



Decoupling of water and air temperature in winter causes warm season bias of lacustrine brGDGTs temperature estimates

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15 Abstract

It has been frequently found that lacustrine brGDGTs-derived temperatures are warm season biased relative to measured annual mean air temperature (AT) in the mid to high latitudes, the mechanism of which, however, is not very clear. Here, we investigated the brGDGTs from catchment soils, and suspended particulate matter (SPM) and surface sediments in the Gonghai Lake in north China to explore this question. Our results showed that the brGDGTs distribution in sediments resembled that in 20 the SPM but differed from the surrounding soils, suggesting a substantial aquatic origin of the brGDGTs in the lake. Therefore, established lake-specific calibrations were applied to estimate local mean annual AT. As usual, the estimates were significantly higher than the measured mean annual AT. However, they were similar to, and thus actually reflected, the mean annual lake water temperature (LWT). Interestingly, the mean annual LWT is close to the measured mean warm season AT, hence suggesting 25 that the apparent warm season bias of lacustrine brGDGTs-derived temperatures could be caused by the discrepancy between AT and LWT. In our study region, ice forms at the lake surface during winter, leading to isolation of the underlying lake water from air and hence higher LWT than AT, while LWT follows AT during warm seasons when ice disappears. Therefore, we believe what lacustrine brGDGTs actually reflected is the mean annual LWT, which is higher than the mean annual AT in our study 30 location. Since the decoupling between LWT and AT in winter due to ice formation is a universal physical phenomenon in the mid to high latitudes, we propose this phenomenon could be also the reason





for the widely observed warm season bias of brGDGTs-derived temperatures in other lakes, especially the shallow lakes.

35 Keywords: lake sediments, aquatic brGDGTs, temperature proxy, seasonality, ice formation

1 Introduction

The branched glycerol dialkyl glycerol tetraethers (brGDGTs), including 0–2 cyclopentyl moieties (a–c) and four to six methyl groups (I–III) (Weijers et al., 2007a), are components of the cell membranes of microorganisms ubiquitously found in marine and continental environments and sensitive to ambient environmental conditions (Sinninghe Damsté et al., 2000; Weijers et al., 2006a; Schouten et al., 2013). The relative amount of methyl groups and cyclopentyl moieties (expressed as MBT/CBT or MBT'/CBT) in soil brGDGTs, has been proposed to reflect mean annual air temperature (AT) (Weijers et al., 2007a; Peterse et al., 2012). Accordingly, mean annual AT can be estimated by the MBT/CBT (or MBT'/CBT) indices calibrated using globally distributed surface soils (Weijers et al., 2007a; Peterse et al., 2007a; Peterse et al., 2012).

al., 2012), which have been widely used for continental AT reconstruction (Weijers et al., 2007b; Niemann et al., 2012).

BrGDGTs in lake environments were initially thought to be derived from soil input (Hopmans et al., 2004; Blaga et al., 2009), allowing the mean annual AT to be reconstructed from lake sediments.

50 However, when the soil-based calibrations are applied to the lake materials, the estimated temperatures



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are significantly lower than local actual AT (Tierney and Russell, 2009; Tierney et al., 2010; Blaga et al., 2010; Loomis et al., 2011, 2012; Pearson et al., 2011; Sun et al., 2011; Russell et al., 2018), suggesting an intricate brGDGTs response to ambient temperature in aquatic environments. Later, more and more studies reveal that brGDGTs could be produced in situ in lake environments, which differ significantly from soil derived brGDGTs in molecular distributions (Wang et al., 2012; Loomis et al., 2014; Naeher et al., 2014; Hu et al., 2015; Cao et al., 2017) and stable carbon isotope composition (Weber et al., 2015, 2018). The findings of intact polar lipid of brGDGTs, indicative of fresh microbial products, in lake water suspended particulate matter (SPM) and surface sediments (Tierney et al., 2012; Schoon et al., 2013; Buckles et al., 2014a; Qian et al., 2019) further confirm the in-situ production of brGDGTs. Nevertheless, the composition of brGDGTs in lake surface sediments has been found to be still strongly correlated with AT. Subsequently, quantitative lacustrine-specific calibrations have been established at regional and global scales (Tierney et al., 2010; Pearson et al., 2011; Sun et al., 2011; Loomis et al., 2012; Shanahan et al., 2013; Foster et al., 2016; Dang et al., 2018; Russell et al., 2018), which have been widely used for AT reconstruction. These lacustrine-specific calibrations may reflect mean annual AT well in low-latitude regions (Tierney et al., 2010; Loomis et al., 2012), such as in the Lake Huguangyan (21°09′ N, 110°17′ E) in south China (Hu et al., 2015), Lake Donghu (30°54′ N, 114°41′ E) in central China (Qian et al., 2019) and Lake Towuli (2.5° S, 121° E) on the island of Sulawesi (Tierney and Russell, 2009). However, they usually yield estimates biased to the warm/summer seasons in mid-





and high-latitude regions (Shanahan et al., 2013; Foster et al., 2016; Dang et al., 2018), such as in Lake
Qinghai (36°54′ N, 100°01′ E) in the northeastern Tibetan Plateau (Wang et al., 2012), in Lower King
pond (44°25′ N, 72°26′ W) in temperate northern Vermont, U.S.A. (Loomis et al., 2014), and in the
Arctic lakes (Peterse et al., 2014). The warm biased temperature estimates in the mid- and high-latitude
lakes have been postulated to be caused by the higher brGDGTs production during warm seasons (e.g.,
Pearson et al., 2011; Shanahan et al., 2013).

