September 12, 2018

Dear Editor Rousseau,

We are re-submitting the revised version of the manuscript "*A 900-year New England temperature reconstruction from* in situ*, seasonally produced branched glycerol dialkyl glycerol tetraethers (brGDGTs)*" for publication in *Climate of the Past*. Two referees, J. Hou and Anonymous, provided helpful feedback and comments that we utilized to improve the manuscript. Per their requests, major adjustments were made to the manuscript, particularly in the discussion section, to increase clarification and facilitate easier interpretation of our study. The major changes include: 1) the addition of two figures (Figures 7 & 8) to better clarify differences in brGDGT distributions between Basin Pond and other studies, 2) an expanded and re-organized Discussion section, addressing the utility of two published brGDGT calibrations using the same UHPLC method we used here (Section 5.2), and 3) the potential for human impacts on the brGDGT signal since the 1950s (Section 5.7). In addition, numerous minor revisions helped improve the readability of the manuscript and the figures. Overall, we feel that these revisions have resulted in a substantially improved manuscript.

The major critique both reviewers had of our work was the presentation of our data in terms of the MBT'_{5ME} index, rather than as an inferred temperature based on applying a published calibration. The two new figures (Figures 7 and 8) and a section in the Discussion (Section 5.2) have been added to address this. We note that while the two published brGDGT temperature calibrations of Russell et al. (2018) and Dang et al. (2018) show similar trends over the last 900 years, they differ in the expression of decadal- and centennial-scale variability. Furthermore, we now show that Basin Pond brGDGTs have a different distribution than those measured at other locations around the globe, underlining the fact that a local calibration is likely needed to provide the accurate temperature reconstructions. Although the current study has laid the groundwork for this (i.e. Supp. Fig. S1) the development of a proper local calibration is beyond the scope of this study, which is mainly focused on reconstructing climate over the past 900 years.

Overall, this work is important because it contributes to our knowledge of Northeast US Late Holocene climate using a brGDGT-based temperature proxy. Our interpretations are strengthened by detailed, *in situ* assessment of the production, transport, and deposition of brGDGTs in Basin Pond. For this reason, we feel our study is of interest to both the paleoclimate and proxy-development communities and is thus especially suited for *Climate of the Past*. It is clear from both reviewer comments that they fundamentally agree about the importance and potential impact of this work, and we believe that the changes we have made following their suggestions have made our study even stronger. We wish to sincerely thank them for their thoughtful reviews!

A document detailing the specific changes made in response to the comments of both reviewers has been provided along with the revised manuscript, and a manuscript with track changes. We look forward to your decision regarding our manuscript!

Sincerely,

Daniel R Miller

Daniel R. Miller (on behalf of all co-authors)

Point-by-point Response to Referee Comments

Referee #1 J. Hou

We would like to thank Dr. J. Hou for the insightful comments on our manuscript. We feel these comments have aided in creating a more well-rounded publication, and we have addressed these comments in the revised manuscript.

Miller et al. presented a well-designed experiment to investigate the seasonality of brGDGT proxies in this paper, which is helpful to understand the mechanism of the potential temperature proxy. The authors reconstructed temperature variation in the past 900 years and suggested they could differentiate anthropogenic and natural changes. I think it is a good try to understand the seasonality of brGDGT proxies, which is worthy to be published. However, there are some problems that the authors need to address before it is accepted for publication. Main comments:

1. The authors did not construct a transfer function between MBT'5ME and temperature, as they claim their proxy likely reflect September temperature. I suggest the authors try to construct a transfer function to show the temperature variation quantitatively.
This is addressed in the supplementary information provided with the manuscript. Although a temperature to MBT'5Me transfer function would be ideal, creating a temperature calibration based on four data points (see supplement), from our four SPM sampling dates, would be dubious. To help address this point, we have added a new section to the discussion (section 5.2) along with two new figures (7 and 8) comparing our MBT'5Me record to published temperature calibrations. However, constructing a regional temperature calibration is beyond the scope of this manuscript.

2. The authors compared their temperature reconstruction with pollen, hydrogen isotope and other records. The authors better explain difference between September T and pollen-inferred T. If they represent T variation in different seasons, why do they show similar variation?
In response to a comment by Referee #2, we have clarified the differences and similarities between temperature reconstructions based on pollen and brGDGTS and possible mechanisms for the differences in proxies (Page 13 Lines 19 – 24). In general, summer and fall temperature fluctuations share some variation, and the differences in the proxy reconstructions presented in Figure 9 are unlikely to be solely due to differences in the exact timing of proxy production. Rather, some of these differences are likely attributable to discrepancies between the age models and the sampling resolution of the published records. We have updated the text to reflect this (Page 13 Lines 19 – 24).

3. The authors attributed different trends in reconstructed T and measured T at the Basin Pond to Rotenone treatment. It seems that the Rotenone affected the algal community. What would the changes in algal community affect the bacteria? **Figure 11 shows relative abundances of both algal biomarkers and higher plant biomarkers (ß-sitosterol/stanol) to illustrate a widespread response of the biota in Basin Pond to the 1955 Rotenone treatment. We have added text (section 4.6; page 17 line 17 – page 18 line 2) to speculate on the response of brGDGT producers in Basin Pond to this treatment. However, it is unclear howrotenone treatment may have affected brGDGT-producing bacteria, which do not exhibit any clear changes in concentration before/after treatment. Because other aspects of lake productivity changed,**

we speculate that this may have affected the Basin Pond microbial community , including brGDGT producers. We have added a few sentences at Page 17, Line 29 – Page 18, line 2 to better clarify this point. Further work to quantify the impacts of anthropogenic changes on brGDGT producers, as well as to identify brGDGT producers (which remain unknown), is needed to better understand these relationships.

If bacterial community changed, why the proxy did not reflect temperature? In this case, why the proxy MBT'5ME would reflect over the past 900 years. **This is a good point, and its one that has generated much discussion. The veracity of our 900-year brGDGT-based temperature reconstruction is supported by its comparison to other paleorecords, and the clear relationship between MBT'_{5ME} and local temperature measured at Basin Pond. However, if we focus on simply the last 100 years, we observe cooling since 1970, in contrast to instrumental records of temperature change for the state of Maine (Figure 11). We have added much text in Section 5.6 detailing a few possible mechanisms for this effect (Page 16, Lines 19 – Page 17, Line 16). We note that all of these mechanisms may be affected by changes to the Basin Pond ecosystem initiated by the addition of Rotenone in 1955, which could have affected only the upper ~3.5 cm of the sediment column. Thus, the great majority of the 900-year brGDGT-based temperature reconstruction likely would not have been altered by anthropogenic impacts. This is supported by our comparison of the brGDGT-based record to other regional records, as well as by other published data (i.e. the age model for the Basin Pond cores BP2014-5D and BP2014-3D, which show no ^{14}C age reversals) (Miller et al. 2017).**

The examples that the author listed in Section 5.1 were all from surface sediment. Were they affected by anthropogenic activities? **We have made substantial changes to the manuscript – section 5.1 now discusses Sources and seasonal production of brGDGTs, while section 5.2 addresses the downcore calibration to temperature. The answer to this question posed by the referee deals with a number of previously published studies that are location-specific and vary regionally in terms of the type and extent of anthropogenic influence. It is beyond the scope of this study to revisit all of the existing studies for signs of anthropogenic influence. In addition, we do not think that the signal in the top ~3.5 cm compromises the veracity of our 900-year reconstruction, nor do we think that potential anthropogenically-influenced overprinting of brGDGT distributions in surface sediments compromises the robust correlation between brGDGT distributions and temperature that has been noted by an array of published studies (see Sections 5.3 and 5.4). Furthermore, ongoing research to calibrate the Basin Pond brGDGTs to temperature is being performed (see Supplementary materials). Nevertheless, this is an interesting question and merits future study.**

Overall, it seems to me that *the interpretation is not convincing.* **We hope that our responses to Referee #1's comments have clarified and supported our interpretation. We have made major changes to all discussion sections (5.1, 5.2, 5.3, 5.5, and 5.6) so that it clearly lays out our interpretation of the 900-year brGDGT-based record. We also note that while uncertainties to some aspects of the interpretation exist and may not be conclusively resolved at this time, our brGDGT and algal biomarker records from Basin Pond add a new and high-resolution record to available paleoclimate records for the NE US. In particular, there are relatively few terrestrial temperature reconstructions from Maine and our study helps to fill this gap. It is likely that as the brGDGT temperature proxy becomes better understood, and**

as new temperature calibrations are developed, the interpretation of our Basin Pond record will evolve accordingly. By presenting our data as MBT'$_{5ME}$ index values, we have made this easier for future studies ,which may revisit these data.

