. For instance, the ratios of GDGT-0/GDGT-4 were always >2, indicating a substantial methanogenic origin for isoGDGTs (Blaga et al., 2009). The seasonal changes in O_2 and S^{2-} concentration in the bottom water might trigger an important switch in the archaeal community favourable for producing methanogen-derived isoGDGTs. In fact, methanogenic archaeal groups have been identified in Montcortés sediments (Compte-Port et al., 2017), but whether or not they contribute significantly to the isoGDGT stratigraphic record needs to be established. The little warm bias from water column to the sediment trap and surface sediments confirms that decreased DO concentration can result in higher TEX_{86} values, then warm-biased LST (Qin et al., 2015; Zhang et al., 2016).

4.4 Implication for the TEX_{86} index used in paleotemperature

As noted earlier, the surface sediment TEX_{86} value (15.7 °C) fits well with the global regression of Powers et al. (2010), and is similar to the mean annual average lake surface temperature (14.6 °C). Moreover, the sedimentary value is also similar to those of the mean annual values of $TEX_{86(w)}$ and $TEX_{86(trap)}$ which also consequently fit the global regression of TEX_{86} vs LST (R^2=0.89, $p<0.01$) (Fig.5), suggesting that this proxy can be applied with confidence. Our findings in Lake Montcortés agree well with other studies showing that TEX_{86} temperatures reflect a subsurface temperature where thermocline is well developed (Huguet et al., 2007a; Lee et al., 2008; Lopes dos Santos et al., 2010; Rommerskirchen et al., 2011; McClymont et al., 2012). Whereas the findings also support our interpretation that the warm biased TEX_{86} temperatures can be attributed to the contributions of isoGDGTs synthesized within the oxygen-depleted zone, which differ by an increase in the relative abundance of GDGT-2 and GDGT-3 from the isoGDGT pools formed in surface waters, indicating a different physicochemical response of thaumarcheotal communities in oxygen-depleted waters can influence the TEX_{86} thermometry, resulting in a seasonal warm bias in estimated-LST during the mixing period. This underlines that water column oxygenation as an environmental factor needs to be considered in paleoclimate studies when the TEX_{86} calibration is carried out in lakes with mixed or stratified water column.

Therefore, our data from the study of SPM, sediment trap and surface sediments suggest that the sedimentary TEX_{86} has potential for evaluating paleoclimate changes in an oligotrophic lake. Even though a dominance of GDGT-0 is present in all lake samples, the TEX_{86} values are still significantly temperature-controlled. While decreased DO concentration in the deep water, especially in the surface sediment yields TEX_{86} to be slightly warm signal.

5. Conclusions

The data presented here reveals that the isoGDGT concentrations in the SPM and sediment trap showed a marked seasonal variation and the highest values in summer and autumn in the upper water column. The production of isoGDGTs occurs throughout the year but it was more abundant in summer and autumn, which might be controlled by the phytoplankton occurrence. The data have highlighted the environmental factors such as temperature and DO exert effects on isoGDGT-based proxies. In particular, the isoGDGT proxy TEX_{86} in SPM and sediment trap showed a marked seasonal variability which matched the temperatures of the upper water column and fit the published global lake trend between TEX_{86} and mean annual lake surface temperature (LST). Subsurface rather than surface temperatures appear to be the most important factor in determining water column TEX_{86} signals. In the hypolimnion, we found a relationship between TEX_{86} and DO. This confirms with field data a previous claim in culture experiments (Qin et al., 2015) and Norwegian coastal lake (Zhang et al., 2016) that the sedimentary TEX_{86}-LST signal may be confounded by DO, which makes TEX_{86} values increased, thus results in warmer estimated LST temperature. However, this influence is too slight to be neglected. Our results herein help to span an important observational gap related to lake temperature reconstructions by isoGDGTs. Lacustrine isoGDGTs show potential to be applied to reconstruct paleoclimate even though there are some interferences. Future studies should focus on high-resolution lake sedimentary records that would help solve whether TEX_{86} can be available on different time scales.