BrGDGTs-producing bacteria in soils could be metabolically active, hence producing abundant brGDGTs in warm and humid season, but suppressed in cold and/or dry environments (Deng et al., 2016; De Jonge et al., 2014; Naafs et al., 2017). However, it is presently unclear whether the brGDGTs in lacustrine sediments are mainly produced during the warm season. Investigations on lake water SPM reveal higher concentration of brGDGTs in the water column may occur in different seasons, e.g., in winter in Lake Lucerne in central Switzerland (Blaga et al., 2011), Lake Challa in tropical Africa (Buckles et al., 2014a) and Lake Huanguangyan in subtropical southern China (Hu et al., 2016), in spring and autumn in Lower King Pond in temperate northern Vermont, U.S.A. (Loomis et al., 2014), and in warm season in Lake Donghu in central China (Qian et al., 2019). Moreover, the contribution of the aquatic brGDGTs to the sediments is quantitatively unknown, and likely minor considering that brGDGTs producers favor anoxic conditions (Weijers et al., 2006b; Weber et al., 2018), which may discount the application of SPM-derived findings to the sedimentary brGDGTs.





In fact, brGDGTs-based temperature indices should directly record lake water temperature (LWT), rather than AT, if the brGDGTs in lake sediments solely or mainly sourced from the lake environments (Tierney et al., 2010; Loomis et al., 2014). So, the mean annual AT estimate based on lake sedimentary 90 brGDGTs is valid only when LWT is tightly coupled with AT. However, the relationship between LWT and AT is potentially complex in cold regions, as well as in deep lakes, and the coupling between the two is not always the case, which would hamper the application of brGDGTs for temperature estimates (Pearson et al., 2011; Loomis et al., 2014; Weber et al., 2018). In deep lakes, bottom water temperature usually decouples with AT, together with the predominant production of brGDGTs in deep water and sediments, causing weak correlations between brGDGTs-derived temperature and AT (Weber et al., 95 2018). For shallow lakes, LWT does not always follow AT either, specifically in winter when AT is below freezing, in cold regions, as has been shown in the Lower King pond (Loomis et al., 2014). However, the decoupling between LWT and AT has not been recognized as a key mechanism for the warm bias of brGDGT-derived temperatures observed widely in the mid- and high-latitude lakes, and 100 seasonal production or deposition of brGDGTs is usually invoked as a cause (e.g., Pearson et al., 2011; Shanahan et al., 2013; Loomis et al., 2014). Here, we hypothesized that the decoupling between LWT and AT in mid- and high-latitude shallow lakes, rather than the warm season production, could have caused the frequently observed warmer temperature estimates from the lacustrine brGDGTs. To test this hypothesis, we investigated the Gonghai Lake (a shallow alpine lake) in north China by collecting SPM





and surface sediments in the lake and soils in its catchment in a hot summer and a cold winter. We analyzed the composition distribution of brGDGTs in these materials to determine the sources of brGDGTs in the lake and further to discuss the possible reasons for the seasonality of brGDGTs-estimated temperatures.

110 2 Materials and methods

2.1 Gonghai Lake

The Gonghai Lake [38°54', 112°14', ca. 1860 m above sea level (a.s.l.); Fig. 1a and 1b] is located on a planation surface of the watershed between the Sang-kan River and the Fenhe River at the northeast margin of the Chinese Loess Plateau. The location is close to the northern boundary of the modern East Asian summer monsoon (EASM, Chen et al., 2008; Fig. 1a). The modern local climate is controlled mainly by the East Asian monsoon system, with a relatively warm and humid summer resulting from the prevailing EASM from the south and east, and a relatively cold and arid winter under the prevailing East Asian winter monsoon (EAWM) from the north and west (Chen et al., 2013, 2015; Rao et al., 2016). The mean annual precipitation is ca. 482 mm, concentrating (75%) between July and

September (Chen et al., 2013). Its total surface area is ca. 0.36 km² and the maximum water depth is ca. 10 m. There is no water column stratification whether summer or winter. Based on a nearby weather station, the measured mean annual AT is 4.3 °C for the past 30 years. From November to March, ice





forms in the lake surface, and LWT under ice remains stable at ca. 4 °C, which is significantly higher than AT that is much below the freezing point (Fig. 1c). From April to October, ice disappears and LWT follows AT closely, demonstrating a coupling between them (Fig. 1c). The vegetation type of the planation surface belongs to transitional forest-steppe, dominated by *Larix principis-rupprechtii*, *Pinus tabulaeformis* and *Populus davidiana* forest, *Hippophae rhamnoides* scrub, *Bothriochloa ischaemum* grassland and *Carex spp.* (Chen et al., 2013; Shen et al., 2018).

2.2 Sampling

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In September 2017, five surface soils samples in the catchment and five surface sediment samples in Gonghai Lake were collected (Fig. 1b). At each soil sample site, we collected 5–6 subsamples (top 0–2 cm) within an area of ca. 100 m² with contrasting micro-topography or plant cover and then mixed to represent a single sample. To avoid possible human disturbance, the soil and sediment sampling sites were distant from roads and buildings. All samples collected in the field were stored in a refrigerated container during transportation and then freeze-dried for >48 h in the laboratory. Details of all the sampling sites, including locations, sample depth and vegetation type, are listed in Table 1.

In addition, we also collected two batches of SPM samples at water depth of 1 m, 3 m, 6 m and 8 m by filtering 50 L water through a 0.7 μ m Whatman GF/F filter on site in September 2017 and January 2018, respectively. SPM samples were also stored in the refrigerated container during transportation and then freeze-dried for >48 h in the laboratory. At the same time of SPM sampling, we measured water





column parameters in the lake using an YSI water quality profiler.