I wish the authors address the concerns in revision. We have tried to address all of **Referee #1's concerns in the revision.**

Referee #2 Anonymous

Referee #2 requested several revisions, primarily within the discussion section. One of the main issues that referee #2 addressed was the lack of applying a current published temperature calibration to the MBT'$_{5ME}$ record. In response, we have provided our Basin Pond MBT'$_{5ME}$ record plotted with 2 different temperature calibrations (Dang et al. 2018 and Russell et al. 2018; Figure 7) that were developed using analytical methods directly comparable to our own, i.e. separating 5-methyl and 6-methyl brGDGTs during HPLC analysis (Figure 7, Discussion section 5.2). Referee #2 stated that we should develop a calibration of our brGDGT observations to local temperatures, while also noting that we do not have enough data for such a calibration to be robust. We agree that we do not have enough data for such a calibration, and we would like to emphasize that the primary goal of this study was not to provide a brGDGT to temperature calibration for Basin Pond. Rather, our goal was to (1) present a new 900 year record and (2) understand the timing and depth profile of brGDGT production in Basin Pond in order to address potential seasonal bias in the 900-year brGDGT reconstruction. We agree with the referees in their assertions that a focused effort to develop a local calibration would be a useful contribution to the paleoclimate community's understanding of brGDGTs. Although this is beyond the scope of this manuscript, our preliminary data have been plotted against local temperature in the supplementary materials (Figure S1), as future efforts to develop a local calibration should incorporate these data. The main purpose of including this in the supplement was to highlight the potential of Basin Pond for future paleoclimate reconstructions.

- The interpretation of the brGDGT data along the sedimentary core is only based on the MBT5Me index. Absolute temperatures based on the calibration developed by Sun et al. (2011) or Russell et al. (2018) are comparable (difference of ca. 1 °C, within the range of the uncertainty associated with brGDGT calibration) and should be provided in the main text, all the more as it does not change the interpretation of the data.

In the original manuscript, we presented our data as MBT'$_{5ME}$ values rather than applying a temperature calibration because the two existing calibrations based on methods that separate 5-methyl and 6-methyl brGDGTs were developed from lakes located in different regions (China and Africa) (Dang et al. 2018, Russell et al. 2018) than mid-latitude Basin Pond. We feel that these calibrations should be treated with caution when attempting to interpret absolute temperatures at Basin Pond. However, based on the request of the reviewer, we have plotted our data on these 2 different temperature calibrations (Dang et al. 2018, Russell et al. 2018) in a new figure (Figure 7), along with additional discussion (Section 5.2), in the main text of the manuscript. To summarize, this is presented in the revised manuscript as 1) an additional figure with MBT'$_{5ME}$, growth temp (Dang et al. 2018), and mean annual air temp (Russell et al. 2018), and 2) a ternary plot showing that brGDGT distribution in the Basin Pond samples and African Lakes samples are distinct (Figure 8). These figures highlight that applying either previously published brGDGT temperature calibration to Basin Pond samples may be misleading, and therefore we present our data as the MBT'$_{5ME}$ index values in Figures 9 and 10. Other temperature calibrations mentioned by the referee (e.g., Sun et al. 2011) are based on different analytical methods that did not fully separate 6-methyl isomers (MBT/CBT proxy; Weijers et al., 2007), and are therefore not suitable calibrations to apply to our MBT'$_{5ME}$ record.

- I would be very cautious about the preliminary calibration between MBT derived from SPM samples and temperature, as it is based on only 4 samples.

We agree and because we are also very cautious about this preliminary calibration based on few data points, we placed it in the supplement rather than the main text. We have re-emphasized this in the main text to better state this important point (Page 12, Line 27 – Page 13, Line 2).

- A local calibration between seasonal temperature (fall temperature, when brGDGTs are preferentially produced in this New England lake) and brGDGT distribution should be developed and used for temperature reconstruction along the sedimentary core.

We agree, and this is an area of our ongoing research. However, this is beyond the scope of the present work. Please see specific comments below for more details.

- The discussion section, especially the *comparison of the present record with other regional ones*, is sometimes difficult to follow, as some explanations are missing and all the data necessary for the understanding of the reasoning are not presented. I recommend a *more careful and more detailed interpretation* of the data.

We agree and thank the referee for this suggestion, and have revised the discussion text to make it easier to followand more detailed. Changes to the text to address this point include several substantial changes, as well as numerous minor revisions, of the discussion section 5.3 (Page 13, Line 15 – Page 14, Line 17). These are outlined in detail below.

- Several lipid biomarkers were analyzed in the lacustrine sediments and revealed some variations in the lake productivity over time, related to anthropogenic influence. Nevertheless, the authors should better discuss the *potential human impact on the brGDGT signal*.

We agree, and text discussing the potential human impact on the brGDGT signal, as well as clarification of our interpretation involving anthropogenic impacts, has been added in Section 5.6. Furthermore, we have added an additional section discussing human impact in the region (section 2.1, Page 4 Lines 19-29). We have also addressed this in our response to Referee #1. However, we note that there is a general lack of knowledge on brGDGT producers, we therefore do not wish to speculate too much on this subject. We hope that in the revised manuscript we achieved a good balance between complete discussion of the potential influences without being overly speculative.

- Disentangling natural and anthropogenic signals in lacustrine records is a key question which should be addressed.

We agree that this point needed better in-depth discussion. We have noted the potential anthropogenic influence on the upper 3.5 cm of our reconstruction following the addition of Rotenone to the lake in 1955 (Section 5.6, Page 17, Line 17 – Page 18, Line 2). Furthermore, we have added text detailing anthropogenic influence at Basin Pond in Section 2.1 (Page 4 Lines 19-29), and have provided evidence that the majority of our 900 year record is not subject to this kind of anthropogenic disruption seen in the 20th century (sections 5.3-5.4). Unfortunately, the precise impact of any kind of anthropogenic disturbance on brGDGT reconstructions is hindered by an incomplete understanding of the organisms responsible for

brGDGT production in general. We leave this to future work in the brGDGT scientific community.

Other detailed comments are given below.

Page 2

Line 18. Late fall rather than early spring.
fixed.

Line 20. De Jonge et al., 2014 instead of 2013.
fixed.

Lines 25-30. Please also add some recent papers examining the distribution of 5- and 6-methyl brGDGTs in lakes: Russell et al., 2018 and Dang et al., 2018 both in Organic Geochemistry. **These references, which have been published since the first draft of this paper was composed, have been added and discussed in detail throughout the paper.**

Page 3

Line 21. How long were the cores kept refrigerated? What about the evolution of organic matter (and especially brGDGTs) during storage?
The cores were collected in March 2014 and were stored unsplit and refrigerated in conditions similar to those at the lake floor (4ºC, in the dark) for one month prior to subsampling (this information has been added to Page 5, lines 8-9). Although growth and alteration of the brGDGT signal during storage is a potentially important form of diagenesis, the sample processing in question is relatively rapid compared to some other existing studies that have utilized brDGTs (i.e. these cores were not stored for years prior to subsampling). This core storage information has been added to the manuscript. We note that while this point should be investigated by future studies, many previous brGDGT studies have been done on old sediments and this is not believed to be a significant factor influencing the brGDT records (e.g., Weijers et al. 2007 Science).

Line 29. All samplings were performed after a period of 28 to 40 days, except the last point. What is the reason for such a long accumulation time (264 days)?
The sediment traps, which were designed and constructed at UMass, required us to enter the water to pull up the traps and therefore were only retrieved while the lake was ice-free. During the winter we were not able to pull out the sediment traps because entering the water was not possible. Additionally, cutting numerous large holes into the ice would have presented a safety hazard for the people utilizing Basin Pond for winter recreation and we were advised not to do this. We have added text discussing this in Section 2.3 (Page 5, Lines 18-23).

Page 4

Lines 5-6. These 5 dates should be specified once again in the present manuscript to make easier the reading of the manuscript. **We agree – we have restated these 5 dates with much more clarity in the methods (Section 2.3, Page 5, Lines 18-23) and in the discussion, and have endeavored to make it clear when sampling took place throughout the manuscript. To facilitate easiest reading of the manuscript, we refer to each sampling period as the month at the midpoint of the period occurs.**

Line 9. According to Fig. 1, 20 soil samples were collected around the lake, which is not consistent with the number given in the text. This should be corrected. **Thank you- this is now correct, and the number of soil samples (10 samples) we analyzed matches the number of samples in Fig. 1.**

Lines 14-17. Why were the TLE from SPM/soils on the one hand and lake sediments on the other hand separated differently? **For the purposes of this study, we are only interested in compounds that eluted in the apolar and polar fractions. Another study using the ketone fraction of the sediment core has already been published (Miller et al., 2017) and initially was designed to look for lacustrine alkenones (they were not present). The SPM/soil samples were measured solely for this study, after we determined separating out the ketone fraction was unnecessary. However, we note that our separation procedure does not omit any compounds. For the SPM/soil samples, any compounds that would have eluted in the ketone fraction end up in the polar fraction.**

Line 19. Please specify here the different algal biomarkers which will be analyzed. Lines 21-26. **This has been added in a new section of the results (section 4.6, page 9, line 26 – page 10, line 4).** Please specify if the GC injections were made in split or splitless mode. **Injections were made in splitless mode. This has been added to section 3.2 (page 6, line 27).**

Page 5

Lines 1-10. A short introduction of 5- and 6-methyl brGDGTs and the related indices should be added. Were some samples injected in duplicate/ triplicate? *What is the analytical uncertainty on the MBT, CBT and IR indices?* **We have added an introduction to 5- and 6-methyl brGDGTs (Page 3, Lines 3-14). In addition, section 4.5 "BrGDGT isomer ratios" also discusses this topic (page 9, lines 19-25). A subset of the samples (n=32) were analyzed in duplicate. The analytical uncertainty from these measurements has been added to this section (page 7, lines 18-20).**

Lines 20-25. The relative abundances of brGDGTs in all the samples (soils, SPM, lake sediments) should be given in a supplementary table. **All Basin Pond data presented in this manuscript will be archived at the NOAA Paleoclimate Data Center when the manuscript is accepted for publication.**

Acyclic and cyclic brGDGTs (Ia, Ib and Ic; IIa, IIb and IIc; IIIa, IIIb and IIIc) cannot be distinguished in Fig. 2. The figure should be modified to take this comment into account. **We have noted relative abundances of the b and c compounds (although they are very small) on Page 8 lines 13-14. As this manuscript does not explicitly discuss the differences in abundances of**

the a b, and c, we chose not to display them in Figure 2 to make the figure more readable. Interested parties can access the a, b, and c data in the data tables available upon publication.