ACKNOWLEDGMENTS

This work was supported by Spanish Ministry of Research (projects TETRACLIM ref. CGL2010-15000, Montcortés-500 ref. CGL-2012-33665; and Maria de Maeztu award MDM-2015-0552), and a studentship to M.C, from the China Scholarship Council (CSC). Fieldwork was performed with the collaboration of E. Safont, N. Cañellas and J. Gomà. Fieldwork permits were provided by the Territorial Service of the department of Agriculture, Livestock, Fishing and Natural Environment of Catalunya. Meteorological data in Pobla de Segur were provided by J. Sigró. We also thank N. Moraleda, C. Huguet and the UAB Analytical Service for technical support.

Author contributions: A.R.-M. designed the project and funded the research; M.C. planned the research, performed the biomarker analysis and processed the data; T.V.-V. and V.R. designed the sediment trap and organized its deployment and retrieval; M.C., A.R.-M., P. R.-R., T.V.-V., M.C.T. provided samples and data; M.C and A.R.-M. wrote the manuscript with contributions from all other co-authors.

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Figure capitals

Fig. 1 A, The location of the study area; B, the sampling site of sediment trap (the yellow triangle)

Fig. 2 Meteorological data from September 2013 to November 2014 from a weather station at La Pobla de Segur for monthly mean values in (a) monthly accumulated precipitation (grey bar), (b) mean monthly air temperatures (MMAT, black line), and (c) wind velocity (black line). Water column data from Lake Montcortés were obtained by means of a CTD probe (Trapote and Vega, unpublished data) once per month. In here we show CTD values at the depths where water samples were taken once per month; blue, orange and green crosses stand for samples from the surface (~0.5m), metalimnion (5-17m) and the bottom (~20m) for (b) water temperature and for (c) dissolved oxygen (DO). Bulk sediment mass fluxes in the sediment trap in Lake Montcortés are shown as dark grey bars in the upper most graph (more details about the limnological variabes from 2013-2015 see Trapote et al., (2018).

Fig. 3 (a) Flux of isoGDGTs in the sediment trap; (b) isoGDGT concentration of SPM in the water column; (c) TEX_{86}-derived lake temperature from SPM at three depths of water column; (d) Comparison of CTD-measured temperature at DCM (5-12 m depth) and reconstructed temperatures from SPM in the water column and sediment trap from October 2013 to November 2014

Fig. 4 Fractional abundance of isoGDGTs in (a) soils surrounding the Lake Montcortès (Ms1-Ms6, see Cao et al., 2018), (b) in SPM at three depths (0 m, 5-17 m, 20-22 m), the sediment trap and surface sediment (0-2 cm).

Fig. 5 The relationship of global lake surface temperature and TEX_{86} (Powers et al., 2010; Tierney et al., 2010; Blaga et al., 2011)

Fig. 6 Linear regression and correlation of TEX_{86} vs temperature and DO vs TEX_{86} in Lake Montcortès. (a) TEX_{86} and SPM Temperature at three depths in the water column; (b) DO and SPM TEX_{86} at three depths in the water column (blue, orange and green diamonds stand for SPM samples from 0m, 5-17m and 20-22m) ; (c) The relationship between SPM TEX_{86} and CTD temperatures in situ in the hypolimnion; (d) DO and SPM TEX_{86} in the hypolimnion (the samples collected when DO is depleted in the hypolimnion were removed at c and d)

Fig. S1 Chemical structures of the isoprenoidal GDGTs

Tables

Table 1 Concentrations of isoGDGTs, TEX_{86}, and reconstructed temperatures for SPM (suspended particulate matter) at three depths (~0.5m, ~5-17m, ~20m) from October 2013 to November 2014