2.3 Sample treatment and GDGT analysis

Soil and sediment samples were freeze-dried, homogenized at room temperature, and accurately weighed. Each filter with SPM attached was freeze-dried and then cut into small pieces using sterilized scissors. Each sample was placed in a 50 mL tube and then ultra-sonicated successively with 145 dichloromethane/methanol (1:1, v/v) four times. After centrifugation and combined all the extracts of a sample, an internal standard consisting of synthesized C46 GDGT was added with a known amount (Huguet et al., 2006). Subsequently, the total extracts were concentrated using a vacuum rotary evaporator. The nonpolar and polar components in the extracts were separated via silica gel column chromatography, using pure *n*-hexane and dichloromethane/methanol (1:1, v/v), respectively. The polar 150 components containing GDGTs was dried in a gentle flow of N₂, dissolved in *n*-hexane/ethyl acetate (EtOA) (84:16, v/v) and filtered through a 0.45 µm polytetrafluoroethylene filter before instrumental analysis. We performed GDGTs analysis by high performance liquid chromatography-atmospheric pressure chemical ionization-mass spectrometry (HPLC-APCI-MS; Agilent 1200 series 6460 QQQ). Following the method of Yang H et al. (2015), the separation of 5- and 6-methyl brGDGTs was 155 achieved using two silica columns in tandem (150 mm \times 2.1 mm, 1.9 μ m, Thermo Finnigan; U.S.A.) maintained at 40 °C. The following elution gradient was used: 84/16 A/B to 82/18 A/B from 5 to 65 min and then to 100% B in 21 min, followed by 100% B for 4 min to wash the column and then back to





84/16 A/B to equilibrate it for 30 min. The flow rate was at a constant 0.2 ml/min throughout. BrGDGTs

were ionized and detected with single ion monitoring (SIM) at m/z 1050, 1048, 1046, 1036, 1034, 1032, 1022, 1020, 1018 and 744. The brGDGTs were quantified from comparing retention time and peak areas with the C_{46} GDGT internal standard.

2.4 Calculation of GDGT-related Proxies

The MBT'_{5ME} and MBT'_{6ME} index are calculated following Eq. (1) and (2) as in De Jonge et al.

165 (2014):

$$MBT'_{5ME} = (Ia+Ib+Ic)/(Ia+Ib+Ic+IIa+IIb+IIc+IIIa)$$
(1)

$$MBT'_{6ME} = (Ia+Ib+Ic)/(Ia+Ib+Ic+IIa'+IIb'+IIc'+IIIa')$$
(2);

The isomer ratio (IR) of 6-methyl is calculated as in De Jonge et al. (2014). The $\Sigma IIIa/\Sigma IIa$ ratio is calculated and modified from Xiao et al. (2016). The weighted average number of ring moieties

170 (#Rings_{tetra}, #Rings_{penta 5ME}, #Rings_{penta 6ME}), are following Sinninghe Damsté (2016)





$IR_{6ME} = (IIa'+IIb'+IIc'+IIIa'+IIIb'+IIIc')/ (IIa+IIa'+IIb+IIb'+IIc+IIc'+IIIa+IIIa'+IIIb+$ IIIb'+IIIc+IIIc') (3) $\Sigma IIIa/\Sigma IIa = (IIIa+IIIa'+IIIa')/ (IIa+IIa') (4)$ $\# Rings_{tetra} = (Ic*2+Ib)/ (Ia+Ib+Ic) (5)$

175 $\#\text{Rings}_{\text{penta 5ME}} = (\text{IIc}*2+\text{IIb})/(\text{IIa}+\text{IIb}+\text{IIc})$ (6)

$$#Rings_{penta 6ME} = (IIc'*2+IIb')/(IIa'+IIb'+IIc')$$
(7);

The Roman numerals represent different brGDGTs homologues referred to Yang et al. (2015) and Weber et al. (2015).

In this study, we used two silica columns in tandem and successfully separated 5- and 6-methyl

brGDGTs. However, many previous brGDGTs studies on lake materials used one cyano column, which cannot separate 5- and 6-methyl brGDGTs (e.g., Wang et al., 2012; Loomis et al., 2014; Hu et al., 2015, 2016; Cao et al., 2017). In order to facilitate comparison with previous studies, we reanalyzed the published brGDGTs data in the Gonghai Lake (Cao et al., 2017). For temperature estimations, we listed the Eqs. (8–16) used in this study in Table 2.

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3 Results

3.1 Seasonal changes in environmental parameters

The AT in our study area ranged from -12.2 to 21.6 °C, below freezing in winter (November to





February) and at 4.3 °C for the mean in the year 2018 (Fig. 1c). Surface LWT ranged from 3.4 to 21.9 °C (average 10.6 °C), and remained stable at ca. 4 °C in winter (Fig. 1c). In September, water 190 column temperature ranged from 16.9 to 17.8 °C, exhibiting a gradual and slight decrease with depth (Fig. 2). In January, the lake surface water was frozen and LWTs under ice were 4 °C at all depths (Fig. 2).

3.2 Concentration and distribution of brGDGTs

- BrGDGTs were detected in all samples, and their total concentration ranged between 15–70 ng/g 195 dry weight (dw) in surface soils from Gonghai catchment, 33-692 ng/g dw in surface sediments, 5-10 ng/l in September and 3-8 ng/l in January for SPM (Table 1 and Fig. 2). The average content of brGDGTs in lake surface sediments (291 ng/g dw) was higher than in surface soils (31 ng/g dw). In SPM, there was no significant difference in average concentration of brGDGTs in water column between September and January (t = 1.2, p = 0.26). 200

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The brGDGTs in soils, sediments and SPM were dominated by brGDGTs II and III series, with acyclic compounds dominant in every series (Fig. 3a). In comparison, the mean $\Sigma IIIa/\Sigma IIa$ ratio value in sediments (1.30) was higher than in SPM (0.99) and soils (0.70). In addition, 6-methyl brGDGTs dominated over 5-methyl brGDGTs in soils, exhibiting mean IR_{6ME} of 0.62; whereas the two isomers were similar in contents in sediments (IR_{6ME} = 0.51) and SPM (IR_{6ME} = $0.47 \sim 0.48$) (Fig. 3a). Notably, the compound IIIa", which was regarded typical for lacustrine brGDGTs (Weber et al., 2015), was





also identified in the Gonghai Lake sediments and SPM, but not found in catchment soils (Fig. 3a).