The different types of green are difficult to distinguish in Fig. 2. Please choose more contrasting colours. **We have updated this figure to use more contrasting colors.**

The brGDGT distributions are not consistent through the four collection periods: the relative abundance of GDGT I decreases from June 2014 to January 2015, in contrast with brGDGT III. **We originally made this observation on Page 6, lines 12–14. However, in June and July 2014, Group I brGDGTs were the most abundant, whereas in September 2014 and January 2015, reductions in Group I brGDGTs were accompanied by increases in Group III brGDGTs. We removed the sentence about distributions being consistent through time, and added additional sentences that accurately describe the changes (Page 8, Lines 14-19).**

Page 6

Lines 4-5. These sentences are redundant with those in lines 1-3. **This paragraph was rearranged for clarity and to reduce redundancy. However, we note that we separately discuss brGDGT fluxes and brGDGT distributions in this paragraph (which now appears at page 8, line 20-Page 9, Line 2); while it may seem like there is redundancy, we find upon careful reading of these lines that all of the information presented is new and necessary.**

Lines 24. These concentrations are not present either in a Fig. or a Table. Please provide the bulk data as Supplementary material. **All Basin Pond data will be archived at the NOAA Paleoclimate Data Center when the manuscript is accepted for publication.**

Lines 27-29. These multidecadal events are difficult to distinguish. **Thank you - to aid the reader in distinguishing these events, we have listed the specific timing of the multidecadal events in the manuscript (Page 9, Lines 13-16).**

Page 7

Line 1. Please add also the recent paper by Russell et al. (2018) to the list of brGDGT lacustrine calibration. **In the original manuscript, the first sentences of the paragraph were discussing older lakes calibrations. The revised manuscript has an entirely new section (section 5.2) discussing the Russell et al. (2018) calibration for African lakes, as well as the Dang et al. (2018) calibration for Chinese lakes.**

Lines 9-13. The different arguments provided here are not convincing. The recent lacustrine calibration by Russell et al. (2018) could be applied to the NE US lakes, with all the caution needed (not the same region, difference in terms of stratification/mixing etc.). This is indeed the only calibration based on the recent analytical method proposed by Hopmans et al. (2016) allowing the separation of 5- and 6-methyl brGDGTs. Furthermore, as shown in Supp. information, the temperature variations inferred from the Russell et al. calibration are similar to those derived from the calibration by Sun et al. (2011). Therefore, the different calibrations provide different absolute temperatures (still very close, ca. 1 °C difference) but similar trends.

We have made major revisions to the Discussion, including adding a new section (5.2) and presenting our data in Figure 7 with the Russell et al. 2018 African Lakes calibration and the Dang et al. 2018 Chinese Lakes calibration, as these are the only calibrations based on the analytical method used in this study. In order to highlight the caution needed when interpreting these results, we have also added a ternary diagram to this section (Figure 8) as well as a new paragraph of information (page 12, line 21 – page 13, line 2), which shows that brGDGT distributions of the samples in this study fall well outside those of the African Lake and Chinese Lake samples. This means the brGDGT producers in Basin Pond, and their sensitivity to temperature, are potentially different from those in the lakes studied by Russell et al. 2018 and Dang et al. 2018. We therefore wish to emphasize that presenting the data in this way requires caution, as it invites a suite of misinterpretations for readers who are not familiar with the proxy. Because of this, we decided to present our data as MBT'$_{5ME}$ values in Figures 9 and 10, and indicated with words and colors in these figures that higher MBT'$_{5ME}$ values indicate higher temperatures, and vice versa.

Line 18. Only group I and III brGDGTs can be distinguished, not the individual compounds. **We have corrected the text to reflect this. We note that the b and c compounds make up <2% of the relative abundance in our samples. The full data will be available online with the NOAA Paleoclimate Data Center for interested parties.** CBT'5Me and MBT'5Me were inverted in Fig. 6. **Thank you - this has been fixed.**

Line 22. Lower instead of higher. **Thank you - this has been fixed.**

Page 8

Lines 1-6. This is redundant with the sentences above. **Thank you – we have edited this paragraph to eliminate redundancy.**

Lines 6-10. In addition to the brGDGT distribution, the brGDGT concentrations in soils, lake and SPM should also be compared. **brGDGT fluxes are explicitly discussed with reference to the SPM samples (e.g. Section 4.2, Page 8, Lines 12 – Page 9, Line 2, Figure 3). brGDGT concentrations in soils (Section 4.1, Page 8, Lines 7-10) and sediments (sections 4.3-4.4, Page 9, Lines 3-17) are also noted. These quantities do not have the same units and are thus not directly comparable. Furthermore, brGDGT concentrations have a wide range of values in the literature, making it difficult to interpret how the soil, sediment, and SPM concentrations compare and how they represent relevant environmental parameters. However, we have added in text stating that brGDGT concentrations in the Basin Pond sediment record do not correlate with MBT'5Me values, indicating that they are decoupled (Page 13, Lines 7-9).**

Lines 11-12. I would be very cautious about the MBT'5Me/temperature local calibration, as it is based on only 4 points. **We agree - this reasoning is why we put it in the supplement and noted that future work should address this promising but presently thin calibration.**

Lines 13-14. Where are the water temperature data? **Water temperature data are presented in Figure 4(a), and we have added a citation (Frost, 2005) which details the yearly cycle of water temperatures as a function of depth in Basin Pond.**

Lines 25-26. Such a calibration should have been developed in the present study and then applied to the downcore brGDGT reconstruction. **We have removed this sentence. Because of the limited number of SPM samples we were able to collect for this study, it is not a calibration experiment and should not be considered as such. Instead it is a detailed assessment of seasonal production biases coupled with the downcore application of a powerful emerging paleotemperature proxy.**

Line 31. These concentrations should be provided as Supp. Material. **These concentrations are included in the data tables that we will archive at the NOAA Paleoclimate Data Center upon publication.**

Line 33. Please remove the last sentence which is not useful. **This sentence has been removed.**

Page 9

Line 9. Please be more explicit about similarities and differences between pollen and MBT'5Me reconstructions. **Text further discussing the differences and similarities, as well as expected differences in proxies, has been added in Section 5.3 (Page 13, Lines 16-24).**

Line 16. Please provide some references here. Are hydrogen isotopes from leaf waxes not mainly used are hydrological proxies? **Hydrogen isotopes of leaf waxes can reflect changes in temperature (e.g. high-latitude sites) changes in hydrological processes (e.g. tropical sites), changes in the dominant moisture source, or a mix of these and other processes, and interpretation is dependent on site-specific parameters. This is briefly discussed in the text (Page 2, Lines 15-17) but the details of these processes are beyond the scope of this study. We provide the δD record from Gao et al. 2017 with its published interpretation (as a temperature proxy) because it is one of the few available records from New England.**

Lines 16-21. This paragraph should be more developed. How are temperatures reconstructed from delta D of leaf waxes? **We have attempted to clarify the manuscript text that Gao et al. (2017) interpret their δD record as a temperature proxy (at page 13, lines 25-26). We provide these data simply for comparison to our own record. We do not wish to question the published interpretation of Gao et al. (2017) of δD as a temperature proxy.**

Line 28. Where are this information derived from? Fig. 7d? **This information is derived from comparison between Figure 9g and Figure 9d–f. This has been updated in the text (Page 14, Lines 12-13).**

Lines 29-32. The conclusion about the predominant human impact on fires remains speculative and is difficult to apprehend. **We agree. The speculative sentence about the causes of fire changing through time has been removed.**

Page 10

Lines 13-15. The similarities between Basin Pond reconstruction and other northern hemisphere reconstructions are difficult to visualize. **We have made the text more explicit about the similarities and differences between the Basin Pond reconstruction and northern hemisphere reconstructions (Page 14, Lines 24-29).**

Page 11

Line 2. What do the authors mean by "not a strong cross correlation? *Please provide r and p values.* **Fixed. r and p values have been added to text (Page 15, Line 21; Page 16, Line 5).**

Lines 13-14. This trend is difficult to visualize. **We are unsure exactly which trend the referee is referring to but all the trends discussed are shown in Figure 10. Additional text was added to Section 5.4 to guide the reader to see all the trends we describe (Page 14, Lines 24-29; Page 15, Line 8). We have also clarified this paragraph by removing superfluous information regarding other trends that are not relevant to the present manuscript.**

Lines 17-18. What is the interest of presenting local data since the authors consider them as inaccurate? I would only present statewide trends. **We agree. We have adjusted the text(Page 16, Lines 11-17) and Figure 11 to remove local data and to only show statewide averages.**

