Associate Editor comment:

First of all, I would like to thank both reviewers for their reviews and you for your reply. I have read you manuscript with great pleasure, but agree with the comments of the reviewers. So please do address these in you next version of the manuscript.

Response: Thank for your handling our manuscript. We found your comments below are very constructive for improving our manuscript. The reviewers' and your comments have been address in the updated version.

I do have a few other questions or suggestions. I totally agree that if the majority of your brGDGTs are produced within the lake, lake water temperature is probably more important than air temperature. That being said, there is still the option that soil derived brGDGTs create part of the observed bias, right? In soils I would assume production is highest during the warm season and decreases or even completely stops in the cold season, when the soils are probably also frozen? What is the catchment of this lake and when does soil derived material end up in the lake? I could imagine soil brGDGTs with a warm season bias being stored in soils over winter ending up in the lake with the melting of snow and ice transporting soil derived material with meltwater to the lake ending up in the sediment. If something like this might happen, you would probably see such as soil signal in mainly the spring SPM and maybe only in certain areas of the lake. Did you sample in spring? So big question is the soil contribution always small and insignificant relative to the lake contribution? Or might there be a small, but significant, contribution to the sediment creating this warm bias? I totally agree with your lake temperatures and how they deviate from the air temperatures in winter, so a very valid explanation, but can you completely rule out the soil contribution based on the data set you have presented here?

Response: (1) We admit that we cannot estimate soil contribution to lake sediment due to lack of any suitable index to completely separate the two brGDGT pools at present. So what we do in our work is to compare brGDGT contents and distributions between sediment and soils, and qualitatively say that soil contribution is quite minor to sediments (please see Line 250-290 in the revision). (2) The Gonghai Lake is a closed alpine lake without river input and output. The catchment soil input to the lake occurs mainly from May to September (the warmest months), when ca. 80% annual rainfall and enhanced erosion take place. Spring is not an important season for soil input. (3) We have been also interested in the assumption of highest brGDGT production during the warm season in catchment soils, which, as you said, may finally create part of the observed bias. However, our data do not support this idea, because the brGDGT-derived temperature in the Gonghai catchment soils using global and regional calibrations are close to or even lower than the mean annual temperature (please see Line 278-284 in the revision).

That was one potential issue. What is reflected in you SPM, is there the potential for resuspension, for instance? I would expect activity and/or growth also to be reduced at 5 °C relative to the 14, 15, 20 °C in summer. Agreed potentially not zero, which would most likely be the case for the frozen soils. Your lake temperature lag behind the air temperature a little, the brGDGTs possibly integrate a relatively long(er) time period, even in the SPM, and therefore lag behind even more or average out a longer time period. Add to that the possibility of soil derived material which could be seasonally varying and possibly resuspension. Could it be that the relatively stable amount of brGDGTs in SPM reflects these process, slow growth and a "fossil" component leading to averaging out of the extremes and resulting in an apparent warm bias?

Response: (1) You are right. We have elaborated the "fossil" nature of brGDGTs in our SPM samples (Please see Line 386-409 in the revision). (2) Your comment of slow growth of bacteria under low temperatures and hence causing warm bias of brGDGT distribution is suggestive. However, in our results brGDGT-derived temperatures in SPM were close to mean annual water temperature and lower than the mean annual warm water temperature. So our data do not support this idea. We add this point in our text (Please see Line 446-449 in the revision).

There one last remark, would it be possible that the population growing and active at 5 °C does something different than the one growing in summer in the lake? Something like this is happening in soils where the observed differences are related to population changes and not adaptations to changing conditions by the same population. If so, how would that interfere with your ideas?

Response: This is a clever comment. We admit we cannot give a perfect answer to this question due to lack of supported data. Nonetheless, we tried to make a simple discussion on this idea. Please see Line 419-433 in the revision.

Again, I think your idea is very valid, but I do think some of these other complicating mechanisms could be discussed. I assume you did not analyse a spring sample, or a sample from during or right after a major ice and snow melt. ^{14}C age data of brGDGTs from different samples would also be very interesting, I think, but that is a completely different topic, never mind.

Response: Thanks for your constructive comments that help improve our manuscript greatly.

Anonymous Referee #1

Received and published: 19 February 2020

The authors of this manuscript examine the brGDGT distributions in the water column and surface sediments of the Lake Gonghai and its catchment. They address a critical issue for brGDGT studies which is the warm season bias of brGDGT-derived temperatures obtained in lakes. They propose a new very interesting mechanism to explain this bias implying the decoupling of air and lake water temperature during the cold season due to ice formation. This finding will be useful for the community and is worthy to be published. However, some improvements can be made before publication.

Response: Thanks for the comments. We have made substantial improvements according to reviewers' suggestions. Besides, some improvements were made beyond those suggestions during our revision, including title rephrasing, reanalysis sedimentary data instead of presenting mean brGDGT values (line 1, 22-24, 216-217, 224-225, 241-242, 244-246), and reorganization of discussion (line 258-259, 382-418, 426-433, 441-483). We think the manuscript has been greatly improved in logic.

Main comments:

1. The new separation method of the 5 and 6-Me isomers should be mentioned in the introduction.

Response: We agree and have added related contents about 5 and 6-Me isomers in the introduction. Please see line 48-55 in the revision. The revised sentences are following:

'With improved analytical methods, a series of 6-methyl brGDGTs, previously co-eluted with 5-methyl brGDGTs, were identified (De Jonge et al., 2013), which may introduce scatter in the original MBT'/CBT calibration for the mean annual AT (De Jonge et al., 2014). Thus, exclusion of the 6-methyl brGDGTs from the MBT', i.e. the newly defined MBT'_{5ME}, results in improved calibrations (De Jonge et al., 2014; Wang et a., 2016; Wang et al., 2019). Calibrations using globally distributed surface soils for the MBT/CBT, MBT'/CBT or MBT'_{5ME} indices (Weijers et al., 2007a; Peterse et al., 2012; De Jonge et al., 2014) have been widely used for continental AT reconstruction (e.g., Weijers et al., 2007b; Niemann et al., 2012; Lu et al., 2019)'.

2. A figure with the different forms of brGDGTs could be included in appendix.

Response: Done. Figure A1 showing different forms of brGDGTs has been added in Appendix 1.

3. Why don't you use recent regional soil calibrations for China as the one of Wang et al., 2016 for your soil samples?

Response: Thanks for your suggestion. The regional soil calibration from Wang et al. (2016) has been applied to the Gonghai Lake, yielding −2.42 ± 1.19 °C from soils, −5.86 ± 1.30 °C from lake sediments (Table 1), −6.20 ± 0.60 °C in Sept (Table 1) and −6.25±0.54 °C in Jan from SPM (Table 1). These values are significantly different from actual values, suggesting that the regional soil calibration was not suitable for soil and lake temperature reconstruction in the Gonghai Lake basin.

We have added the results about brGDGT calculated temperature values from Wang et al. (2016) in the text, Table 1 and calibration in Table 2. Please see Line 279-284, Table 1 and 2 in the revision.

4. The conclusion is incomplete, you could add that soil temperature reconstructions reflect the MAAT and I think that it is important to mention that brGDGT distributions in the water column change with seasons while brGDGT productivity does not seem to significantly change. This allows you to propose an alternative explanation to warm season bias in brGDGT-derived temperature that is currently mainly considered as linked with changing brGDGT productivity.

Response: Thanks for your suggestion. The conclusion has been rewritten accordingly. Please see lines 524-542 in the revision.

5. The manuscript should be carefully checked for grammar and language issues.

Response: Done, thanks for your suggestion.

Abstract

l17 mean annual

Response: Done. Please see line 17 in the revision.

l18 There are too many ‘and’.

Response: This sentence has been rephrased to ‘we investigated the brGDGTs from catchment soils, suspended particulate matter (SPM) and surface sediments in the Gonghai Lake in north China to explore this question’. Please see line 19 in the revision.

l29 I think that the use of ‘believe’ should be avoided and the sentence should be rewritten. Suggestion: we think that lacustrine brGDGTs actually reflect the mean annual LWT (. . .).

Response: Done as you suggested. Please see line 32 in the revision.

Introduction

l42 The abbreviations MBT and CBT should be defined.

Response: Done. Please see line 45-46 in the revision.

l46 Some references could be added in particular, recent ones using the new separation method.

Response: Done. References ‘De Jonge et al. (2014), Wang et al. (2016), Wang et al. (2019)’ have been added in line 52.

l53 Suggestion: brGDGTs could be produced in situ in lake environments and differ significantly from soil derived brGDGTs (. . .)

Response: Done as you suggested. Please see line 63 in the revision.

l106 ‘composition distribution of brGDGTs’ sounds odd to me, I suggest you to change it in the entire manuscript and replace it by ‘brGDGT distribution’.

Response: Done. Please see line 63, 69, 116-117, 254, 260, 524, 527, 812 in the revision.

l107 and further discuss . . .

Response: Done. Please see line 118 in the revision.

Materials and methods

l112 Mention ‘N’ and ‘E’ for latitude and longitude.

Response: Done. Please see line 123 in the revision.

l119 concentrated

Response: Changed. Please see line 130 in the revision.

l146 combination of

Response: Changed. Please see line 161 in the revision.

l146 and 150 ‘DCM’ and ‘MeOH’ could be used for dichloromethane and methanol defining the acronym at the first appearance.

Response: Done. Please see line 160 and 165 in the revision.

l157 Mention what are ‘A’ and ‘B’.

Response: Done. Please see line 172 in the revision.

l167 Remove the ‘;’ after(2)

Response: Done. Please see line 183 in the revision.

l169 The authors could mention Martin et al., 2019 who modified the initial definition of the IIIa/IIa ratio proposed by Xiao et al., 2016.

Response: Done. Please see line 184-185 in the revision.

l170 A word is missing as well as a punctuation mark.

Response: Done. Please see line 186 in the revision.

l177 Add a figure in appendix describing the different brGDGT structures and refer to it here.