3.3 Cyclisation ratio, methylation index of brGDGTs

The #Rings_{tetra} values varied from 0.26 to 0.45 (average 0.36) in surface soils of the lake

The MBT'_{5ME} values varied from 0.31 to 0.36 (average 0.35) in surface soils of the lake

210 catchment, 0.37–0.43 (average 0.40) in September and 0.39–0.42 (average 0.40) in January in SPM, and 0.45–0.47 (average 0.45) in surface sediments (Fig. 3b). The #Rings_{penta 5ME} showed the same increasing trend as #Rings_{tetra} from soils to SPM and then to sediments (Fig. 3b). In contrast, #Rings_{penta 6ME} in soils was similar to that in sediments and SPM (Fig. 3b).

catchment, 0.23–0.29 (average 0.26) in surface sediments, 0.23–0.28 (average 0.26) in September and 0.24–0.26 (average 0.25) in January in SPM (Fig. 3b). The MBT'_{6ME} values varied from 0.20 to 0.33 (average 0.25) in surface soils of the lake catchment, 0.22–0.27 (average 0.25) in surface sediments, 0.24–0.32 (average 0.28) in September and 0.26–0.28 (average 0.27) in January in SPM (Fig. 3b).

220 4 Discussions

4.1 Different sources of lacustrine brGDGTs from surrounding soils

Although brGDGTs have a strong potential to record temperature in lacustrine regions (Tierney et al., 2010; Pearson et al., 2011; Sun et al., 2011; Loomis et al., 2012; Dang et al., 2018; Russell et al., 2018), the sources of brGDGTs in lake sediments should be carefully identified. There are two





- 225 potential sources, including allochthonous input from soil and autochthonous production in lake water or surface sediments, which can be distinguished by comparison of brGDGTs concentration and compositional distribution between surface sediments and soils (Tierney and Russell, 2009; Loomis et al., 2011; Wang et al., 2012; Hu et al., 2015; Sinninghe Damsté, 2016).
- In the Gonghai Lake, the average content of brGDGTs in surface sediments was significantly 230 higher than that in surface soils (Table 1), suggesting a possible autochthonous contribution, even though soil brGDGTs input cannot be ignored. Moreover, the composition distribution of brGDGTs in surface sediments was similar to SPM, but quite different from soils (Fig. 3a). Several lines of evidence could suggest a substantial in situ production of brGDGTs in the Gonghai Lake. (I) The presence of IIIa" in the Gonghai Lake sediments (Fig. 3a), which has been only identified in lake sediments but not found in catchment soils previously (Weber et al., 2015), could be a direct evidence 235 of in situ production in lake. (II) The values of $\Sigma IIIa / \Sigma IIa$ in sediments was higher than 0.92, which was regarded as the evidence of aquatic production as previous reported (Xiao et al., 2016; Martin et al., 2019; Zhang et al., 2020). In the Gonghai Lake, $\Sigma IIIa / \Sigma IIa$ was higher than 0.92, and significantly higher than that in catchments (Fig. 3a). (III) The average values of IR_{6ME} in surface sediments is significantly lower than in catchment soils (Fig. 3a), suggesting at least some of 5-methyl brGDGTs 240 in lake sediments were produced in situ. (IV) The cyclisation ratio of brGDGTs has been also used to distinguish the aquatic production, although applied to marine sediments, from soil input (Sinninghe





Damsté, 2016). In the Gonghai Lake, #Rings_{tetra} and #Rings_{penta 5ME} were clearly higher in sediments than in catchment soils, although #Rings_{penta 6ME} in sediments was similar to that in catchment soils (Fig. 3b).

4.2 Soil brGDGTs reflect mean annual AT

Based on the new global soil calibration of Eq. (9) excluding 6-methyl brGDGTs, the brGDGTs-derived AT in the Gonghai catchment soils ranged from 1.18-2.75 °C (average 2.33 ± 0.65 ; Fig. 4a). Considering the ± 4.8 °C uncertainty of the calibration, thus estimated temperature is close to

250 the mean annual AT of 4.3 °C, thereby reflecting mean annual AT in our study lake catchment.

For some lakes, soil brGDGTs input may be significant and predominant over aquatic production, yielding similar brGDGTs composition distributions between lake sediments and surrounding soils. In such cases, soil calibrations could be still applicable to lake sediments for AT reconstruction (Niemann et al., 2012; Li et al., 2017; Ning et al., 2019; Tian et al., 2019). In our results, using soil-derived calibration of Eq. (9), the estimated temperatures from surface sediments (-0.50 ± 0.78 °C; Fig. 4a) and SPM (-0.55 ± 0.52 °C; Fig. 4a) were much lower than those from surface soils (2.33 ± 0.65 °C; Fig. 4a). Similarly, temperature underestimation has been widely reported in global lakes (e.g., Tierney et al., 2010; Loomis et al., 2012; Pearson et al., 2011; Russell et al., 2018), which is likely associated with in situ production of brGDGTs in the lakes.





4.3 Lacustrine brGDGTs reflect warm season AT

The above evidence suggests that the application of temperature calibrations based on soil brGDGTs (by De Jonge et al. (2014)) to lake sediments is risky. Therefore, lake-specific temperature calibrations, although not differentiated quantitatively the relative contributions of aquatic vs. soil-derived brGDGTs, are likely to be more appropriate than soil calibrations. In fact, in situ aquatic production of brGDGTs has been noticed by numerous authors in their works for making lake-specific calibrations (Tierney et al., 2010; Pearson et al., 2011; Sun et al., 2011; Loomis et al., 2012; Dang et al., 2018; Russell et al., 2018). Therefore, we preferred application of lake-derived calibrations to our lacustrine brGDGTs.