Lines 24-27. This is a little too short. What are exactly the mechanisms which could explain the lower MBT'5Me values in surficial sediments? **We have added discussion, which lists possible mechanisms to explain this trend without speculating too much about our own data (Page 17, Lines 4-7). Furthermore, we have cited other studies (e.g. Tierney et al., 2012; Sinninghe Damste et al., 2012) that show a similar trend in the uppermost surface sediments, and discussed the fact that the responsible mechanisms are not known (Page 17 Line 30 – Page 18, Line 2).**
Some of these "mechanisms" may be lake-/region-dependent. **We agree.**

Page 12

Lines 4-16 / Fig. 9a. The different algal biomarkers are difficult to distinguish in Fig. 9a. Please use contrasting colours for each biomarker. **We agree with the referee that the way it was arranged made it difficult to distinguish the colors and link them to the respective biomarkers. We have edited this figure to make it more reader-friendly in response to the referee's request. However, in order to present data in a color-blind friendly manner, we decided to stick with shades of gray. After uploading this figure to an online color blindness simulator, we have confirmed that it is viewable in its current format to all readers.**

Supplementary information

Page 1

Line 17. Where is Table S1? **Table S1 is the first table in the supplement, but was mislabeled as S2. This has been fixed.**

Line 27. Where are the fall measurements? **The average measured temperatures for each of the sediment trap collection periods are listed in Table S2.**

Page 2

A MBT'5Me-temperature calibration should have been developed in the present study. **We agree with several of your comments above that while this is a fantastic goal, we found that a correlation based on only four scattered points would be spurious (see following comment). Nevertheless, we do present a preliminary calibration in the supplement and supplementary figure S1 plots the Basin Pond brGDGT record on this calibration.**

The correlation presented in Fig. S1, based on only 4 scattered points, is not reliable. We agree. **This was our reasoning as to why we chose to include it in the supplement and not actually apply it to the data in the main text.**

A 900-year New England temperature reconstruction from *in situ* seasonally produced branched glycerol dialkyl glycerol tetraethers (brGDGTs)

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Abstract. Paleotemperature reconstructions are essential for distinguishing anthropogenic climate change from natural variability. An emerging method in ~~paleoclimatology~~paleolimnology is the use of branched glycerol dialkyl glycerol tetraethers (brGDGTs) in ~~lacustrine~~ sediments to reconstruct temperature but their application is hindered by a limited understanding of their sources, seasonal production, and transport. ~~We~~Here, we report seasonally resolved measurements of brGDGT production ~~within~~in the water column, in catchment soils, and in a sediment ~~sequence~~core from Basin Pond, a small, deep inland lake in Maine, USA. ~~BrGDGT distributions in the water column are distinct from catchment soils but~~ We find similar ~~to the~~brGDGT distributions in both water column and lake ~~sediments,~~sediment samples but the catchment soils have distinct brGDGT distributions suggesting that (1) brGDGTs are produced within the lake and (2) this in situ production dominates the downcore sedimentary signal. Seasonally, depth-resolved measurements indicate that ~~the dominant~~most brGDGT production ~~of brGDGTs~~ occurs in late fall~~/early spring~~, and at intermediate depths (18-30 meters) in the water column. We ~~apply~~utilize these observations to help interpret a ~~900-year-long~~Basin Pond brGDGT-based temperature reconstruction ~~and find that it shows~~spanning the past 900 years. This record exbibits similar trends to a pollen record from the same site and also to regional and global syntheses of terrestrial temperatures over the last millennium. However, the Basin Pond temperature record ~~also~~ shows higher-frequency variability than has previously been captured by such an archive in the Northeastern United States, potentially attributed to the North Atlantic Oscillation and volcanic~~/~~ or solar activity. This ~~is the~~ first brGDGT- based multi-centennial ~~paleoreconstruction~~paleo-reconstruction from this region ~~and~~ contributes to our understanding of the production and fate of brGDGTs in lacustrine systems.

1 Introduction

~~Climate~~Anthropogenic climate change is one of the most complex and challenging issues facing the world today~~. The~~ and its impacts ~~of anthropogenic climate change~~ will likely be exacerbated in heavily populated ~~regions~~areas, such as the Northeastern United States (NE US) (Fig. 1), ~~which is~~a region comprised of communities that have been historically susceptible to climate change (Horton et al., 2014). Here, over the past 120 years~~,~~ average temperatures have increased by ~1°C, precipitation has increased by 10%, and sea levels have ~~also~~ risen by ~40 cm (Kunkel, 2013; NOAA, 2014). While historical records document the temperature increase of the past century, they are not long enough to capture the underlying variability of the pre-anthropogenic period. Therefore, high-resolution paleotemperature records, such as those developed from lacustrine sedimentary sequences, are needed to investigate how current climate change compares to long-term natural variability. A regional synthesis of NE US late Holocene climate variability by Marlon et al. (2017) reviews~~ previous~~ temperature reconstructions from terrestrial sediment records using methods such as pollen (Gajewski, 1987; Webb et al., 2003; Oswald et al., 2007), testate amoeba (Clifford and Booth, 2013), and leaf wax hydrogen isotopic ratios (Huang et al., 2004, Shuman et al., 2006; Gao et al., 2017). However, these climate proxies may also reflect changes in parameters other than temperature (i.e., precipitation~~ trends~~, humidity, evapotranspiration, and vegetation ~~changes~~) (Gajewski, 1988; Hou et al., 2008; Marlon et al., 2017). Therefore, additional quantitative paleotemperature records are needed to accurately assess ~~the history of~~past temperature ~~variations~~variability in ~~this region~~the NE US (Marlon et al~~.~~., 2017).

Branched glycerol dialkyl glycerol tetraethers (brGDGTs), found globally in lakes, soils, rivers, and peats, provide an independent terrestrial paleothermometer well-suited to this task (e.g. Weijers et al~~.~~., 2007; Peterse et al~~.~~., 2012; De Jonge et al~~.~~., 2013; Buckles et al., 2014; De Jonge et al., 2015). BrGDGTs are comprised of two ether-linked dialkyl chains containing zero to two methyl branches (prefixes I, II, and III) and zero to two cyclopentane moieties (suffixes a, b, and c~~).~~) (Sinninghe Damsté et al., 2000). Although the source organisms are unknown, ~~the~~these compounds are thought to be ~~bacterial membrane lipids~~produced by Acidobacteria (e.g., Sinninghe Damsté et al., 2011~~).~~; Sinninghe Damsté et al., 2018). Noting a strong correlation between mean annual air temperature (MAAT) and the ~~distribution~~degree of methylation of brGDGTs in global soils, Weijers et al. (2007) proposed that sedimentary brGDGTs could be used as a proxy for past soil temperature, which in many cases is similar to mean annual air temperature. This motivated the development and later refinement of two indices, based on the degree of methlyation and cyclization of brGDGTs (MBT and CBT), which ~~are used~~were correlated to ~~reconstruct past climate~~temperature and pH, respectively (e.g. Weijers et al., 2007~~,~~; Peterse et al., 2012~~,~~; De Jonge et al., ~~2013~~2014a).

More recently, improved chromatographic separation techniques for brGDGTs have been developed and indicated the presence of 5- and 6-methyl brGDGT isomers (De Jonge et al., 2013; De Jonge et al., 2014; Hopmans et al., 2016). The 6-methyl isomers may be abundant in environmental samples (De Jonge et al., 2014b), and failure to account for the presence of these compounds can have a significant influence on reconstructed temperatures (De Jonge et al., 2013; De Jonge et al., 2014a). Importantly, De Jonge et al. (2014a) demonstrated that soil pH (CBT) does not have an influence on the degree of methylation (MBT) and that earlier observations suggesting an influence of pH on methylation (Weijers et al., 2007) were the result of incomplete isomer separation. A new index based on the 5-methyl brGDGTs (MBT'_{5ME}) was developed and calibrated to temperature using a global soils dataset (De Jonge et al., 2014). MBT'_{5ME} has recently been calibrated for temperature reconstruction in lakes from East Africa (Russell et al., 2018) and China (Dang et al., 2018).

Initially, brGDGTs were presumed to be exclusively produced in soils, and subsequently washed into lakes or marine environments via erosion by rivers and streams (Hopmans et al., 2004). Further research ~~has indicated~~demonstrated these compounds are also produced *in situ* in lakes and rivers (e.g. Tierney and Russell, 2009; Bechtel et al., 2010; ~~Buckles~~Tierney et al., ~~2014; De Jonge~~2010; Zhu et al., ~~2015~~2011; Loomis et al., 2012; Schoon et al., 2013; ~~Tierney et al., 2010; Tierney and Russell, 2009;~~ Zell et al., 2013~~; Zhu et al., 2011~~). Although some studies suggest that distinct brGDGTs are produced within the water column of lakes (~~Weber et al., 2015;~~ Colcord et al., 2015; Weber et al., 2015) and show that their production is seasonally biased (e.g. Buckles et al., 2014; Loomis et al., 2014), relatively limited work has been done to understand their in-situ production and its consequences for the sedimentary brGDGT record (Zhang et al., 2016). Knowledge of brGDGT production and seasonality is important for appropriately calibrating and ~~understanding~~interpreting downcore records, yet ~~to date little to no~~few studies have combined modern observations of brGDGT distributions in the environment with a paleoclimate reconstruction for a temperate lake system.