Response: Done. We have added the figure about brGDGT structures in Appendix 1.

Results

l206 typical for in situ produced lacustrine (. . .)

Response: Done. Please see line 221 in the revision.

Discussion

l221 This title is not very clear, maybe ‘Different sources of brGDGTs in the Gonghai Lake‘ or ‘In situ production of brGDGTs in the Gonghai Lake‘.

Response: Thanks for your suggestion. We have changed ‘Different sources of lacustrine brGDGTs from surrounding soils’ to ‘In situ production of brGDGTs in the Gonghai Lake’. Please see line 249 in the revision.

l226 and/or surface sediments. I would not mention brGDGT concentrations as a discriminant factor between soils and in situ production, differences of concentrations, alone, would not be a proof of the occurrence of in situ production as several other parameters could be involved.

Response: We found content of brGDGTs in surface sediments is significantly higher than that in surface soils (Table 1), and increases with water depth (Table 1). Therefore, we think it suggests a possible autochthonous contribution in Gonghai Lake. We have added ‘Moreover, they exhibited a clearly increasing trend with water depth’ in the revision, please see line 258-259.

l227 comparison of brGDGT distribution

Response: Changed. Please see line 260 in the revision.

l232 was similar to that of SPM . . . from that of soils

Response: Changed. Please see line 260-261 in the revision.

l236 The ΣIIIa/ΣIIa values in sediments and SPM were

Response: Changed. Please see line 266 in the revision.

l238 the ΣIIIa/ΣIIa ratio in sediments and SPM was significantly higher than in catchment soils.

Response: Changed. Please see line 266 in the revision.

l239 sediments are

Response: Changed. Please see line 269 in the revision.

l243 It does not appear very clearly that #Ringstetra were higher in sediments than in soils, a statistical test would be appreciated.

Response: Thanks for your suggestion. We have added *t*-test in the revised sentence, please see '… $\#Rings_{tetra}$ and $\#Rings_{penta\ 5ME}$ were clearly higher in sediments than in catchment soils (p<0.05 for $\#Rings_{tetra}$, p<0.01 for $\#Rings_{penta\ 5ME}$), although $\#Rings_{penta\ 6ME}$ in sediments was similar to that in catchment soils (p=0.11 for $\#Rings_{penta\ 6ME}$; Fig. 3b)' in line 273-275.

l257-258 in globally distributed lakes?

Response: We have changed 'in global lakes' to 'in many modern lake sediments'. Please see line 288 in the revision.

l270 You should provide the reader with the analytical error associated with the MBT indices in the method section for a better evaluation of the changes discussed here.

Response: We have added the analytical error in the method. Please see 'Based on duplicate HPLC/MS analyses, the analytical errors of both the MBT'_{5ME} and MBT'_{6ME} index were ±0.01 units' in line 177-178 in the revision.

l274 You should add a reference to Fig. 2. You should at least mention that the deepest SPM shows an opposite trend which seems to indicate that at this depth, temperature is not the only parameter controlling brGDGT distributions.

Response: In revised Fig. 2, the MBT'_{5ME} and MBT'_{6ME} index trace the water temperature changes at different depth in Sept and in Jan, and it seems that MBT'_{5ME} and MBT'_{6ME} index could response to water temperature changes to some extent. However, the seasonal changes of SPM brGDGT derived temperature between Sept and Jan were small, which could be influenced by the several reasons in addition to water temperature, such as residence of "fossil" brGDGTs and sediment resuspension, as evidence of smaller differences in MBT'_{5ME} and MBT'_{6ME} between sediments and SPM at deeper sites. We have discussed the detailed reason about it in the later paragraph. Please see line 391-409 in the revision.

l275 seasonal temperature changes?

Response: This paragraph have been rephrased. Please see line 383-390 in the revision.

l276 previously

Response: This paragraph have been rephrased. Please see line 383-390 in the revision.

l276-277 The phrasing sounds odd to me. Suggestion: suggest that both . . . could respond to temperature changes.

Response: This paragraph have been rephrased. Please see line 383-390 in the revision.

l278-279 African ; the phrasing is not very clear here.

Response: This paragraph have been rephrased. Please see line 383-390 in the revision.

l283 I suppose that 0.3 corresponds to the difference of the mean temperatures obtained for September and July? You could specify it.

Response: We have revised sentence as

'Although the MBT'_{5ME} and MBT'_{6ME} in SPM in the lake seem to reflect temperature changes in the water column to some extent, the differences of brGDGT-derived temperatures based on lake-specific calibrations between September and January (−0.93–1.21 °C) are much lower than the measured difference (~13 °C), independent of the calibration of (15), (16) or (17) (Tables 1 and 2)'. This could be clear for reader. Please see line 391-394 in the revision.

l284 remove the '.' after (16).

Response: Done. Please see line 394 in the revision.

l286 multi-seasonal

Response: Changed. Please see line 401 in the revision.

l287 previously

Response: This paragraph have been rephrased. Please see line 391-409 in the revision.

l292 could also be

Response: This paragraph have been rephrased. Please see line 391-409 in the revision.

l293 the shallow water depth of the lake

Response: This paragraph have been rephrased. Please see line 391-409 in the revision.

l293-294 The sentence is not very clear and too long, you should maybe cut it into two sentences.

Response: This paragraph have been rephrased. Please see line 391-409 in the revision.

l296-299 Terrestrial inputs are almost not discussed, could they have a role in seasonal changes of brGDGTs?

Response: Just as discussed in the text, several parameters, such as $\sum$IIIa/ΣIIa, IR_{6ME}, $\#Rings_{tetra}$ and $\#Rings_{penta}$ in SPM were in-between the soil and sediment values, we speculate terrestrial inputs may be a factor, if any, to reduce the seasonal changes of brGDGTs in SPM. Please see line 407-409 in the revision.

l297 Be coherent with the notation of ΣIIIa/ΣIIa.

Response: Done. Please see line 407 in the revision.

l300-304 You should mention here or in the previous paragraphs that SPM samples also reflect temperatures close to warm season AT.

Response: Done. Sedimentary brGDGTs in Gonghai Lake reflected temperature close to warm season AT. Due to sediment resuspension, the warm season bias also occurred in SPM. We have discussed it in line 446-448 in the revision.

l302 You could add a reference to the table 1. Is it 13.2 or 13.5?

Response: Done. The number of 13.5 is correct according to the results in Table 1.

l305 correlated significantly

Response: Done. This paragraph have been rephrased and this word has been deleted.

l314 are thought to . . .

Response: Done. This sentence has been rephrased. Please line 356-358 in the revision.

l314-325 You say in situ production is thought to be the main source of brGDGTs in many lakes so why do you only consider six lakes in fig 5? What about the others?

Response: We selected these five lakes for several reasons. (i) The brGDGTs-related data from both the lake surface sediments and the catchment surface soils were available. (ii) The lakes are in different regions, and together with Gonghai Lake in this study, they span a relatively large environmental gradient. (iii) The authors of these studied lakes have claimed that brGDGT distribution in lake sediments differed from catchment soils as we do in Gonghai Lake in this study.

As to others lakes, due to the lack of catchment soil brGDGT data, they are not shown in revised Figure 5, although brGDGT-derived temperatures are also warm season biased. We have added related content in the revised manuscript. Please see line 358-381 in the revision.

l319-325 Rephrase

Response: Done. Please see line 371-381 in the revision.

l332 You should also mention that brGDGT distribution in water column seems to change seasonally in agreement with temperature, what you discussed in the 4.3 section.

Response: Although the MBT'_{5ME} and MBT'_{6ME} in water SPM mirror the water temperature change in Sept and Jan, the calculated seasonal temperature offsets was quite small in Gonghai Lake. So we don't emphasize this phenomenon. We have added related content in the revised manuscript. Please see line 391-409 in the revision.

l339 Rephrase

Response: Done. Please see line 454-456 in the revision.

l350 Most of stratified lakes . . .

Response: Done. This paragraph has been rephrased and this word has been deleted.

l365 Can you add a reference?

Response: Done. Please see line 486 in the revision.

l378 universal

Response: Changed. Please see line 499 in the revision.

l383 compatible with the mechanism that we propose here

Response: Changed. Please see line 504 in the revision.

l391 Use cold season rather than ‘winter’.

Response: This paragraph has been deleted.

Conclusion

l403 from that in soils

Response: Changed. Please see line 528 in the revision.

l403-404 indicating that lacustrine brGDGTs are mainly produced in situ . . .

Response: Changed. Please see line 528 in the revision.

l404 in surface sediments of Lake Gonghai

Response: Changed. Please see line 534 in the revision.

l406 water-air decoupling in Lake Gonghai

Response: We don’t add “in Lake Gonghai” here because we think the sentence is ok.

Figure 1

(a) northern limit ? (b) For the latitude replace ‘E’ by N l655 represent

Response: Changed. Please see in the revised Figure 1.

Figure 3

fractional abundance Maybe specify: water column (SPM).

Response: Changed. Please see line813 in the revision.

l667 Use degree of cyclisation rather than ‘cyclisation ratio’.

Response: Done. Please see line 813-814 in the revision.

Figure 4

l670 soil calibration.

Response: This figure have been replace, please see revised caption Figure 4.

Figure 5

l679 A comma missing before Lake Donghu.

Response: Changed. Please see line 830 in the revision.

l676 Mention the number of the equation used.

Response: Done. Please see line 825-831 in the revision.

Table 1

l695 For b et c, mention the number of the equation used.

Response: Done. Please see the note of Table 1 in the revision.

Table 3

l705-708 Mention the number of the equation used.

Response: Done. Please see the note of Table 3 in the revision.

Anonymous Referee #2

Received and published: 2 March 2020

General comments

The mechanism of season bias of lake brGDGTs-derived temperature is not very clear, hence limit the application of brGDGTs index in lakes. The manuscript proposes a new idea about this hot topic. They conclude that decoupling of water and air temperature in winter causes warm season bias of lacustrine brGDGTs temperature estimates. Therefore, I recommend this manuscript for publication in the journal after improvement.