In September, the values of MBT'_{5ME} and MBT'_{6ME} in SPM gradually decreased with depth, similar to the measured water temperature profile in the water column (Fig. 2). In January, the values of MBT'_{5ME} and MBT'_{6ME} in SPM remained constant at different depths, also similar to the measured water temperature profile in water column (Fig. 2). In addition, the values of MBT'_{5ME} and MBT'_{6ME} in SPM remained constant at different depths, also similar to the measured water temperature profile in water column (Fig. 2). In addition, the values of MBT'_{5ME} and MBT'_{6ME} in SPM in September were higher than in January, corresponding to the warmer water temperature in September (Table 1). This suggests that brGDGTs in SPM can record lake water temperature changes, as previous reported (Loomis et al., 2014; Hu et al., 2016; Zhang et al., 2016; Qian et al., 2019). Our results suggest both MBT'_{5ME} and MBT'_{6ME} could work well to indicate temperature change. However, air temperature has been found to be correlated well with 5-methyl brGDGTs in Africa lakes (Russell





et al., 2018), but with 6-methyl brGDGTs in East Asian lakes (Dang et al., 2018; Qian et al., 2019), which remains elusive.

Although the MBT'_{5ME} and MBT'_{6ME} in SPM in the lake may reflect temperature changes in the water column, the difference of brGDGTs-derived temperatures based on lake-specific calibrations between September and January (0.3 °C) were much smaller than the measured difference (~13 °C), independent of the calibration of (14), (15) or (16). (Tables 1 and 2). We suspected that the reduced seasonal difference in the estimated temperatures in SPM could have resulted from a long residence 285 time of SPM, although not exactly known, in the water column, which may imprint multi-season brGDGTs signals on the SPM, as previous reported in Lower King pond (Loomis et al., 2014). Such a scenario may lead to more "fossil" brGDGTs in SPM than those produced within a specific season or month, as evidenced by an observation showing that only a small proportion of intact polar lipid of brGDGTs, indicative of fresh brGDGTs, was detected in total brGDGTs in SPM in a shallow lake 290 (Qian et al., 2019). Sediment resuspension, which may admix to the SPM the sedimentary brGDGTs that are both in-situ produced and deposited from the water column, could be also important for smoothing the temperature signal in SPM due to its shallow water depth (<10 m) and hence prone to be dynamic, as evidenced by the lack of water column temperature stratification in the whole year 295 (Fig. 2). Both residence of "fossil" brGDGTs and sediment resuspension in SPM may cause the reduced seasonal difference in the estimated temperatures in SPM of Gonghai Lake. Besides, the





indices such as IIIa/IIa, IR_{6ME} , $\#Rings_{tetra}$ and $\#Rings_{penta}$ in SPM were all in-between the soil and sediment values, suggestive of more impact of soil input on brGDGTs in SPM than in sediments, which could also reduce the seasonal contrast in estimated temperatures.

300 Using the new proposed 5- and 6-methyled brGDGTs temperature calibrations, we got temperature estimates from the Gonghai surface sediments in ranges of 6.9–8.0 °C (average 7.5 ± 0.4 °C; Eq. (14); Fig. 4b) and 10.1–13.2 °C (average 11.4 ± 1.4 °C; Eq. (15); Fig. 4b). These values are significantly warmer than the mean annual AT and close to the mean warm season AT in the Gonghai Lake region (Fig. 4b). This is consistent with the recent results from Dang et al. (2018), who investigated 35 Chinese lakes and found that warm season AT correlated well with brGDGTs composition in relatively cold regions.

Many previous brGDGTs instrumental analyses on lake materials used one cyano column, which cannot separate 5- and 6-methyl brGDGTs. Using the data published in the same lake from Cao et al. (2017), we re-calculated temperature using different calibrations. The results showed that the absolute

temperature estimates were all significantly warmer than the mean annual AT (Table 3), with the temperature offsets varying from 4–10 °C, which cannot be fully explained by the uncertainty of each calibration. Therefore, it appears that sedimentary brGDGTs-derived temperature is warm season biased in the Gonghai Lake irrespective of whether or not 5- and 6-methyl brGDGTs are separated.





Globally, brGDGTs in many lake sediments are believed to be mainly sourced from aquatic production, including Lower King pond (Loomis et al., 2014), Qinghai Lake (Wang et al., 2012), Lake Donghu (Qian et al., 2019), Huguangyan maar (Hu et al., 2015, 2016) and Lake Towuli (Tierney and Russell, 2009). Applying the global lake surface sediment calibration (Eq (10); Sun et al., 2011) to these lakes, we also re-calculated temperatures from published data of sedimentary brGDGTs (Fig. 5). Interestingly, the brGDGTs-inferred temperatures were generally higher than the measured mean

- annual AT, with greater differences in higher latitude lakes (including the Gonghai Lake in this study)
 and close to the mean annual AT in low-latitude or low-altitude lakes (i.e. the warm region; Fig. 5a).
 Investigations on specific lake studies have also pointed out that brGDGTs-inferred temperatures are
 higher than mean annual AT, close to warm season AT or summer AT in mid- and high-latitude lakes
 (Shanahan et al., 2013; Peterse et al., 2014; Foster et al., 2016; Dang et al., 2018), but close to mean
 annual AT in low-latitude lakes (Tierney et al., 2010; Loomis et al., 2012).
 - 4.4 Ice cover formation as a mechanism for the apparent warm bias of lacustrine brGDGTs-derived temperature