Here we examine brGDGT abundances and distributions in catchment soil samples and at varying depths in the water column throughout the year at an inland lake in ~~Maine,~~the NE US (Fig.

1). We collected samples from 2014–2015 to assess the seasonality and location of brGDGT production in and around Basin Pond, ME. We then appliedused our observations to the interpretation ofhelp interpret a 900 year--long relative temperature record, providing the first decadally-resolved brGDGT-derived lacustrine paleoclimate reconstruction for this region.

2 Site information, and field sampling, and laboratory methods

2.1 Study Site

Basin Pond, located in Fayette, ME (44º 28' N, 70º 03' W, elevation 124 m above sea level), is a small, deep lake with an area of 0.14 km^2 and a maximum depth of 32.6 m (Fig. 1). Basin Pond is fed from groundwater and precipitation, with one small, dammed, outlet stream running westward into the adjacent David Pond (Frost, 2005). Most of the 0.53 km^2 catchment area is dominated by a well-developed deciduous hardwood and evergreen forest, with only one residential building. Mean annual air temperature at Basin Pond is ~5.9°C and average annual precipitation is ~1150 mm (NOAA, 2014).

Basin Pond contains a unique sedimentary sequence comprised of annual laminations (varves) due to permanent water column stratification (Wetzel, 1983; Frost, 2005) resulting from a persistent thermocline. This stratification causes permanent bottom water anoxia, which enhances the preservation of annual laminations throughout the record (O'Sullivan, 1983). The Basin Pond varves are biogenic, with couplets comprised of a lighter, diatom-rich summer layer and a darker, humic winter layer (Frost, 2005).

The extent of anthropogenic impacts to Basin Pond and its catchment area have varied over the study interval. Although people were certainly present in Maine for the past 900 years, European-settler land clearance did not begin until the mid-1700s (Foster and Aber, 2004). It is uncertain whether the Basin Pond catchment was affected by this process. Due to its relatively remote location in New England, Maine experienced substantially less deforestation compared with the other NE US states (Foster and Aber, 2004). However, polycyclic aromatic hydrocarbons (PAHs) reflecting regional anthropogenic activity indicate that industrialization is notable in the Basin Pond sedimentary record (Miller et al., 2017). Furthermore, the lake's natural chemistry was disrupted in the 1950s, when Basin Pond was treated with a chemical piscicide, Rotenone (United

States Geological Survey, 1996). Today, the lake is lightly used for recreation by members of the Basin-David-Tilton Ponds Association.

2.2 Sediment Coring

Sediment coring was performed from ice ~~(~~in March 2014~~)~~, in the deepest part of the lake at 32 m (44º 27’ 27” N, 70º 03’ 09” W~~)~~), using a UWITEC gravity coring system. Core BP2014-3D (52 cm) captured an undisturbed sediment-water interface and was subsampled in the field at 0.5 cm resolution for radioisotopic dating. Core BP2014-5D (174 cm) was immediately capped upon retrieval. Cores were split, photographed, and non-destructive down-core logging was performed using an Itrax XRF core scanner with a Molybdenum tube at 100 µm resolution in the Department of Geosciences at University of Massachusetts Amherst. Cores were kept refrigerated for one month prior to subsampling. Subsamples were stored frozen in WhirlPak bags until ~~analysis~~extraction.

2.3 Sediment trap construction, deployment and retrieval

Sediment traps were designed and constructed at University of Massachusetts Amherst. Sediment trap collection cones were made of high density polyethylene (HDPE~~),~~) with a diameter of ~1 m (Fig. 1~~),~~) and attached to 4L bottles for~~ the~~ settling particulate matter (SPM) collection (Fig. 1). Note that our definition of SPM includes both material suspended in the water column and settling into the traps. Five sediment traps were deployed on May 27, 2014 at 6, 12, 18, 24, and 30 ~~m depths in the deepest part of the lake (Fig~~meter depth (Fig. 2). SPM was collected from all traps on 7/2/14, 8/16/14, 9/14/14 and 6/5/15. Each trap continuously accumulated SPM from deployment until collection and therefore each sample represents material collected over 36, 40, 28, and 264 days, respectively. ~~Thus, samples collected on a given date represent the previous month (or longer) of sedimentation. Catchment soil samples were also taken~~The length of the last sampling period of 264 days was due to ice cover at the lake; sediment trap recovery was not possible until ice out. SPM labels on Figures 2, 3, & 5 and throughout the discussion are referred to by the month that was the midpoint of each collection period. Thus, the four sampling periods listed above are referred to respectively as June, July, September, and January SPM. Catchment soil samples were also collected around the perimeter of the lake at the time of initial trap deployment. All soil and water SPM samples were kept frozen until analysis.

3 Methods

3.1 Sedimentary Age Model

Subsamples for ~~downcore~~past climate reconstruction were taken every 0.5 cm from the uppermost 68 cm of core BP2014-5D. The age model for ~~this core~~Basin Pond is based on ^{210}Pb, varve counts, and five ^{14}C dates and was previously published by Miller et al., (2017). The sediment examined here ranges in age from modern to ~1100 BP, with a sampling resolution of 4 to 13 years (median: 7) (Miller et al., 2017).

3.2 Laboratory Methods

Overall, ~~5~~10 catchment soil, 19 SPM sediment trap samples, and 136 sediment core samples were analyzed. Soil and lake sediment samples were freeze-dried and homogenized prior to extraction. For SPM samples, water from each collection bottle was filtered through a 47mm, 0.3-µm combusted Sterlitech glass fiber membrane filter, and dried prior to extraction. For most samples, a total lipid extract (TLE) was obtained using a Dionex Accelerated Solvent Extractor (ASE 200) with a mixture of dichloromethane (DCM)/ methanol (MeOH) (9:1, v/v). For four SPM samples, plastic filters were washed and sonicated with HPLC-grade water, which was subsequently extracted with DCM three times~~ to avoid contamination. The TLE~~. TLEs from SPM and catchment soil samples ~~was~~were separated into apolar (9:1 DCM/hexane v/v) and polar (1:1 DCM/MeOH v/v) fractions, while the lake sediment samples were separated into apolar, ketone (1:1 hexane/DCM) and polar fractions using alumina oxide column chromatography. For all samples, one half of each polar fraction was filtered through 0.45µm PTFE syringe filters using 99:1 hexane/isopropanol (v/v). 0.1 µg of C$_{46}$ GDGT internal standard was added to each polar fraction prior to analysis. The other half of each polar fraction was derivatized using bistrimethylsiyltrifluoroacetamide (BSTFA), and algal biomarkers were identified with a Hewlett-Packard 6890 Series gas chromatograph coupled to an Agilent 5973 mass spectrometer (GC-MS) using a Restek Rtx-5ms (60m x 250µm x 0.25 µm) column. Algal biomarkers, (iso)loliolide, C$_{30}$ 1, 13 *n*-alkyl diol, dinosterol/stanol, and β-sitosterol/stanol, were quantified with an Agilent 7890A dual gas chromatograph-flame ionization detector (GC-FID) equipped with two Agilent 7693 autosamplers and two identical columns (Agilent 19091J-416: 325 °C: 60m x 320µm x 0.25 µm, HP-5 5% Phenyl Methyl Siloxan). For both the GC-MS and GC-FID, ~~Helium~~helium was used as the carrier gas. The ovens began at a temperature of 70 °C, increased at 10 °C min $^{-1}$ to 130 °C, increased again at 4 °C min $^{-1}$ to 320 °C, and then held for 10 minutes. The GCs were run in splitless mode. Compounds were quantified using an external calibration curve where squalane was injected at multiple concentrations ranging from 2 to 100 ng/μl~~,~~; r^2 values for linearity tests were >0.99.

3.3 brGDGT analysis

Polar fractions were analyzed on an Agilent 1260 high performance liquid chromatograph (HPLC) coupled to an Agilent 6120 Quadrupole mass selective detector (MSD). ~~Separation of compounds~~Compound separation was achieved using the ~~UHPLC~~ method of Hopmans et al. (2016). The technique uses two Waters UHPLC columns in series (150 mm × 2.1 mm × 1.7 μm) and isocratically elutes brGDGTs using a mixture of hexane (solvent A) and hexane: isopropanol (9:1, v:v, solvent B) in the following sequence: 18% B (25 minutes), linear ~~ramp~~increase to 35% B (25 minutes), linear ~~ramp~~increase to 100% B (30 minutes). Mass scanning was performed in selected ion monitoring (SIM) mode. brGDGTs were quantified with respect to the C_{46} standard, assuming equal ionization efficiency for all compounds. For calculation of MBT'$_{5ME}$, CBT'$_{5ME}$, and the Isomer Ratio (IR), the following equations were used~~.~~ from De Jonge et al. (2014a&b):

~~$$MBT'_{5Me} = \frac{Ia+Ib+Ic}{IIIa+IIIb+IIIc+IIa+IIb+IIc+Ia+Ib+Ic} \quad (1)$$~~

$$MBT'_{5ME} = \frac{Ia+Ib+Ic}{IIIa+IIa+IIb+IIc+Ia+Ib+Ic} \quad \text{Eq. (1)}$$

~~CBT'$_{5Me}$~~

$$CBT'_{5ME} = -\log\left(\frac{Ib+IIb}{Ia+IIa}\right) \quad \text{Eq. (2)}$$

$$IR = \frac{IIa' + IIb' + IIc' + IIIa' + IIIb' + IIIc'}{IIa+IIa' + IIb+IIb' + IIc+IIc' + IIIa+IIIa' + IIIb+IIIb' + IIIc+IIIc'} \quad \text{Eq. (3)}$$

For samples measured in duplicate (n=32), the maximum MBT'$_{5ME}$ difference was < 0.01, while the maximum CBT'$_{5ME}$ was 0.01; thus analytical error associated with proxy application is insignificant.