0 m	**isoGDGT** μg·$^{-1}$L	**GDGT-0/ GDGT-4**	**TEX_{86}**	**LST** ºC
Dec-13	0.08	17.5	0.50	4.9
Jan-14	0.71	9.3	0.55	16.5
Feb-14	0.51	18.3	0.35	5.1
Mar-14	0.19	22.2	0.37	6.4
Apr-14	0.11	10.0	0.37	6.3
May-14	0.19	11.1	0.43	22.8
Jun-14	0.32	33.3	0.48	12.8
Jul-14	0.77	16.3	0.65	22.1
Aug-14	1.70	17.2	0.47	11.8
Sep-14	1.46	18.2	0.48	12.6
Oct-14	1.81	16.8	0.48	12.4
Nov-14	0.76	9.1	0.48	12.3
Oct-14	1.12	13.5	0.45	10.7
Nov-14	2.29	20.5	0.44	10.2
5-12 m				
Oct-13	0.22	13.9	0.53	15.2
Nov-13	0.67	12.3	0.45	11.0
Dec-13	0.55	11.7	0.47	11.7
Jan-14	0.21	18.8	0.35	5.3
Feb-14	0.15	20.8	0.39	7.3
Mar-14	0.20	12.8	0.48	12.7
Apr-14	0.13	8.2	0.43	9.8
May-14	0.19	9.4	0.50	13.7
Jun-14	0.89	11.9	0.52	14.6
Jul-14	0.77	11.7	0.48	12.6
Aug-14	2.20	15.1	0.49	13.1
Sep-14	1.12	12.8	0.54	16.1
Oct-14	0.52	9.0	0.53	15.4
Nov-14	1.27	13.9	0.60	19.1
20-22 m				
Oct-13	0.88	17.7	0.47	11.8
Nov-13	0.66	15.6	0.50	13.5
Dec-13	0.47	15.3	0.51	14.0
Jan-14	0.36	13.6	0.46	11.6
Feb-14	0.28	17.6	0.33	4.4
Mar-14	0.21	16.9	0.42	9.2
Apr-14	0.15	17.6	0.39	7.5
May-14	0.16	9.9	0.47	12.0
Jun-14	0.26	16.3	0.46	11.5
Jul-14	0.42	19.1	0.40	8.0
Aug-14	0.63	16.6	0.42	9.1
Sep-14	1.12	16.4	0.61	19.5
Oct-14	1.04	16.9	0.49	12.8
Nov-14	0.76	19.3	0.48	12.5

Table 2 Concentrations of isoGDGTs, TEX_{86}, and reconstructed temperatures for sediment trap from October 2013 to November 2014, and surface sediment

Sampling types	isoGDGT	GDGT-0/GDGT-4	TEX_{86}	LST
Sediment trap	$\mu g \cdot m^{-2} \cdot day^{-1}$			ºC
Oct-13	0.66	15.2	0.52	14.5
Nov-13	0.78	13.4	0.51	14.2
Dec-13	1.06	13.1	0.50	13.4
Jan-14	0.37	11.8	0.45	10.9
Feb-14	0.15	13.5	0.39	7.7
Mar-14	0.12	15.1	0.47	12.1
Apr-14	0.22	9.6	0.62	20.3
May-14	0.30	9.2	0.57	17.7
Jun-14	0.32	15.3	0.56	17.0
Jul-14	0.67	13.2	0.53	15.2
Ago-14	0.83	16.3	0.53	15.2
Sep-14	0.94	16.8	0.56	16.9
Oct-14	0.69	15.4	0.54	15.9
Nov-14	0.63	14.5	0.51	14.1
Dic-14	1.08	19.1	0.53	15.3
Feb-15	0.43	17.5	0.39	7.8
Mar-15	0.15	19.6	0.44	10.3
Apr-15	0.28	15.7	0.63	20.8
	isoGDGT	GDGT-0/GDGT-4	TEX_{86}	LST
Surface sediments	μg/g TOC			ºC
Feb-13	7,3	22.7	0.54	15.7
Soils				
Ms1	1.6	1.0	-	-
Ms2	0.1	1.6	0.66	-
Ms3	2.0	1.0	0.75	-
Ms4	0.1	1.1	0.77	-
Ms5	0.4	0.9	0.70	-
Ms6	1.0	3.5	-	-