Response: Thanks for the comments. We have made substantial improvements according to reviewers' suggestions. Besides, some improvements were made beyond those suggestions during our revision. Please see the response and revised manuscript below.

Detailed comments

1/ Many pervious researchers suggested that soil calibrations could not be applicable to lake sediments for temperature reconstruction, if aquatic production of brGDGTs is predominant over soil input (e.g. many papers). It is no new, and not necessary to discuss too much in this point in your manuscript. And to focus on SPM.

Response: We agree. Some related sentences have been deleted and some related content has merged into the Section 4.1, as evidences of the in situ production of brGDGTs in the lakes. Please see Line 284-290 in the revision.

2/ Seasonality is a major feature for almost all organic proxies. For example, Lake Huguangyan (Hu et al., 2016; Chu et al., 2017). Lake limnology is most important, for example, Lake Huguangyan is a monomictic lake.

Response: We agree. Seasonality has been discussed in lines 421-444 in our manuscript and we are inclined to rule it out as a cause in our case. Lake Huguangyan has been used as a reference in many places in our paper. However, due to its location in the tropical area it is not the focus of our discussion. We give a special mention on proxy seasonality in the Lake Huguangyan. Moreover, we propose deep/bottom waters might influence brGDGT temperature signal in the lake. Please see lines 467-483 in the revision.

3/ “Line 147-148: “There is no water column stratifification whether summer or winter”. You must revise this sentence. Based on the location and depth of the lake, it might be stratified in summer. And figure 2 shows a little stratifification occurred in September (autumn).

Response: You are right. We changed these sentences. Please see lines 133-135 in the revision.

4/ Line 360-365: I don't think the estimated temperature using the calibration of Dang et al. (2018) are close to the mean warm season AT in GH, even if the RMSE is being considered. It seems that the calibration of Russell et al. (2018) may be more suitable for your explanation, and you'd get more discuss about this point.

Response: You are right. We rephrase these sentences. Please see lines 309-315 in the revision.

5/ Line 450: The definition of warm season should be given earlier, and change "monthly temperature" to "average monthly temperature".

Response: Done. The warm season is defined in the head of Section 4.2 '4.2 Lacustrine brGDGT-derived AT are warm season biased (average monthly temperature >0 °C)'. Please see line 300-301, 313 in the revision.

6/ Line 464-465: "For example, MBT/CBT-derived temperature 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)". To improve the discussion of seasonality in the paper, I recommend authors should detailed read the paper of Sun et al. (2011) carefully. And the author should see discussion about the seasonality of brGDGTs in Lake Huguangyan from Hu et al. (2016) and Chu et al. (2017). Seasonal biases may be due to seasonal brGDGTs production, and link to lake limnology and local climate.

Response: Thanks for the comment. We misunderstood the results from the Lake Huguangyan and made changes accordingly. The sentence has been corrected as 'The MBT/CBT-derived temperature in the Lake Huguangyan was thought to reflect mean annual AT (Hu et al., 2015, 2016); however, has recently been proposed to be winter/cool biased (Chu et al., 2017)'. Lake Huguangyan is located in the tropical region, which is not the focus of our discussion. Nonetheless, we give a special mention on proxy seasonality of Lake Huguangyan and other tropical lakes in second paragraph in Section 4.4. Please see line 470-475 in the revision.

7/ Please provide the component specific content of brGDGT as a Supplement.

Response: The brGDGT data had been showed in the data repository as journal recommends, please see https://figshare.com/s/a4f324247ecd9d1ac575.

8/ This manuscript is worth publish because something is new. But, authors should mention that the limited data in your manuscript, and more works are need to verify this question.

Response: Thanks for your suggestion. We add a sentence “Of course, considering limited data in this study, more investigations are needed to test our viewpoint in future studies.” at the end of discussion.

Ice formation on lake surface in winter causes warm season bias of lacustrine brGDGT temperature estimates

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Abstract

It has been frequently found that lacustrine brGDGT-derived temperatures are warm season biased relative to measured ~~annual mean~~mean annual 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 different water depths in the Gonghai Lake in north China to explore this question. Our results showed that the brGDGT distribution in sediments resembled that in the SPM but differed from the surrounding soils, suggesting a substantial aquatic origin of the brGDGTs in the lake. Moreover, the increase of brGDGT content and decrease of methylation index with water depth in sediments suggested more contribution of aquatic brGDGTs produced from deep/bottom waters. 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 that the apparent warm season bias of lacustrine brGDGT-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 basically follows AT during warm seasons when ice disappears. Therefore, we ~~believe~~think what lacustrine brGDGTs actually reflected is the mean

annual LWT, which is higher than the mean annual AT in our study 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 brGDGT-derived temperatures in other seasonally surface ice-forming lakes, especially the shallow lakes.

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 amounts of methyl groups and cyclopentyl moieties, expressed as methylation index and cyclization ratio of brGDGTs (such 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). With improved analytical methods, a series of 6-methyl brGDGTs, previously co-eluted with 5-methyl brGDGTs, were identified (De Jonge et al., 2013), which may introduce scatter in the original MBT'/CBT calibration for the mean annual AT (De Jonge et al., 2014). Thus, exclusion of the 6-methyl brGDGTs from the MBT', i.e. the newly defined MBT'$_{5ME}$, results in improved calibrations (De Jonge et al., 2014; Wang et al., 2016; Wang et al., 2019). Calibrations using globally distributed surface soils for the MBT/CBT, MBT'/CBT or MBT'$_{5ME}$ indices (Weijers et al., 2007a; Peterse et al., 2012; De Jonge et al., 2014) have been widely used for continental AT reconstruction (e.g., Weijers et al., 2007b; Niemann et al., 2012; Lu et al., 2019).

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. However, when the soil-based calibrations are applied to the lake materials, the estimated temperatures are usually significantly lower than actual local 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~~,~~ and~~which~~ differ significantly from soil derived brGDGT~~s 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~~brGDGT distribution in lake surface sediments has been found to be still strongly correlated with AT. Subsequently, quantitative lacustrine-specific calibrations for AT 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 brGDGT production during warm seasons (e.g., Pearson et al., 2011; Shanahan et al., 2013).

BrGDGT-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 Huguangyan 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 brGDGT producers favor anoxic conditions (Weijers et al., 2006b; Weber et al., 2018) that usually prevail in bottom water and sediments, which may discount the application of SPM-derived findings to the sedimentary brGDGTs.

In fact, brGDGT-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 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 brGDGT-derived temperature and AT (Weber et al., 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 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 different depths in the lake and soils in its catchment in a hot summer and a cold winter. We analyzed brGDGT distributions~~the composition distribution of brGDGTs~~ in these materials to determine the sources of brGDGTs in the lake and further~~ to~~ discussed the possible reasons for the seasonality of brGDGT-estimated temperatures.

2 Materials and methods

2.1 Gonghai Lake

The Gonghai Lake [38°54′ N, 112°14′ E, 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 southeast, and a relatively cold and arid winter under the prevailing East Asian winter monsoon (EAWM) from the northwest (Chen et al., 2013, 2015; Rao et al., 2016). The mean annual precipitation is ca. 482 mm, concentrated~~concentrating~~ (75%) between July and September (Chen et al., 2013). Its total surface area is ca. 0.36 km^2 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. The warm season lasts from May to September (Fig. 1c), when column stratification develops with an upper-bottom temperature difference >1 °C. During the winter from November to March, ice forms on the lake surface, and LWT under ice vertically constant at ca. 4 °C, which is significantly higher than AT that is much below the freezing point (Fig. 1c). From April to October, the 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

In September 2017, five surface soil samples in the catchment and five surface sediment samples at different depths (1.0, 2.5, 5.5, 6.7, 8.0 m) 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 m^2 with contrasting micro-topography or plant cover and then mixed them to represent a single sample. To avoid possible human disturbances, the soil sampling sites were distant from roads and buildings. All samples collected in the field were stored in a refrigeration 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 μm Whatman GF/F filter on site in September 2017 and January 2018, respectively. SPM samples were also stored in a refrigeration 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

Freeze-dried soil and sediment samples were homogenized at room temperature, and accurately weighed. Each freeze-dried filter with SPM attached was cut into small pieces using a sterilized scissor. Each sample of soil, sediment and SPM was placed in a 50 mL tube and then ultra-sonicated successively with dichloromethane/methanol (DCM/MeOH, 1:1, v/v) four times. After centrifugation and combination of~~combined~~ all the extracts of a sample, an internal standard consisting of synthesized C_{46} 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 fractions in the extracts were separated via silica gel column chromatography, using pure *n*-hexane and DCM/MeOH~~dichloromethane/methanol~~ (1:1, v/v), respectively. The polar fraction containing GDGTs was dried in a gentle flow of N_2, 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 GDGT 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 et al. (2015), the separation of 5- and 6-methyl brGDGTs was achieved using two silica columns in tandem (150 mm × 2.1 mm, 1.9 μm, Thermo Finnigan; U.S.A.) maintained at 40 °C. The following elution gradient was used: 84/16 *n*-hexane/EtOA (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. Based on duplicate HPLC/MS analyses, the analytical errors of both the MBT'_{5ME} and MBT'_{6ME} index were ±0.01 units.

2.4 Calculation of GDGT-related Proxies

The MBT'_{5ME} and MBT'_{6ME} index were calculated following Eq. (1) and (2) as in De Jonge et al. (2014):

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

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

The isomer ratio (IR) of 6-methyl was calculated as in De Jonge et al. (2014). The ΣIIIa/ΣIIa ratio was calculated as in Martin et al. (2019), which is modified from Xiao et al. (2016). The weighted average number of ring moieties (#$Rings_{tetra}$, #$Rings_{penta\ 5ME}$~~,~~ and #$Rings_{penta\ 6ME}$) followed Sinninghe Damsté (2016):

$$IR_{6ME} = (IIa'+IIb'+IIc'+IIIa'+IIIb'+IIIc')/\ (IIa+IIa'+IIb+IIb'+IIc+IIc'+IIIa+IIIa'+IIIb+IIIb'+IIIc+IIIc') \qquad (3)$$

$$\Sigma IIIa/\Sigma IIa = (IIIa+IIIa'+IIIa'')/\ (IIa+IIa') \qquad (4)$$

$$\#Rings_{tetra} = (Ic*2+Ib)/\ (Ia+Ib+Ic) \qquad (5)$$

$$\#Rings_{penta\ 5ME} = (IIc*2+IIb)/\ (IIa+IIb+IIc) \qquad (6)$$

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

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

Weber et al. (2015) (see Appendix 1).