3.4 Time Series Analysis

To analyze the variance in the data presented here, we used the *Astrochron* R package (Meyers, 2012). Pre-processing of the data was kept to a minimum to avoid introducing spurious signals. The downcore brGDGT reconstruction was re-interpolated to 7-yr resolution (equivalent to median resolution of the raw data, see results) prior to spectral analysis. The published PAGES2k datasets were analyzed with their published chronologies, which is 1 year resolution for most regions and 10 years for the North American tree-ring based reconstruction (PAGES2k, 2013). Each of these reconstructions were smoothed to 7 year averages for easier comparison to our record.

4 Results

BrGDGTs were present in all soil, SPM and sediment core samples analyzed. In contrast, isoprenoid GDGTs, on which the TEX_{86} temperature proxy is based (Schouten et al., 2002), were absent in a majority of samples or present in very low abundances compared to the brGDGTs. Therefore, TEX_{86} could not be utilized as a temperature proxy at Basin Pond.

4.1 Catchment Soils

BrGDGTs Ia and IIa dominated distributions in the catchment soil samples, with relative abundances of 65% ±13% and 28% ±7%, respectively (Fig. 2). The next largest relative abundances were IIIa and Ib, comprising 3% ±6% and 3% ±1%, respectively (Fig. 2). Total brGDGT concentrations in soils ranged from 1.5 to 7.3 (median = 2.2) µg $gsed^{-1}$.

4.2 SPM

BrGDGTs Ia, IIa and IIIa dominated distributions in the SPM samples, with relative abundances of 28% ±8%, 37% ±7%, and 30% ±8%, respectively (Fig. 2). The next largest relative abundances were Ib and IIb, each comprising 2% ±<1%. Through the four collection periods, the distributions are relatively consistent. However, in In June and July and August 2014, group I brGDGTs were the most abundant, whereas in September 2014 and June January 2015 reductions in group I brGDGTs were accompanied by increases in group 3 III brGDGTs (Fig. 2). Overall, fluxes of brGDGTs were highest in September 2014 (ranging from 0.36 to 15.2 ng m^2 day^{-1} at different depths) (Fig. 3). In June and July and August 2014, total brGDGT fluxes at various depths ranged from 0.009 to 0.04 ng m^2 day^{-1} and 0.04 to 0.14 ng m^2 day^{-1}, respectively (Fig. 3).

BrGDGT fluxes and distributions also varied as a function of depth (Fig. 3,4, 5). In general, summed brGDGT fluxes increase with depth, with up to an order of magnitude higher fluxes at 30 m compared to 6 m for all dates (Fig. 3).

BrGDGT fluxes and distributions also varied as a function of depth (Fig. 4,5). BrGDGT fluxes in the upper and lower water column peaked in September with fluxes of 0.4 to 0.6 ng m^2 day^{-1} and 7 to 16 ng m^2 day^{-1}, respectively. The average distributions also changed as a function of depth. Group I brGDGTs comprised 30% of the distributions at all depths. Group II brGDGTs had the greatest abundance at 12 and 18 m water depth (Fig. 5), comprising up to 50% of the distribution. Group III brGDGTs peaked comprised an average of 30% with a peak of 35% at 30 m, comprising 35% of the distribution, and showed a minimum at 18 m of <20%. These distributions lead to variations in MBT'$_{5ME}$ and CBT'$_{5ME}$indicesCBT'$_{5ME}$ indices as a function of depth (Fig. 5). MBT'$_{5ME}$ varied from 0.34 to 0.46, and peaked at 24 m water depth (Fig. 4). CBT'$_{5ME}$ varied from 1.1 to 1.6, peaked at 12 m and then decreased with depth (Fig. 4).

4.3 Sediment Surface sediment samples

To represent surface sediments, we averaged the measurements from the uppermost 5 cm of Core BP2014-5D, corresponding to approximately 35 years (Miller et al., 2017). BrGDGTs Ia, IIa, and IIIa dominate the distribution, with relative abundances of 27%, 32%, and 33%, respectively (Fig. 3). The next largest relative abundances wereare IIb, Ib, and IIIb (3%, 2%, and 1%, respectively). Reconstructed MBT'$_{5ME}$ values in surface sediments rangedrange from 0.35 to 0.45 (Fig. 6).

4.4 Sediment Core

BrGDGT **isomer ratios**

The chromatographic separation of brGDGTs allows for the separation of penta- and hexa-methylated brGDGT isomers, and improves the error associated with temperature reconstruction (DeJonge et al., 2013; DeJonge et al., 2014). Analysis of the relative abundances of these isomers has also been used to identify different production sources of brGDGTs (DeJonge et al., 2014; Weber et al., 2015). The summed IR for soils, lake water and sediments at Basin Pond were significantly different. The IR value for soils averaged 0.03, while the water samples and sediments averaged 0.26 and 0.30, respectively (Fig. 6).

~~**4.5 Downcore reconstruction**~~

~~Sampling every 0.5 cm in Core BP2014-5D yielded a record of brGDGT distributions with a resolution of 4 to 13 years (median: 7). brGDGT~~ concentrations in these samples ranged from 1.~~16~~2 to 21.~~07~~1 (median: 8.09) µg gsed^{-1}. ~~-~~MBT'$_{5ME}$ ranged from 0.34 to 0.50 (median: 0.39). MBT'$_{5ME}$ values fluctuate around a stable mean from 1100-1400 AD, then broadly decrease from ~1400 AD until the present day (Fig. 7). Decadal variability is superimposed on the long-term decreasing trend (Fig. 7). Prominent, multi-decadal low- MBT'$_{5ME}$ value events are apparent from 1420–1444, 1500–1520, 1593–1627, 1762-1829, and 1908–1950 AD (Fig. 7). Multidecadal high- MBT'$_{5ME}$ events are observed from 1261–1283, 1317–1351, 1556–1583, 1632–1657, 1829–1846 and 1958–1987 AD(Fig. 7). ~~(Fig. 7).~~The brGDGT concentrations in the core range from 1.2-21.1 µg gsed^{-1}, with a median of 8.2 µg gsed^{-1}.

4.5 BrGDGT isomer ratios

The UHPLC method we utilized for brGDGT analysis (Hopmans et al., 2016) allows for the separation of 5- and 6-methyl brGDGT isomers (DeJonge et al., 2013; DeJonge et al., **2014). Analysis of the relative abundances of these isomers has also been used to identify different production sources of brGDGTs (e.g. soils vs. water column; DeJonge et al.,** 2014; Weber et al., 2015). ~~**5. Discussion**~~

~~**5.1 Calibration of the brGDGT paleothermometer**~~

~~Several lacustrine brGDGT calibrations have been developed (Tierney et al.,~~ The summed IR (equation 3) for soils, lake water and sediments at Basin Pond are significantly different. The IR value for soils is very low and averages 0.03, while the water samples and sediments are higher and average 0.26 and 0.30, respectively (Fig. 6).

4.6 Algal biomarkers

Samples in the upper 17cm of the sediment core were analyzed for the following algal lipid biomarkers: (iso)loliolide, C_{30} 1, 13 *n*-alkyl diol, dinosterol/stanol, and β-sitosterol/stanol. Concentrations of (iso)loliolide ranged from 31-426 µg gsed^{-1} (median=171). C_{30} 1, 13 *n*-alkyl diol concentrations ranged from 8-1378 µg g sed^{-1} (median=475). Dinosterol/stanol concentrations ranged from 12-5663 µg g sed^{-1} (median= 1384). Concentrations of β-sitosterol/stanol concentrations ranged from 3-7955 µg g sed^{-1}(median=1465).