One explanation for the warm season biases of the lacustrine brGDGTs-derived temperature has been proposed as the excessive production of brGDGTs during the warm/summer season relative to 330 winter season (Pearson et al., 2011; Shanahan et al., 2013; Peterse et al., 2014; Foster et al., 2016; Dang et al., 2018). In the Gonghai Lake, the average concentration of brGDGTs in SPM is 7.1 ± 2.0



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ng/l in September and 5.2 ± 2.3 ng/l in Jannuary (Fig. 2) with no significant difference. It appears not to support preferential production of brGDGTs in warm season, although the interference from fossil brGDGTs due to longer residence time and sediment resuspension cannot be fully ruled out. Besides, the season of higher brGDGTs concentration has been found different in different lakes, e.g., in spring and autumn in Lower King pond (Loomis et al., 2014), in winter in Lake Huguangyan (Hu et al., 2016) and Lake Lucerne (Blaga et al., 2011), and in summer in Lake Donghu in central China (Qian et al., 2019). However, in all these lakes, brGDGTs-derived temperatures have been found to be slightly or obviously warm season biased. The inconsistency of seasonality of particulate brGDGTs concentrations suggests that other than seasonality in the production of brGDGTs in the lakes, there should be another factor responsible for the bias of brGDGTs-inferred temperature toward warm season (Fig. 5a and b).

Another explanation is that lake water depth (wd), especially water stratification, can affect molecular distribution of brGDGTs, and thus the temperature estimates (Ajiako et al., 2014; Buckles et al., 2014b; Loomis et al., 2014; Weber et al., 2018). The bio-precursors of brGDGTs have been proposed to be bacteria with an anaerobic heterotrophic lifestyle (Sinninghe Damsté et al., 2000; Weijers et al., 2006b, 2010; Weber et al., 2015, 2018), implying that a potentially anoxic environment in deep water favors the production of brGDGTs (Woltering et al., 2012; Zhang et al., 2016; Weber et al., 2018), which could lead to higher proportion of 'colder temperature' brGDGTs in surface





sediments. Normally, stratified lakes are deep, which is not the case for the Gonghai Lake, as well as for Lower King pond (Loomis et al., 2014) and Lake Donghu (Qian et al., 2019) that have maximum water depths of ca. 8 m and 6 m, respectively. Therefore, the influence of lake water depth on the molecular distribution of brGDGTs can be ruled out in these shallow lakes. In deeper lakes, such as Lake Huguangyan (20 m wd), Qinghai Lake (27 m wd) and Lake Towuli (200 m wd) (Tierney and Russell, 2009; Wang et al., 2012; Hu et al., 2016), the relatively high concentration of brGDGTs in bottom water (Hu et al., 2016) could record relatively low temperature of deep water in sediments. However, the MBT/CBT-inferred temperature in these lakes' sediments are higher, not lower than the mean annual AT, irrespective of whether the global or regional calibrations are used (Fig. 5a and Table 3). Consequently, lake water stratification should be not responsible for the warm bias of MBT/CBT-inferred temperature of surface sediments, at least in these lakes.

Since the brGDGTs in surface sediments of the Gonghai Lake mainly derived from in situ production, the brGDGTs-derived temperature proxies should directly record LWT, rather than AT, as has been demonstrated by the study of Lower King Pond in temperate northern Vermont, U.S.A. (Loomis et al., 2014) and Loch Lomond in north-west of Glasgow, UK (Buckles et al., 2014b). However, previous studies assumed that the estimated temperatures can still reflect AT due to the tight coupling between LWT and AT. In fact, such tight coupling can be found in tropical-subtropical lakes such as Lake Huguangyan and Lake Donghu (Fig. 6c and d), where AT is always above freezing, but





is not true in higher-latitude lakes such as Lower King pond and Gonghai Lake with lake surface freezing in winter (Fig. 6a and b). The reason is that lake surface ice prevents the thermal exchange 370 between water and air, leading to decoupling between LWT and AT in winter in those cold regions. The decoupling makes annual mean LWT higher than mean annual AT. Therefore, the greater warm biases of brGDGT-derived temperatures from surface sediments in higher latitudes (Fig. 5a) could be due to the stronger decoupling (e.g., longer freezing time) between LWT and AT. Nevertheless, annual mean LWT appears close to the mean AT in warm season (monthly temperature >0 °C) (Fig. 6f), which could be the reason why the brGDGTs-inferred temperatures are similar to the mean warm 375 season AT. Due to lack of detailed AT and LWT data in literature, we failed to show more examples than as shown in Fig. 6, especially those from even higher latitudes. However, we proposed a simple model for the relationship between LWT and AT in a year cycle (Fig. 7), which may be a universe physical phenomenon in shallow lakes. In mid- and high-latitude region, we believe the decoupling between AT and LWT caused by ice formation in winter may be applied to explain the observed 380 seasonality of the brGDGTs temperature records. For example, the biases of brGDGTs derived temperatures toward summer AT observed extensively in the Arctic and Antarctic lakes (Shanahan et al., 2013; Foster et al., 2016) are compatible with our suggested mechanism here.

We noticed that the seasonality of brGDGTs-derived temperature occurs also in tropical lakes; however, there are disagreements in related studies. For example, MBT/CBT-derived temperature



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correlated better with warm season AT than with annual mean AT in the tropical Lake Huguangyan, suggesting a warm season bias (Sun et al., 2011). However, the brGDGTs-inferred temperatures reflect cold season temperature in some tropical lakes, such as Lake Challa, Lake Albert, Lake Edward and Lake Tanganyika (Tierney et al., 2010; Loomis et al., 2012; Buckles et al., 2014a). It is certain that the ice cover mechanism proposed here cannot be applied to these tropical lakes because ice cover does not form even in winter except for high altitudes. In such cases, other environmental conditions might determine the seasonality of brGDGT-based temperature proxies, such as seasonal soil erosion from lake catchments, seasonal production of brGDGTs and different production rate of brGDGTs at water depths (Sinninghe Damsté et al., 2009; Sun et al., 2011; Buckles et al., 2014a). Although these environmental conditions likely also occur in mid to high latitudes, they should become secondary in comparison with the great impact of ice formation on the air-water thermal

contrast, especially in shallow lakes, like the Gonghai Lake.