In this study, we used two silica columns in tandem and successfully separated 5- and 6-methyl brGDGTs. However, many previous brGDGT studies on lake materials used one cyano column, which did not 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 brGDGT data without separation of 5- and 6-methyl brGDGTs in the Gonghai Lake (Cao et al., 2017). For temperature estimations, we listed the Eqs. (8–17~~6~~) used in this study in Table 2.

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 2017, water column stratification was weak with temperature ranging from 16.9 to 17.8 °C and exhibiting a gradual and slight decrease with depth (Fig. 2). In January 2018, 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 16–75 ng/g dry weight (dw) in surface soils from Gonghai catchment, 42–707 ng/g dw in lake surface sediments, 5–10 ng/l in September and 3–8 ng/l in January in water SPM (Table 1 and Fig. 2). The average content of brGDGTs in lake surface sediments (291 ng/g dw) was significantly higher than in surface soils (31 ng/g dw) and particularly exhibited an increasing trend with water depth. In SPM, ~~there was no significant difference in~~ the average concentration of brGDGTs in water column showed no significant difference between September and January (t = 1.2, p = 0.26) but there was a clearer trend of increase with depth in September than in January (Fig. 2). Notably, the compound IIIa'', which was regarded typical for in situ produced lacustrine brGDGTs (Weber et al., 2015), was also identified in the Gonghai Lake sediments and SPM but not found in catchment soils (Table1 and Fig. 3a). There was no significant difference in average concentration of IIIa'' in water column between September and January (t = 0.62, p = 0.28). The change patterns of IIIa'' with water depth in SPM and sediments were the same as those of the total brGDGTs (Table 1).

The brGDGTs in soils, sediments and SPM were dominated by brGDGT II and III series, with acyclic compounds dominant in every series (Fig. 3a). In comparison, the mean ΣIIIa/ΣIIa ratio value in sediments (1.14–1.52 range, 1.30 average) was higher than in SPM (0.84–1.11 range, 0.99 average) and soils (0.56–0.86 range, 0.70 average). 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 content in sediments (IR_{6ME} = 0.47–0.60 range, 0.51 average) and SPM (IR_{6ME} = 0.45–0.50 range, 0.48 average) (Fig. 3a).

3.3 Cyclisation ratio, methylation index of brGDGTs

The $\#Rings_{tetra}$ values varied from 0.26 to 0.45 (0.36 average) in catchment soils, 0.37–0.43 (0.40 average) in September and 0.39–0.42 (0.40 average) in January in SPM, and 0.45–0.47 (0.45 average) 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).

The MBT'_{5ME} values varied from 0.31 to 0.36 (average 0.35) in catchment soils, 0.23–0.29 (0.26 average) in surface sediments, 0.23–0.28 (0.26 average) in September and 0.24–0.26 (0.25 average) in January in SPM (Fig. 3b). Generally, the MBT'_{5ME} exhibited decreasing trends with water depth in surface sediments and SPM in September (Fig. 2). The MBT'_{6ME} values varied from 0.20 to 0.33 (0.25 average) in surface soils of the lake catchment, 0.22–0.27 (0.25 average) in surface sediments, 0.24–0.32 (0.28 average) in September and 0.26–0.28 (0.27 average) in January in SPM (Fig. 3b). The MBT'_{6ME} also decreased in SPM in September, but increased in sediments with water depth. Both MBT'_{5ME} and MBT'_{6ME} changed less in SPM in January with water depth (Fig. 2).

4 Discussions

4.1 In situ production of brGDGTs in the Gonghai Lake

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 potential sources, including allochthonous input from soil and autochthonous production in lake water and/or surface sediments, which can be distinguished by comparison of brGDGT~~s 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 higher than that in surface soils (Table 1). Moreover, they exhibited a clearly increasing trend with water depth, suggesting a possible autochthonous contribution, even though soil brGDGTs input cannot be ignored. Moreover, the brGDGT distribution in surface sediments was similar to that of SPM, but quite different from that of soils (Fig. 3a). Several lines of evidence indicate a substantial in situ production of brGDGTs in the Gonghai Lake. (I) The presence of IIIa" in the Gonghai Lake sediments and SPM but the absence in the catchment soils may be a direct evidence of in situ production in the lake (Fig. 3a). A similar conclusion has been drawn in a Swiss mountain lake basin (Weber et al., 2015). (II) In the Gonghai Lake, the $\Sigma IIIa/\Sigma IIa$ ratio in sediments (1.3 average) and SPM (0.99 average) were much higher than in catchment soils (0.7 average) (Fig. 3a). The values of

ΣIIIa/ΣIIa $\geq$0.92 has been regarded as the evidence of aquatic production in previous reports (Xiao et al., 2016; Martin et al., 2019; Zhang et al., 2020). (III) The average values of IR_{6ME} in surface sediments and SPM were significantly lower than in catchment soils (Fig. 3a), suggesting at least some of 5-methyl brGDGTs in lake sediments and SPM 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 (p <0.05 for $\#Rings_{tetra}$, p <0.01 for $\#Rings_{penta\_5ME}$), although $\#Rings_{penta\ 6ME}$ in sediments was similar to that in catchment soils (p = 0.11 for $\#Rings_{penta\_6ME}$; Fig. 3b).

~~**4.2 Soil brGDGTs reflect mean annual AT**~~

The in situ production of brGDGTs in the Gonghai Lake can be also evidenced by the discrepancies in reconstructed temperatures between soils and sediments/SPM. Based on the new global soil calibration of Eq. (9) and regional soil calibration of Eq. (10) for China, the brGDGT-derived AT in the Gonghai catchment soils ranged from 1.18 to 2.75 °C (average 2.33 ± 0.65 °C; Table 1~~Fig. 4a~~) and from −4.22 to −1.21 °C (average −2.42 ± 1.19 °C; Table 1), respectively. Considering the ±4.8 °C uncertainty of the global calibration and ±2.5 °C of the regional calibration, the estimated temperatures from the global calibration are much close to the mean annual AT of 4.3 °C, thereby well reflecting mean annual AT in our study lake catchment. Then, the global calibration Eq. (9) was applied to sediment/SPM data, yielding estimated temperatures −0.50 ± 0.78 °C in surface sediments and −0.55 ± 0.52 °C in SPM and hence much lower than those from surface soils (2.33 ± 0.65 °C; Table 1). Similarly, temperature underestimation using soil-derived calibration has been widely reported in many modern lake sediments (e.g., Tierney et al., 2010; Loomis et al., 2012; Pearson et al., 2011; Russell et al., 2018), which has been attributed to in situ production of brGDGTs in the lakes.

~~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 many modern lake sedimentsglobal 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.~~

4.2 Lacustrine brGDGT-derived ATs are warm season biased (average monthly temperature >0 °C)

~~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,~~ The suggested in situ production of brGDGTs prompts us to use lake-specific temperature 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) to reconstruct AT, although not differentiated quantitatively the relative contributions of aquatic vs. soil-derived brGDGTs. Here, we applied four equations, Eqs. (11) and (15)–(17) in Table 2, to our sedimentary brGDGT data.

As shown in Fig. 4a, the reconstructed temperatures using different equations are >6.4 °C. Despite discrepancies in the temperature values between calibrations, they are comparable considering the uncertainty of each calibration. A prominent feature of the reconstructed temperature is that they, especially those in the shallower sediments, are well above the annual mean AT but more close to the mean warm season AT (average monthly temperature >0 °C). This feature is consistent with numerous studies proposing that lacustrine brGDGT-derived ATs are warm season biased (Shanahan et al., 2013; Peterse et al., 2014; Dang et al., 2018).

~~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 in September were higher than in January, corresponding to the warmer water temperature in~~

~~September (Table 1Fig. 2). This suggests that brGDGTs in SPM can record lake water temperature changes, as previously 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 wellrespond to indicate temperature changes to some extent. However, air temperature has been found to be correlated well with MBT'$_{5ME}$5-methyl brGDGTs in African lakes (Russell et al., 2018), but with MBT'$_{6ME}$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 seem to reflect temperature changes in the water column to some extent, the differences of brGDGT-derived temperatures based on lake-specific calibrations between September and January (~0.3 °C) the measured difference (~13 °C). In fact, similar results have been also reported in other lakes. For example, in the Lower King Pond, the calculated seasonal temperature difference in surface water SPM was 5.4 °C, significantly smaller than the measured difference about 28.3 °C (Loomis et al., 2014); in the Huguangyan maar lake, the brGDGT calculated seasonal temperature difference was 8 °C, also significantly smaller than the measured difference about 16 °C (Hu et al., 2016). a long residence time of SPM, although not exactly known, in the water column. which may imprint multi-seasonal brGDGTs signals on the SPM, as previously 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 (Qian et al., 2019). Sediment resuspension, which may admix to the SPM 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 (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.~~

Many previous brGDGT instrumental analyses on lake materials used one cyano column, which did not 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 brGDGT-derived temperature is warm season biased in the Gonghai Lake irrespective of whether or not 5- and 6-methyl brGDGTs are separated.