5 Discussion

~~2010; Pearson et al., 2011; Sun et al., 2011; Loomis et al., 2012) following strong evidence for *in situ* brGDGT production (e.g. (Tierney and Russell, 2009; Buckles et al., 2014; Loomis et al., 2014). Unfortunately, these are generally either based on relatively few samples (e.g. Zink et al., 2010; Loomis et al., 2012) or are geographically restricted (e.g. Tierney et al., 2010; Foster et al., 2016). Furthermore, under new chromatographic separation schemes (Hopmans et al., 2016), pH no longer affects MBT values (De Jonge et al., 2014) and few lacustrine calibrations have been developed using this new method. Recently, a calibration was developed for African lakes using only the 5 methyl brGDGTs. However, we do not believe it is appropriate to apply an African calibration to lakes in the NE US, as these two regions are climatically different and their lakes differ in terms of stratification/mixing. We thus present our results simply in terms of the MBT'$_{5ME}$ index, which we note shows a strong positive correlation with temperature in all previously published global calibrations (i.e. Weijers et al., 2007; Peterse et al., 2012; De Jonge et al., 2013) and the new African lakes calibration (Russell et al., 2018) as well as in the data we present here (see Supplementary Materials).~~

5.~~2 In situ~~1 Sources and seasonal production of ~~brGDGTs in~~ Basin Pond brGDGTs

It is important to constrain brGDGT sources before interpreting lacustrine sedimentary records. Multiple lines of evidence suggest ~~that~~ brGDGTs deposited in Basin Pond sediments are predominantly produced within the water column, in agreement with prior studies (e.g. Tierney and Russell, 2009; Buckles et al., ~~.~~2014; Loomis et al., 2014). First, we observe significant differences in the fractional abundances of brGDGTs between soil, SPM and lake sediments (Figs. 2, 5), suggesting *in situ* production occurs in both soil and lacustrine environments~~.~~, but that soil-derived brGDGTs do not exert a large influence on the Basin Pond sedimentary record. Average distributions of brGDGTs reveal that lake sediments and SPM are similar in ~~Ia~~group I and ~~IIIa~~III content, while the soils differ substantially (Figs 2, 5). The relative amounts of 5- and 6-methyl brGDGTs also differs between soils and lake water and sediment (Figs 2, 5), and as seen in the average IR values (Fig. 6). MBT'$_{5ME}$ and ~~CBT~~CBT'$_{5ME}$ values for lake sediment and soils are ~~different~~distinct, while SPM samples ~~lie between the respective end members~~are similar to lake sediment samples, consistent with *in situ* brGDGT production within Basin Pond ~~and mixing with soil brGDGTs~~ (Fig. 6). The degree of cyclization (mean ~~CBT~~CBT'$_{5ME}$ = 1.2) is significantly ~~higher~~lower in lake sediments than in soil samples (mean ~~CBT~~ CBT'5$_{ME}$= 1.5) (p value = 0.021 from two-tailed t-test), and brGDGTs are more methylated (p value = 0.003) in lake sediments (mean MBT'$_{5ME}$ = 0.38) than in soils (mean MBT'$_{5ME}$ = 0.7) (Fig. 6). This agrees with differences in brGDGT distributions recorded in other temperate (Tierney et al., 2012; Wang et al., 2012; Loomis et al., 2014) and tropical (Tierney and Russell, 2009; Loomis et al., ~~2011~~2012; Buckles et al., 2014) lakes and catchment area soils, and suggests *in situ* production of relatively more cyclized and methylated brGDGTs within lakes. In agreement with previous studies, we also note higher brGDGT concentrations in lake sediments (median – 8.2 µg $gsed^{-1}$) in comparison to watershed soils (median= 2.2 µg $gsed^{-1}$) (e.g. Sinninghe Damsté et al., 2009; Tierney and Russell, 2009) pointing to *in situ* brGDGT production.

~~Monthly variations in fluxes and distributions of brGDGTs also suggest lacustrine brGDGTs have an *in situ* source. Fractional abundances of brGDGTs vary as a function of depth suggesting brGDGTs in SPM may respond to (and record) temperatures at different depths. Although seasonal precipitation events leading to soil erosion have previously been invoked to explain increased seasonal brGDGT fluxes (Sinninghe Damsté et al., 2009; Vershuren et al. 2000), fluxes of brGDGTs are not higher during summer months, when strong precipitation events generally occur at Basin Pond (NOAA, 2014). Furthermore, SPM samples maintain the distinct lacustrine fractional abundance distribution, suggesting they are not significantly influenced by a flux of terrestrially derived brGDGTs from runoff (Fig. 2). Instead, brGDGT fluxes are orders of magnitude higher in September (Fig. 3).~~ BrGDGT fluxes at all depths are generally low throughout the summer months (June–~~August~~July). A large flux increase at depth (18–30 m) occurs during September~~. BrGDGT distributions in SPM generally do not reflect that of the surrounding soils, suggesting that there is no significant flux of brGDGTs into~~ , when the lake ~~from either summer storm erosion or spring freshet runoff. Permanent lake stratification likely prevents resuspension, thus limiting~~is strongly stratified. Thus any transfer of brGDGTs from ~~greater~~lower depths to the upper water column~~. Overall, this~~ likely would be minimal. This suggests ~~an~~ annual seasonal production of brGDGTs in Basin Pond, with a fall bloom occurring at intermediate (18–30 m) depths. Therefore, brGDGT temperatures recorded in the lake sediments likely reflect a seasonally biased (fall), rather than mean annual, temperature. We ~~observe~~make the following~~: (1)~~ observations based on these results. First, peak brGDGT flux is observed at 18-~~24~~30 m water depth, suggesting that the organisms producing the most brGDGTs thrive in the mid to upper water column (Fig. 3~~); (2)~~). Secondly, peak brGDGT production occurs in September, suggesting that the sedimentary record will be biased toward brGDGTs produced during this period (Fig. 3~~); And (3)~~). Finally, for the four time-periods sampled, brGDGT distributions (as described by MBT'$_{5ME}$) correlate with temperature (Fig. S1). Interestingly, at ~~18-24 m~~ depth the water temperature shows little to no seasonal cycle, remaining at approximately 4 °C for the entire year~~.~~ (Frost, 2005). Therefore, if maximum brGDGT production is indeed occurring here, it is possible that another parameter, which covaries with temperature on a seasonal scale (i.e. light duration, water chemistry, nutrient availability), may drive, or contribute to, the distribution of brGDGTs produced at depth at Basin Pond. However, the sediment trap at this depth represents an integrated signal of SPM produced in the water column, which could also be driving the temperature correlation at depth.

Although few studies are available for comparison, Loomis et al. (2014) studied ~~brGDGT~~brGDGTs in another temperate lake in the NE US (Lower King Pond, Vermont). ~~Whereas~~ brGDGT production in Lower King Pond peaked during fall and spring~~, it~~ and was linked to seasonal full water column mixing events~~,~~ (Loomis et al., 2014), which do not occur at Basin Pond~~.~~ (Frost, 2005). Moreover, Basin Pond is ten times ~~bigger~~larger by area and four times deeper than Lower King Pond. Similar to Lower King Pond, brGDGT production at Basin Pond seems to be seasonal, and calibration of brGDGTs against seasonal (in this case, fall) temperatures is necessary to accurately reconstruct past temperature change for this location. If the ~~behavior~~behaviour of brGDGTs in Lower King Pond and Basin Pond is representative of all temperate lakes, then calibration to fall or spring temperature may be the most appropriate choice for these settings. ~~While we believe that the MBT'$_{5ME}$ trends in our brGDGT-based reconstructions reflect temperature change, future work is necessary to generate properly calibrated (and accurate) paleotemperature records.~~

5.~~3 Downcore~~2 Calibration of the 900 year brGDGT ~~Reconstructions~~ record to temperature

Numerous studies have provided strong evidence for *in situ* brGDGT production in lakes and have shown that application of the global soils calibration to lacustrine sediments often yields temperatures that are unrealistically cold (e.g. Tierney and Russell, 2009; Bechtel et al., 2010; Blaga et al., 2010; Tierney et al., 2010a,b; Tyler et al., 2010; Pearson et al., 2011). Therefore, many lacustrine brGDGT calibrations have been developed (Tierney et al., 2010; Zink et al., 2010; Pearson et al., 2011; Sun et al., 2011; Loomis et al., 2012, Foster et al., 2016). However, many of these are based on relatively few samples or are geographically restricted (e.g. Tierney et al., 2010; Zink et al., 2010; Foster et al., 2016). Furthermore, at present, all available lacustrine brGDGT calibrations except for two (Dang et al., 2018; Russell et al., 2018) were developed using older HPLC methods that did not fully separate brGDGT isomers. As we measured our brGDGTs following the newer method of Hopmans et al. (2016), we investigated Basin Pond temperature reconstructions using only those calibrations based on the same technique. The Dang et al. (2018) calibration is based on alkaline Chinese lakes and reconstructs temperatures ranging from 4-9 °C, while the Russell et al. (2018) calibration is based on African lakes and yields temperatures ranging from 10-14 ºC (Fig. 7). The African lakes calibration from Russell et al. (2018) is based on MBT'$_{5ME}$ while the Chinese lakes calibration of Dang et al., (2018) is based on fractional abundances of brGDGTs; therefore these two calibrations yield somewhat different trends with the Dang et al. (2018) calibration showing muted variability and some discrepancies from the other proxy records (i.e. during the last 50 years) (Figure 7).

Importantly, we caution against interpretation of the Basin Pond reconstructed temperatures using either of these calibrations because application of an African or Chinese calibration to lakes in the NE US is questionable as these regions are climatically different and their lakes differ in terms of stratification and mixing regimes. Furthermore, brGDGTs from Basin Pond are characterized by distinct brGDGT distributions from both the African (Russell et al., 2018) and alkaline Chinese lake sediments (Dang et al., 2018) (Figure 8). This suggests that application of either of these calibrations to Basin Pond sediments may not be appropriate. Local temperature data are available for Basin Pond over the period our measurements were made, but the SPM dataset presented here is not large enough to develop a robust local MBT'$_{5ME}$ to temperature calibration (see Supplement). We thus present our results in the following discussion and figures simply in terms of the MBT'$_{5ME}$ index, which provides a relative temperature indicator, where higher values reflect relatively higher temperatures and vice versa (De Jonge et al., 2014b).