5 Conclusions

We investigated the composition of brGDGTs in catchment soils, surface sediments and water column SPM in September and January in the Gonghai Lake in north China. The lake is characterized by ice formation in its surface and a constant 4 °C condition in the underlying water in winter. The composition distribution of brGDGTs in sediments differed clearly from in soils, indicating their





mainly in situ production in the lake. Based on available lake calibrations, we found that the temperature estimates in surface sediments reflected the mean annual LWT, which are higher than the measured mean annual AT but close to warm season AT. We thereby proposed that water-air temperature decoupling due to ice formation at the lake surface in winter may have caused the apparent bias toward warm AT of lacustrine brGDGTs-derived temperatures. Since the warm AT bias of brGDGTs estimates has been observed extensively in mid- and high-latitude shallow lakes, we believe the mechanism proposed here could be also applicable to these lakes.

Data availability

The raw data of this study can be accessed from https://figshare.com/s/a4f324247ecd9d1ac575.

Author contribution

415 ZR designed experiments, FS and JC collected samples and JC carried experiments out. JC, GJ and ZR prepared the manuscript with contributions from all co-authors.

Conflicts of interest

The authors declare that they have no conflict of interest.

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Captions for Tables and Figures:

Fig. 1. (a) The Gonghai Lake (red circle), other referenced lakes (black circles) and modern Asian summer monsoon limit (dashed line; Chen et al., 2008). (b) SPM from water column (black star), surface soils (red squares) and

- 655
- surface sediments (red triangles) in Gonghai Lake in this study; black squares and triangles represents the sample sites published in Cao et al. (2017) (modified from Cao et al., 2017). (c) Measured local air temperature (AT) and lake water temperature (LWT) during 2018–2019 (this study).





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Fig. 2. Depth profiles of water temperature, brGDGTs concentrations, MBT'_{5ME} , MBT'_{6ME} in the Gonghai Lake in

January and September.







Fig. 3. Composition distribution of brGDGTs in surface soils, water column and surface sediments of the Gonghai









670 Fig. 4. (a) brGDGTs-derived temperatures for surface soils, sediments and SPM using soils calibration from De





Jonge et al. (2014). (b) brGDGTs-derived temperatures for sediments and SPM using lake calibrations Eq. (14)

and Eq. (15) from Dang et al. (2018) and Russell et al. (2018).







Fig. 5. Comparison between brGDGTs-derived temperature and measured AT. (a) Measured mean annual AT and brGDGTs-derived temperatures in surface sediments based on Sun et al. (2011). (b) Measured mean warm season AT and brGDGTs-derived temperatures in surface sediments based on Sun et al. (2011). Data are from Gonghai Lake (GH; Cao et al., 2017), Lower King pond (LK; Loomis et al., 2014), Lake Huguangyan (HML; Hu et al., 2015, 2016) Lake Donghu (DH; Qian et al., 2019), Qinghai Lake (QH; Wang et al., 2012) and Lake Towuli (LT; Tierney and Russell, 2009).







Fig. 6. Measured LWT and AT in (a) Gonghai Lake (GH; this study), (b) Lower King pond (LK; modified from

Loomis et al., 2014), (c) Lake Donghu (DH; modified from Qian et al., 2019) and (d) Lake Huguangyan (HML;

685 modified from Hu et al., 2016). (e) Correlation between mean annual AT and mean annual LWT. (f) Correlation between mean warm season AT and mean annual LWT. In the mid-latitude Gonghai Lake and Lower King pond, the surface LWT follows AT only when the AT is above freezing. In the low-latitude Lake Donghu and Lake Huguangyan, the surface LWT follows AT for the whole year.







Fig. 7. A simple model showing the relationship between LWT and AT in different latitudes





Table 1 Concentration of brGDGTs, calculated indices and estimated temperatures in catchment surface soils,

Code of site	I	Latitude (N)	Vegetation type	Water depth (m)	brGDGTs			МААТ	МААТ	МААТ	Currently
	T				(ng/g dw)	MBT'5ME	MBT'6ME	MAAI	MAA I	MAAI	Growin
	(E)				(ng/L)			"(·C)	°(-C)	·(·C)	$AI^{*}(C)$
Surface soils	in Gonghai catchme	nt									
S 1	112°14′19.039″	38°54′37.343″	grass		74.82	0.31	0.21	1.20			
S2	112°14′18.460″	38°54′28.750″	grass		23.50	0.36	0.20	2.58			
S3	112°14′24.140″	38°54′23.098″	shrub		22.00	0.35	0.33	2.40			
S4	112°14′36.827″	38°54′27.126″	shrub		32.65	0.36	0.26	2.64			
S5	112°14′40.502″	38°54′38.174″	grass		16.06	0.36	0.24	2.82			
Gonghai surface sediments											
D1	112°14′22.963″	38°54′36.357″		1.00	42.03	0.29	0.22	0.70	8.35	13.50	6.91
D2	112°14′24.004″	38°54′35.903″		2.50	33.95	0.27	0.24	-0.13	7.50	11.91	7.33
D3	112°14′25.109″	38°54′35.294″		5.50	327.62	0.23	0.25	-1.19	6.40	10.11	7.70
D4	112°14′27.301″	38°54′34.499″		6.70	374.29	0.24	0.27	-0.93	6.67	10.57	8.00
D5	112°14′28.453″	38°54′33.980″		8.00	706.72	0.24	0.25	-0.95	6.64	10.72	7.67
Gonghai SPM	I in Sept										
Water-1 m	112°14′28.453″	38°54'33.980"		1.00	5.71	0.28	0.32	0.24	7.88	11.19	9.16
Water-3 m	112°14′28.453″	38°54′33.980″		3.00	6.39	0.27	0.28	-0.05	7.57	10.86	8.25
Water-6 m	112°14′28.453″	38°54'33.980"		6.00	6.22	0.26	0.29	-0.35	7.26	10.45	8.55
Water-8 m	112°14′28.453″	38°54'33.980"		8.00	10.07	0.23	0.24	-1.40	6.18	10.60	7.31
Gonghai SPM in Jan											
Water-1 m	112°14′28.453″	38°54'33.980"		1.00	2.88	0.25	0.27	-0.75	6.85	10.40	7.95
Water-3 m	112°14′28.453″	38°54′33.980″		3.00	6.09	0.26	0.26	-0.49	7.12	11.02	7.77
Water-6 m	112°14′28.453″	38°54′33.980″		6.00	8.05	0.25	0.27	-0.65	6.95	10.57	7.99
Water-8 m	112°14′28 453″	38°54'33 980"		8 00	3 71	0.24	0.28	-0.96	6.63	10.20	8 24