~~Similar to our findings~~, ~~brGDGTs in many lake sediments are believed~~thought ~~to be mainly~~

~~sourced from aquatic production,~~Moreover, we found the warm season bias of reconstructed AT is increasingly apparent with the increase of latitude. Here, five lakes, 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), were selected to compare as an example. These lakes are located in different regions spanning a relatively large environmental gradient, and more importantly, brGDGT data from both the lake surface sediments and the surrounding soils are available. We re-calculated temperatures from published data of brGDGTs from these lakes (Fig. 5) by applying the calibration of global soils (Eq (8); Peterse et al., 2012) to the surrounding soils and the calibration of lake surface sediments (Eq (11); Sun et al., 2011) to the lake sediments. As shown in Fig. 5a, the brGDGT-inferred temperatures in catchment soils are similar to local mean annual ATs. In contrast, the brGDGT-inferred temperatures in lake sediments are similar to the local mean annual ATs only in low-latitude lakes, whereas they become increasingly higher than the local mean annual ATs toward higher latitudes (Fig. 5b). In comparison, the brGDGT-inferred temperatures are close to the local mean ATs in warm season (average monthly mean AT >0°C) in all these lakes (Fig. 5c). Besides above discussed lakes,~~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).~~ some investigations have also pointed out that brGDGT-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, or lower than, mean annual AT in low-latitude lakes (Tierney et al., 2010; Loomis et al., 2012). Therefore, it is a global occurrence that sedimentary brGDGT-derived temperatures are warm season biased in lakes at cold regions.

4.3. **Lacustrine brGDGTs reflect deep/bottom water temperature**

Another feature of sedimentary brGDGT-derived ATs in our results is that there is a consistently decreasing trend of reconstructed temperature with depth using Eqs. (11), (15) and (16) (Fig. 4a), albeit less clear using Eq. (15). It is not understandable that AT is correlated with water depth. Interestingly, both MBT'_{5ME} and MBT'_{6ME} in SPM showed decreasing trends with water depth in September, similar to the water temperature profile of the month (Fig. 2). In January, the relatively unchanged MBT'_{5ME} and MBT'_{6ME} (<0.02) also mirror the constant water temperature of the month (Fig. 2). Accordingly, we surmise that brGDGT-derived temperatures in sediments and SPM may actually reflect water temperature.

Although the MBT'_{5ME} and MBT'_{6ME} in SPM in the lake seem to reflect temperature changes in the water column to some extent, the differences of brGDGT-derived temperatures based on lake-specific calibrations between September and January (−0.93– to 1.21 °C) are much lower than the measured difference (~13 °C), independent of the calibration of (15), (16) or (17) (Tables 1 and 2). In fact, similar results have been also reported in other lakes. For example, in the Lower King Pond, the calculated seasonal temperature difference in surface water SPM was 5.4 °C, significantly smaller than the measured difference about 28.3 °C (Loomis et al., 2014); in the Huguangyan maar lake, the calculated seasonal temperature difference was 8 °C, also significantly smaller than the measured difference about 16 °C (Hu et al., 2016). The reduced seasonal contrasts in SPM brGDGT-derived temperatures could result from the existence of "fossil" brGDGTs and sediment resuspension in the water column, which may lead to a long (e.g., multi seasonal) residence time of SPM, although not exactly known (Loomis et al., 2014). The even smaller differences in MBT'_{5ME} and MBT'_{6ME} between sediments and SPM at deeper sites in our results (Fig. 2) suggest the impacts of sediment suspension on SPM. 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 (Qian et al., 2019). Besides, several parameters, such as ΣIIIa/ΣIIa, IR_{6ME}, $\#Rings_{tetra}$ and $\#Rings_{penta}$ in SPM were in-between the soil and sediment values, we speculate terrestrial inputs may be a factor, if any, to reduce the seasonal changes of brGDGTs in SPM.

In addition to reflecting water temperature, the decease trend with depth in sedimentary brGDGT-derived temperature further suggests a controlling influence of deep/bottom water temperature. Similar occurrence has been observed also in Lower King pond in temperate northern Vermont, U.S.A. and Lake Biwa in central Japan, showing that the sedimentary brGDGT-derived temperatures decreased with water depth, co-varied with mean annual LWT at depths (Ajiako et al., 2014; Loomis et al., 2014). Also in Loch Lomond in the UK, the brGDGT-derived temperatures by different MBT/CBT lacustrine calibrations all decreased with water depth (Buckles et al., 2014b). So, a water depth-related production of brGDGTs should be considered when interpreting brGDGT-derived temperatures, which will be discussed below.

We notice recent works suggesting that changes in microbial community composition may be responsible for variations in the distribution of brGDGTs, causing the different responses of soil brGDGTs temperature, as well as pH, under different temperature ranges (e.g., De Jonge et al. 2019). However, little is known about whether this idea is applicable to aquatic environments. According to De Jonge et al. (2019), community change can be indicated by the community index (CI = Community Index~~??~~) in soils, with CI >0.64 indicating warm community cluster and CI <0.64 indicating cold community cluster. Here we applied the CI to lake sediment data including ours and those available for the entire 15 brGDGT compounds in literature, mostly from the east Africa. As shown in Fig. 4b, the putative two community clusters also occur in lake environments, with the Gonghai community belonging to the “cold” cluster. Different from soil data showing that MBT'$_{5ME}$

captures large temperature changes only when the bacterial community shows a strong change in composition (De Jonge et al. 2019), it seems that MBT'$_{5ME}$ changes linearly with LWT, which is less influenced by the bacterial community change (Fig. 4b~~a~~). However, we note that the test of community change here is rather crude, and further studies on the biological sources of brGDGT and their response to temperature in aquatic environments are needed.

4.4 Ice cover formation as a mechanism for the apparent warm bias of lacustrine brGDGT-derived temperature

One explanation for the warm season biases of the lacustrine brGDGT-derived temperature in mid to high latitudes has been proposed as the excessive production of brGDGTs during the warm/summer season relative to 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 ng/l in September and 5.2 ± 2.3 ng/l in January (Fig. 2) with no significant difference. Besides, the compound IIIa'', which is likely specifically of aquatic origin (Weber et al., 2015), also showed no significant seasonal difference (0.36 ± 0.09 ng/l in September vs. 0.31 ± 0.15 ng/l in January). More importantly, the small differences in MBT'$_{5ME}$ and MBT'$_{6ME}$ of SPM and their derived temperatures between September and January suggest that the actual seasonal temperature difference, which may be recorded by the immediately produced brGDGTs, would have been substantially masked or smoothed by the predominance of fossil brGDGTs. In addition, brGDGT-derived temperatures in SPM were close to mean annual water temperature and lower than the mean annual warm water temperature, also did not support the excessive production of brGDGTs during the warm/summer season relative to winter season. Besides, the season of higher brGDGT 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 Lucerne (Blaga et al., 2011), and in summer in Lake Donghu in central China (Qian et al., 2019). However, in all these lakes in temperate climate zones, the brGDGT-derived temperatures have been found to be slightly or significantly warm season biased (Loomis et al., 2014; Qian et al., 2019; Fig. 5b). The above evidence suggests that other factors, other than seasonality in the production of brGDGTs in the lakes, should be responsible for the bias of brGDGT-inferred temperature toward warm season in higher latitudes (Fig. 5b and c).

~~Another explanation is lake water depth (wd), especially water stratification, can affect brGDGT distributionmolecular 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 brGDGT-derived temperature in lake sediments could be influenced by the vertically inhomogeneous production of brGDGTs with maximum in deep/bottom waters. This seems true in the Gonghai Lake as evidenced by the increase of sedimentary brGDGT content and the decrease of brGDGT-derived temperature with water depth as discussed above. 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 (micro)environment in deep/bottom water favors the production of brGDGTs (Woltering et al., 2012; Zhang et al., 2016; Weber et al., 2018). Such an occurrence could lead to higher proportion of 'colder temperature' brGDGTs in lake sediments, which may at least partly interpret the frequently observed cool bias of brGDGT-derived temperatures in many lakes, such as the Lake Challa, Lake Albert, Lake Edward and Lake Tanganyika (Tierney et al., 2010; Loomis et al., 2012; Buckles et al., 2014a). The MBT/CBT-derived temperature in the tropical Lake Huguangyan was thought to reflect mean annual AT (~~Sun et al., 2009;~~ Hu et al., 2015, 2016); however, has recently been proposed to be winter/cool biased (Chu et al., 2017). We suppose that, as a monomictic lake, the lower mean annual temperature than mean annual AT in deep/bottom waters might be a cause for the cool biased brGDGT temperature in the lake. Intriguingly, all the above lakes are in the tropics. Nonetheless, the deep/bottom water bias may be still true for the brGDGT-derived temperature in lakes in higher latitude, as suggested by our data in the Gonghai Lake. However, different from those tropical lakes, in higher-latitude lakes, including the Gonghai Lake (this study), Qinghai Lake (Wang et al., 2012), Lower King pond (Loomis et al., 2014), some cold-region lakes in China (Dang et al., 2018) and some Arctic lakes (Shanahan et al., 2013; Peterse et al., 2014), the sedimentary brGDGT-derived temperatures are all higher, not lower, than the mean annual AT. Therefore, more production of brGDGTs in deep/bottom water alone is not responsible for the warm bias of brGDGT-derived temperature in surface sediments at least in these lakes.

Although brGDGTs in lake sediments were confirmed to be mainly derived from in situ aquatic production, previous studies deemed that the estimated temperatures can still reflect AT by assuming that LWT is tightly coupled with AT (Tierney et al., 2010). In fact, such tight coupling can be found in tropical-subtropical lakes, where AT is always above the freezing point, 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 between water and air, leading to decoupling between LWT (usually ≥4 °C) and AT (<0 °C) in winter in cold regions. The decoupling makes mean annual ~~mean~~ LWT, even at the deep/bottom waters, higher than mean annual AT. Therefore, the greater warm biases of brGDGT-derived temperatures from surface sediments in higher latitudes (Fig. 5b~~a~~) could be due to the stronger decoupling (e.g., longer freezing time) between LWT and AT. Nevertheless, annual mean LWT appears basically close to the mean AT in warm season (average monthly temperature >0 °C) (Fig. 6f), which could be the reason why the brGDGT-inferred temperatures are similar to the mean warm season AT (Fig. 5c). 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 universal~~e~~ physical phenomenon in shallow lakes. In the 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 seasonality of the brGDGT temperature records. For example, the biases of brGDGT-derived temperatures toward summer AT observed extensively in the Arctic and Antarctic lakes (Shanahan et al., 2013; Foster et al., 2016) are compatible with the mechanism that we propose here. Of course, considering limited data in this study, more investigations are needed to test our viewpoint in future studies.

~~We also noticed that the seasonality of brGDGTs-derived temperature occurs in some other lakes also in tropical lakes.; however, there are disagreements in related studies. For example, sedimentary MBT/CBTbrGDGT-derived temperature from lake-specific calibrations was unusual higher than Ning et al., 2019).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 thesethis tropical lakes because ice cover does not form even in cold seasonwinter 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). in mid to high latitudes, they~~ likely~~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~~ brGDGT distribution~~s~~ 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 on its surface and a constant 4 °C condition in the underlying water in winter. The brGDGT distribution in sediments were similar to that in SPM but differed clearly from that in soils, indicating mainly in situ production of brGDGTs in the lake. BrGDGTs in SPM showed little seasonal differences in concentration and MBT'_{5ME}, likely due to a dominant contribution of fossil brGDGTs caused by, e.g., sediment suspension, which may mask any seasonal signals documented in sedimentary brGDGTs. The increase of brGDGT content and decrease of methylation index with water depth in sediments suggested more contribution of aquatic brGDGTs produced from deep/bottom waters. Based on available lake calibrations, we found that the temperature estimates in surface sediments and SPM of the Gonghai Lake were higher than the measured mean annual AT but close to warm season AT, which cannot interpreted by more aquatic production of brGDGTs in warm season and/or in deep/bottom waters. We found that such a warm biased brGDGT-derived temperature was actually close to the mean annual LWT, and therefore proposed that water-air temperature decoupling due to ice formation at the lake surface in winter, which can prevent thermal exchange between lake water and air, may be the cause for the apparent bias toward warm AT of lacustrine brGDGT-derived temperatures. Since the warm AT bias of brGDGT estimates has been observed extensively in mid- and high-latitude shallow lakes, we believe the mechanism proposed here could also 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

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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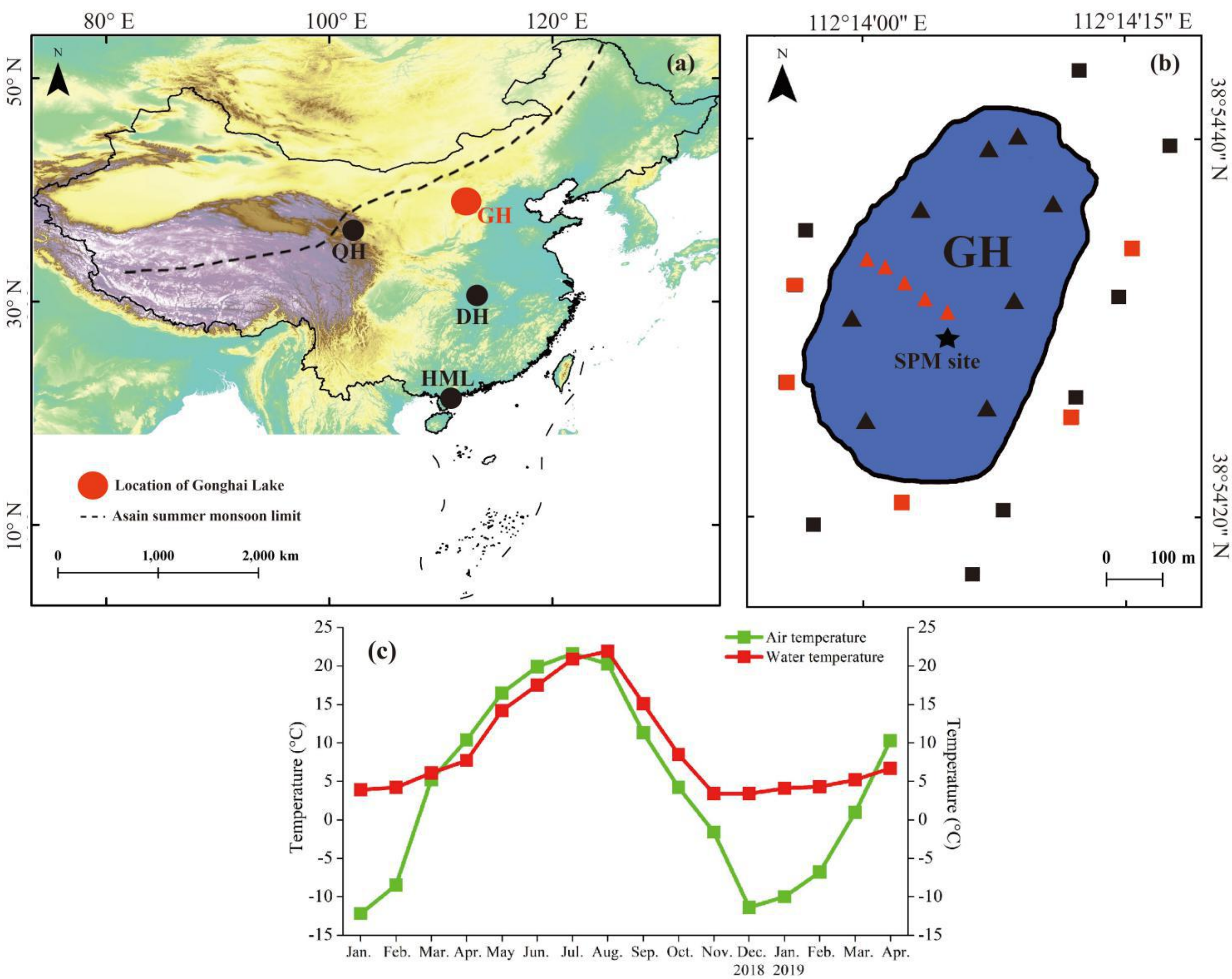

Fig. 1. (a) The Gonghai Lake (red circle), other referenced lakes (black circles) and modern Asian summer monsoon limit (dashed line; Chen et al., 2008). (b) SPM from water column (black star), surface soils (red squares) and surface sediments (red triangles) in Gonghai Lake in this study; black squares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

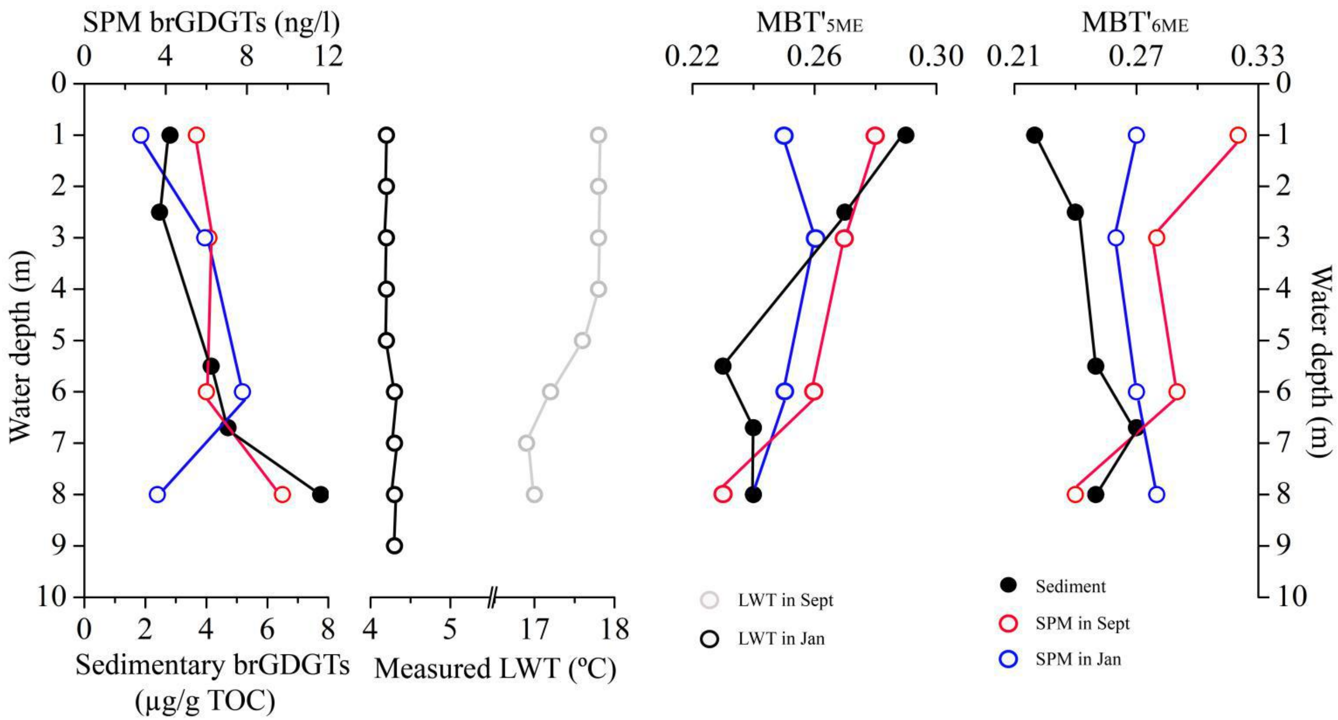

Fig. 2. Depth profiles of water temperature, brGDGTs concentrations, MBT'$_{5ME}$, MBT'$_{6ME}$ ~~in the Gonghai Lake~~ in water SPM from January and September and sediments in the Gonghai Lake.