sediments and water column SPM from Gonghai Lake.

MAAT represents mean annual air temperature.

^a Calculated after De Jonge et al. (2014).

^b and ^c Calculated after Russell et al. (2018).

^d Calculated after Dang et al. (2018).

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Table 2 Calibrations for brGDGTs-derived temperature proxies reported in previous studies.

Calibrations	Equation no. in the text	References
For soils		
MAAT=0.81-5.67*CBT+31.0*MBT' (<i>n</i> =176, r ² =0.59, RMSE=5.0 °C)	(8)	Peterse et al. (2012)
MAAT=-8.57+31.45*MBT' _{5ME} (n=222, r ² =0.66, RMSE=4.8 °C)	(9)	De Jonge et al. (2014)
For sediments		
MAAT=6.803-7.062*CBT+37.09*MBT (<i>n</i> =139, r ² =0.62, RMSE=5.24 °C)	(10)	Global, Sun et al. (2011)
MAAT=8.263-17.938*CBT+46.675*MBT (<i>n</i> =24, r ² =0.52, RMSE=5.1 °C)	(11)	Regional, Sun et al. (2011)
$MAAT^{a}\!=\!50.47\text{-}74.18*f(\mathrm{IIIa})\text{-}31.60*f(\mathrm{IIa})\text{-}34.69*f(\mathrm{Ia}) \ (n\!=\!46, r^{2}\!=\!0.94, RMSE\!=\!2.2\ ^{\circ}\mathrm{C})$	(12)	Tierney et al. (2010)
$MAAT = 22.77 - 33.58 * f(IIIa) - 12.88 * f(IIa) - 418.53 * f(IIc) + 86.43 * f(Ib) (n = 111, r^2 = 0.94, RMSE = 1.9 °C)$	(13)	Loomis et al. (2012)
Growth AT=21.39*MBT' _{6ME} +2.27 (<i>n</i> =39, r ² =0.75, RMSE=1.78 °C)	(14)	Dang et al. (2018)
$MAAT = 23.81 - 31.02 * f(IIIa) - 41.91 * f(IIIb) - 51.59 * f(IIIb') - 24.70 * f(IIa) + 68.80 * f(Ib) (n = 65, r^2 = 0.94, RMSE = 2.14 °C) = 0.04 + $	(15)	Russell et al. (2018)
MAAT=-1.21+32.42*MBT' _{5ME}	(16)	Russell et al. (2018)

AT represents air temperature.

MAAT represents mean annual air temperature.

700 ^a Fractional abundance of brGDGTs is a fraction of only brGDGTs Ia, IIa and IIIa.





Table 3 Comparison of measured air temperature, brGDGTs-derived temperature from catchment soils and

Name	Latitude	Longitude	Depth (m)	MAAT (°C)	Mean warm season AT (°C)	Mean annual LWT (°C)	Surface soils	Surface sediments					
							MAAT ^a	MAAT ^b	MAAT °	MAAT ° MAAT ^d MAAT		References	
							(°C)	(°C)	(°C)	(°C)	(°C)		
Gonghai Lake	38°54′ N	112°14′ E	9	4.3	12.1	10.6	3.96±1.46	10.74±0.33	9.70±0.71	10.86±1.33	7.93±1.46	Cao et al. (2017)	
Lake Towuti	2.5° S	121° E	200	24	24	n.d.	22.52±2.61	26.62±1.10	29.13±1.86	n.d.	n.d.	Tierney and Russell. (2009)	
Lake Huguanyan	21°09′ N	110°17′ E	20	23.2	23.2	24.8	23.80±1.39	25.11±0.60	28.12±0.90	26.47±0.83	26.07±0.73	Hu et al. (2015, 2016)	
Lake Donghu	30°54′ N	114°41′ E	6	16	16	20	15.79±4.37	19.74±0.39	22.82±0.51	25.75±0.34	20.61±0.71	Qian et al. (2019)	
Qinghai Lake	36°54′ N	100°01' E	27	0.65	7	n.d.	3.38±2.40	12.34±0.87	9.92±1.14	13.61±1.49	8.80±1.11	Wang et al. (2012)	
Lower King pond	44°25′ N	72°26′ W	8	6	11.3	11.6	11.50±2.08	14.97±0.42	14.9±0.53	18.75±0.64	15.76±0.84	Loomis et al. (2014)	

brGDGTs-derived temperature from sediments in different lake basins.

AT represents air temperature and MAAT represents mean annual air temperature.

LWT represents lake water temperature.

^a Calculated after Peterse et al. (2012)

^b and ^c Calculated after Sun et al. (2011).

^d Calculated after Tierney et al. (2010).

^e Calculated after Loomis et al. (2012).