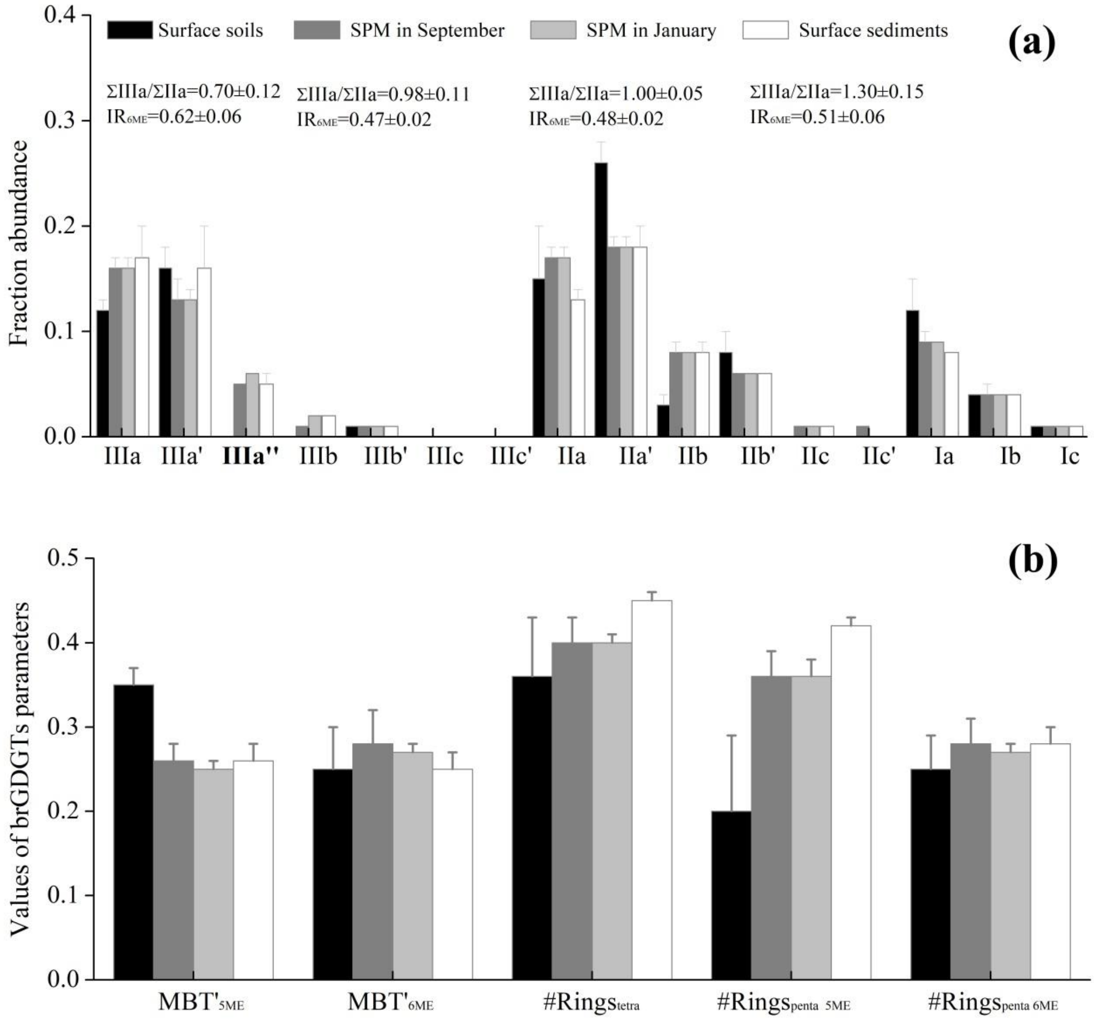

Fig. 3. BrGDGT distribution~~Composition distribution of brGDGTs~~ in surface soils, water column (SPM) and surface sediments of the Gonghai Lake. (a) ~~Relative~~Fracional abundance of brGDGTs. (b) Degree of methylation and cyclisation~~Methylation index and cyclisation ratio~~ of brGDGTs.

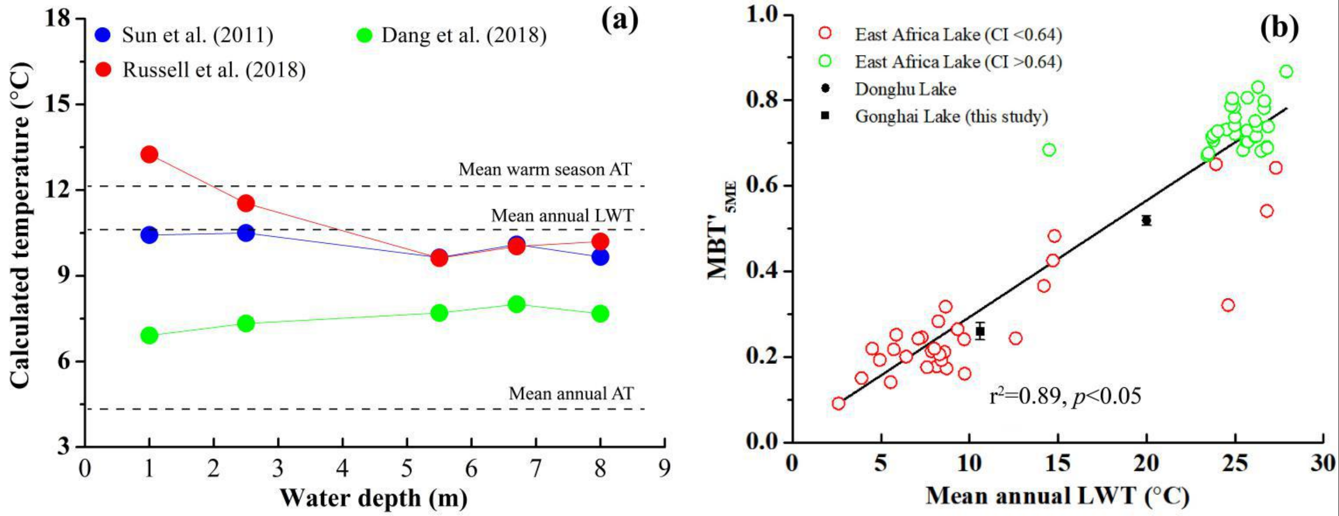

Fig. 4. (a)~~–~~ B~~b~~rGDGT~~s~~-derived temperatures for~~ surface soils,~~ sediments ~~and SPM using soils calibration from De Jonge et al. (2014). (b) brGDGTs-derived temperatures for sediments and SPM~~ using lake calibrations Eqs. (114), (15) and~~ Eq.~~ (16~~5~~) from Sun et al. (2011), Dang et al. (2018) and Russell et al. (2018) respectively. (b) The correlation between MBT'$_{5ME}$ of sedimentary brGDGTs and mean annual lake water temperature (LWT); CI index represents Community Index (De Jonge et al., 2019); the brGDGT data of East Africa Lake, Donghu Lake and Gonghai Lake were sourced from Russell et al. (2018), Qian et al. (2019) and this study.

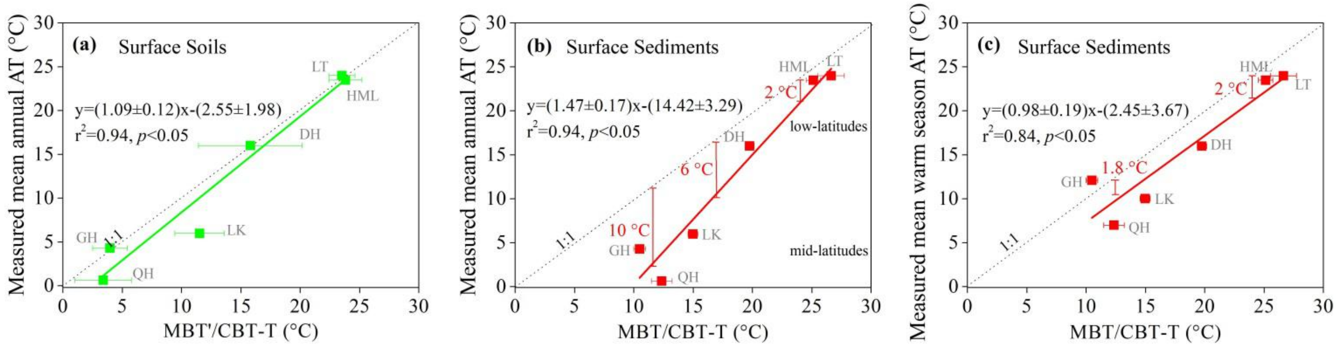

Fig. 5. Comparison of brGDGT-derived temperature and measured air temperature. (a) Measured mean annual AT and estimated temperatures of brGDGTs in surface soils based on soil calibration Eq. (9). (b) Measured mean annual AT and estimated temperatures of brGDGTs in surface sediments based on lake calibration Eq. (11). (c) Measured mean warm season AT and estimated temperatures of brGDGTs in surface sediments based on lake calibration Eq. (11). Data are from Gonghai Lake (GH; Cao et al., 2017), Lower King pond (LK; Loomis et al., 2014), Huguangyan maar (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).~~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).~~

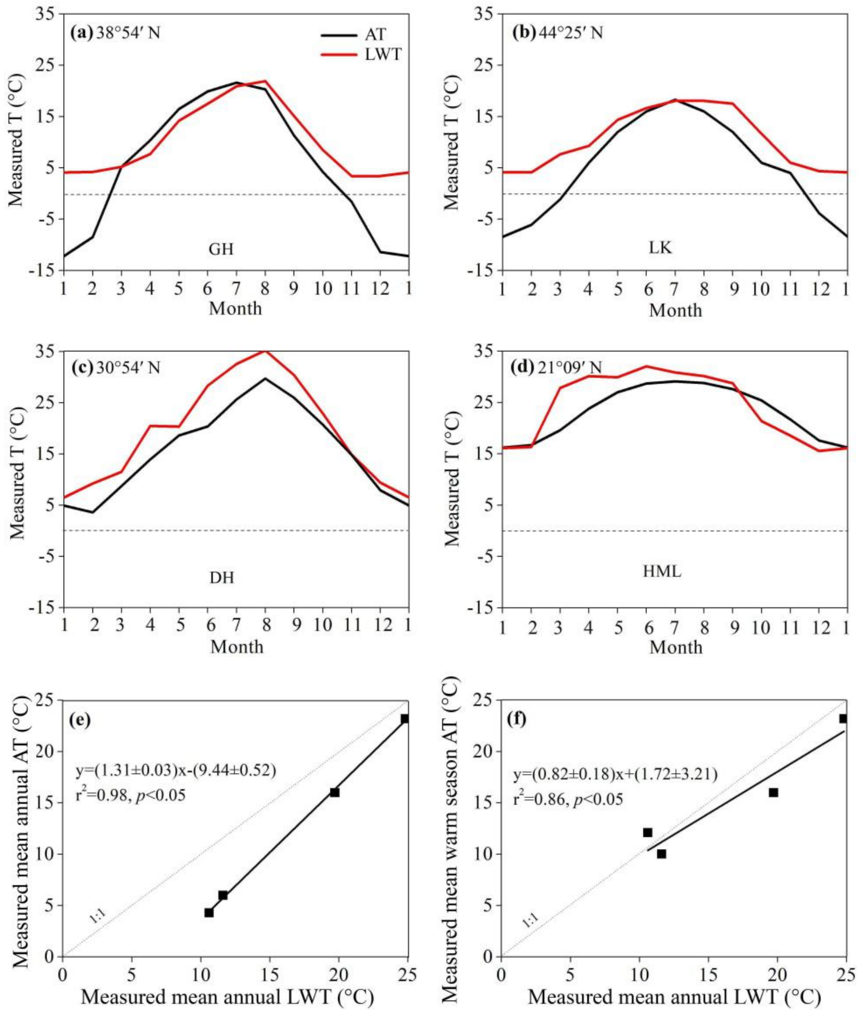

Fig. 6. Measured LWT and AT in (a) Gonghai Lake (GH; this study), (b) Lower King pond (LK; modified from Loomis et al., 2014), (c) Lake Donghu (DH; modified from Qian et al., 2019) and (d) Lake Huguangyan (HML; modified from Hu et al., 2016). (e) Correlation between mean annual AT and mean annual LWT. (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.

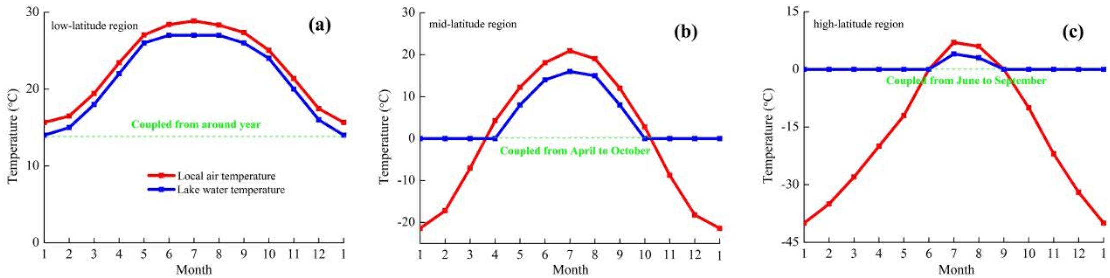

Fig. 7. A simple model showing the relationship between LWT and AT in different latitudes

Table 1 Concentration of brGDGTs, MBT'_{5ME}, MBT'_{6ME}~~calculated indices~~ and estimated temperatures in catchment surface soils, sediments and water column SPM ~~from~~in the Gonghai Lake.

Code of site	Longtitude (E)	Latitude (N)	Vegetation type	Water depth (m)	IIIa''	Total brGDGTs (ng/g dw) (ng/L)	MBT'_{5ME}	MBT'_{6ME}	MAAT [a] (°C)	MAAT [b] (°C)	MAAT [c] (°C)	MAAT [d] (°C)	Growth AT [e] (°C)
Surface soils in Gonghai catchment													
S1	112° 14'19.039"	38° 54'37.343"	grass		0	74.82	0.31	0.21	1.20	-2.90			
S2	112° 14'18.460"	38° 54'28.750"	grass		0	23.50	0.36	0.20	2.58	-1.21			
S3	112° 14'24.140"	38° 54'23.098"	shrub		0	22.00	0.35	0.33	2.40	-4.22			
S4	112° 14'36.827"	38° 54'27.126"	shrub		0	32.65	0.36	0.26	2.64	-2.15			
S5	112° 14'40.502"	38° 54'38.174"	grass		0	16.06	0.36	0.24	2.82	-1.61			
Gonghai surface sediments													
D1	112° 14'22.963"	38° 54'36.357"		1.00	1.46	42.03	0.29	0.22	0.70	-4.24	8.35	13.50	6.91
D2	112° 14'24.004"	38° 54'35.903"		2.50	1.59	33.95	0.27	0.24	-0.13	-4.79	7.50	11.91	7.33
D3	112° 14'25.109"	38° 54'35.294"		5.50	17.87	327.62	0.23	0.25	-1.19	-6.53	6.40	10.11	7.70
D4	112° 14'27.301"	38° 54'34.499"		6.70	25.53	374.29	0.24	0.27	-0.93	-7.32	6.67	10.57	8.00
D5	112° 14'28.453"	38° 54'33.980"		8.00	42.96	706.72	0.24	0.25	-0.95	-6.44	6.64	10.72	7.67
Gonghai SPM in Sept													
Water-1 m	112° 14'28.453"	38° 54'33.980"		1.00	0.29	5.71	0.28	0.32	0.24	-6.00	7.88	11.19	9.16
Water-3 m	112° 14'28.453"	38° 54'33.980"		3.00	0.36	6.39	0.27	0.28	-0.05	-5.46	7.57	10.86	8.25
Water-6 m	112° 14'28.453"	38° 54'33.980"		6.00	0.30	6.22	0.26	0.29	-0.35	-6.55	7.26	10.45	8.55
Water-8 m	112° 14'28.453"	38° 54'33.980"		8.00	0.49	10.07	0.23	0.24	-1.40	-6.79	6.18	10.60	7.31
Gonghai SPM in Jan													
Water-1 m	112° 14'28.453"	38° 54'33.980"		1.00	0.16	2.88	0.25	0.27	-0.75	-6.32	6.85	10.40	7.95
Water-3 m	112° 14'28.453"	38° 54'33.980"		3.00	0.36	6.09	0.26	0.26	-0.49	-5.57	7.12	11.02	7.77
Water-6 m	112° 14'28.453"	38° 54'33.980"		6.00	0.49	8.05	0.25	0.27	-0.65	-6.24	6.95	10.57	7.99
Water-8 m	112° 14'28.453"	38° 54'33.980"		8.00	0.22	3.71	0.24	0.28	-0.96	-6.89	6.63	10.20	8.24

MAAT represents mean annual air temperature.

[a] Calculated according to Eq. (9).

[b] Calculated according to Eq. (10).

[c] and [d] Calculated according to Eq. (16) and (17).

[e] Calculated according to Eq. (15).~~[a] Calculated after De et al. (2014)..~~

~~[b] and [c] Calculated after Russell et al. (2018).~~

[d] ~~Calculated after Dang et al. (2018).~~

Table 2 Calibrations for brGDGT~~s~~-derived temperature proxies ~~reported~~used in ~~previous~~this stud~~ies~~y.

Calibrations	Equation no. in the text	References
For soils		
MAAT=0.81-5.67*CBT+31.0*MBT' (n=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)
MAAT [a]=27.63*Index 1-5.72 (n=148, r2=0.75, RMSE=2.5 °C)	(10)	Wang et al. (2016)
For sediments		
MAAT=6.803-7.062*CBT+37.09*MBT (n=139, r^2=0.62, RMSE=5.24 °C)	(11~~0~~)	Global, Sun et al. (2011)
MAAT=8.263-17.938*CBT+46.675*MBT (n=24, r^2=0.52, RMSE=5.1 °C)	(12~~1~~)	Regional, Sun et al. (2011)
MAAT [~~a~~b]=50.47-74.18*f(IIIa)-31.60*f(IIa)-34.69*f(Ia) (n=46, r^2=0.94, RMSE=2.2 °C)	(13~~2~~)	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)	(14~~3~~)	Loomis et al. (2012)
Growth AT=21.39*MBT'_{6ME}+2.27 (n=39, r^2=0.75, RMSE=1.78 °C)	(15~~4~~)	Dang et al. (2018)
MAAT=23.81-31.02*f(IIIa)-41.91*f(IIb)-51.59*f(IIb')-24.70*f(IIa)+68.80*f(Ib) (n=65, r^2=0.94, RMSE=2.14 °C)	(16~~5~~)	Russell et al. (2018)
MAAT=-1.21+32.42*MBT'_{5ME}	(17~~6~~)	Russell et al. (2018)

AT represents air temperature.

MAAT represents mean annual air temperature.

[a] Index=log[(Ia+Ib+Ic+IIa'+IIIa')/(Ic+IIa+IIc+IIIa+IIIa')].

[b~~a~~] Fractional abundance of brGDGTs is a fraction of only brGDGT~~s~~ Ia, IIa and IIIa.

Table 3 Comparison of measured air temperature, brGDGT~~s~~-derived temperature from catchment soils and brGDGT~~s~~-derived temperature from sediments in different lake basins.

Name	Latitude	Longitude	Depth (m)	MAAT (° C)	Mean warm season AT (° C)	Mean annual LWT (° C)	Surface soils	Surface sediments				References
							MAAT [a] (° C)	MAAT [b] (° C)	MAAT [c] (° C)	MAAT [d] (° C)	MAAT [e] (° 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)

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

LWT represents lake water temperature.

[a] Calculated after according to Eq. (8).~~Peterse et al. (2012)~~

[b] and [c] Calculated according to Eq. (11) and (12)~~after Sun et al. (2011)~~.

[d] Calculated after according to Eq. (13)~~Tierney et al. (2010)~~.

[e] Calculated after according to Eq. (14)~~Loomis et al. (2012)~~.