Our interpretation of the 900-year MBT'$_{5ME}$ record is as follows. Based on the ~~contents of the sediment traps~~SPM samples, we argue that the downcore brGDGT reconstruction is likely weighted toward September temperature change in the NE US~~ over the last ~900 years.~~. We note that brGDGTs are present at all depths measured but peak at ~~24~~18-30 m depth, indicating that the compounds reaching the ~~sediment~~lake floor represent an integrated signal from the entire water column. Although brGDGT concentrations vary down core, they are not correlated with reconstructed MBT'$_{5ME}$ values (p=0.25), indicating that brGDGT production and MBT'$_{5ME}$ variability are largely decoupled. We observe an overall stepped cooling trend recorded by generally decreasing MBT'$_{5ME}$ values over the past 900 years (Fig. 9). ~~The average reconstructed MBT'$_{5ME}$ value over the last 100 years is 0.37. At the beginning of the record (AD 1100), MBT'$_{5ME}$ values are ~0.4 (Fig.~~ Using the calibration of Russell et al. (2018), this overall cooling is on the order of 3.0 º C; however, for the reasons discussed earlier, we advise that caution must be taken when interpreting absolute temperature changes from applying this calibration to Basin Pond sediments. ~~7). Values increase until AD 1340,~~

~~reaching a maximum of 0.5 (Fig. 7). Multi-taper method spectral analysis reveals significant power at periodicities of 80, 63, and 47 years (Meyers, 2012). MBT'$_{5ME}$ values decrease from AD 1340 to AD 1900 with variability of ±0.05 superimposed on this trend.~~

5.~~4~~3 Comparison to Regional Hydroclimate Records in the NE US

Regional hydroclimate in the NE US has been reconstructed at several sites on similar timescales as the Basin Pond record~~. We find that while similarities exist between our record and these hydroclimate records, the Basin Pond MBT'$_{5ME}$ record shows long-term changes that are not observed in other regional reconstructions.~~. The MBT'$_{5ME}$ record ~~infers~~indicates an overall cooling from ~1300 AD to ~1900 AD (Fig. ~~7~~9), which is also observed in pollen-derived temperature reconstructions from Basin Pond (Gajewski ~~1988),~~, 1988). Both records also indicate two major cooling steps, although ~~we note that there~~the exact timing of these differs between records, which may be ~~a difference~~attributable to age model differences (Fig. 9). Apparent differences between the Basin Pond records are likely also associated with sampling resolution; the pollen record has varying and generally much lower sample resolution in comparison to our MBT'$_{5ME}$ record. Furthermore, some of the differences in MBT'$_{5ME}$ and pollen reconstructions may be caused by differences in proxy seasonality~~ between pollen reconstructions and MBT'$_{5ME}$ from Basin Pond. The greatest flux of brGDGTs occurs during September, whereas the published pollen data record reflects~~ , with pollen representing a summer ~~(JJA) temperature. Despite these differences in seasonality, the two records broadly agree. The~~signal (Gajewski, 1988) and MBT'$_{5ME}$ likely representing a fall signal.

The general long-term cooling trend from Basin Pond is also observed in a hydrogen isotope-based temperature reconstruction from Little Pond, Massachusetts (Gao et al., 2017). ~~Although the timing of maximum~~Both records show higher temperatures ~~at that site occurs later than at Basin Pond, both records show the coolest part of the last 900 years occurring at ~1850~~between 1300-1400 AD (Fig. ~~7).~~
~~A potential cause for the discrepancy between the Basin and Little Pond records is that the latter is based on hydrogen isotopes from leaf waxes, which represent an integrated signal of temperature and hydrological change.~~9). Bog records provide additional, high-resolution reconstructions of hydrological conditions in the NE US over this time period via analysis of testate ameoba (a proxy for water table depth) and the *Sphagnum*/Vascular Ratio (SVR) (Nichols and Huang, 2012; Clifford and Booth, 2013~~; Nichols and Huang, 2012~~). The testate ameoba records show that the last 400 years (i.e., 1600–2000 AD) have been generally wetter than the preceding 400 years (1200-1600 AD). However, unlike the temperature reconstructions, these records do not show a long-term linear trend (Fig. ~~7~~9).

These ~~observations~~cooling and wetting trends are surprising given the record of fire history at Basin Pond (Miller et al., 2017), which shows five periods of increased charcoal deposition since 1100 AD (Fig. ~~7~~9). It is important to note that wildfire activity is a complex phenomena, with multiple factors affecting fire occurrence apart from climate variability ~~in the NE US~~ (Marlon et al~~.~~., 2017). However, our data suggest that fire activity in the NE US may be influenced more by shorter-term (multi-decadal) variations in climate, particularly seasonal cooling superimposed on dry conditions, as opposed to longer-term, multi-centennial climate trends. Surprisingly, the first 200 years of the record (1100–1300 AD) are dominated by warm and dry conditions, but no fire events were recognized during this period. Three fire events~~,~~ (Fig. 9g), between ~1300 and ~1700 AD, are associated with regionally dry conditions~~.~~ (Fig. 9d-f). Although average Basin Pond MBT'_{5ME} values are higher on a multi-centennial time-scale during this ~~time period~~interval, the fire events themselves occur synchronously with multi-decadal cold ~~intervals. Two~~periods (Fig. 9a-c). Furthermore, two recent fire events occurred during the historical period, which is reconstructed as relatively cool and wet (Fig. 9). ~~. We suggest these fires to be less climatically driven and are perhaps more strongly associated with human disturbance.~~ Therefore, it appears that at Basin Pond, temperature did not exert a major influence over fire occurrence.

5.~~6~~4 Comparison with Northern Hemisphere ~~Records~~records

A compilation of Northern Hemisphere temperature records for the last 2000 years reveals sustained warmth from ~~AD~~ 830–1100 AD, just prior to the beginning of our reconstructions (PAGES2k, 2013~~) (Fig. 8~~). Northern Hemisphere climate then entered a cooler phase, though the timing of this transition varied regionally between ~~AD~~ 1200 and 1500 AD (PAGES2k, 2013). North American pollen data~~, as well as pollen data from Basin Pond,~~ show elevated, though decreasing, temperatures through ~~AD~~ 1500 AD (Gajewski, 1988; PAGES2k, 2013) (Fig. 10). From 1100-1400 AD, Basin Pond MBT'_{5ME} values are high in contrast with European and Arctic temperature reconstructions. From 1500-1900 AD, MBT'_{5ME} values are lower, in better agreement with other Northern Hemisphere reconstructions. Moreover, the decadal to centennial scale variability observed in MBT and other records during this time may be linked to variability in Atlantic Multidecadal Oscillation (AMO) and North Atlantic Oscillation (NAO) indices (Figure 8). ~~Surprisingly,~~We note that the brGDGT MBT'_{5ME} values are better correlated with regional tree-ring records and compilations of European and Arctic temperatures, which all show warm anomalies, followed by cooling, earlier this century. Thus, the multi-centennial structure of the brGDGT record from Basin Pond is supported by other local, regional, and global records (PAGES2k, 2013). On a multi-decadal scale, there is variability potentially associated with volcanic events recognized as having a global impact. Five intervals during the last millennium were defined as 'volcanic-solar downturns': AD 1251–1310, 1431–1520, 1581–1610, 1641–1700, and 1791–1820 AD (PAGES2k, 2013). All but the most recent (1908–1950 AD) of the cool events are present in the Basin Pond MBT'$_{5ME}$ record during these periods (or within the age model uncertainty) (Fig. 810 highlighted in blue).

There is some similarity between the Basin Pond reconstruction and other northern hemisphereNorthern Hemisphere reconstructions (PAGES2k, 2013) in that we note cooling (low MBT'$_{5ME}$ value) events during (or within age model uncertainty of) five prominent volcanic downturns that occurred during the last millennium (PAGES2k, 2013) (Fig. 810). The brGDGT record is also peppered with warm (high MBT'$_{5ME}$) anomalies; many of these seem to be coherent with tree-ring based reconstructions of North American climate (i.e. AD 1300, 1550, 1830 AD) and are sometimes associated with negative phases of the NAO (Fig. 810). The sensitivity of the Basin Pond sediment record to regional scale climatic variations is highlighted by time series analysis. Multispectral taper method analysis reveals a persistent cycle in the brGDGT-based temperature reconstruction with a period of 57–63 years (Fig. 810). The Northern Hemisphere tree-ring compilation also shows a cyclicity with a period of 60 years (Fig. 810). However, the fact that the two datasets are not significantly correlated indicates the variability at 60-year periods is not exactly in-phase over the 900 year period covered by the two records. Cross-correlation analysis indicates that the correlation between the two datasets is strongest when the tree-ring reconstruction is lagged by 42 years relative to the Basin Pond temperature record (r=0.33, p=0.04). Significant spectral peaks with a similar period exist in the annually-resolved records from Europe (period = 65 yr), Asia (period = 58 yr) and the Arctic (period = 58 yr) (PAGES2k, 2013). However, the same analyses applied to South American, Australasian, and Antarctic reconstructions do not show spectral peaks at this period (PAGES2k, 2013). Thus, it appears that the Basin Pond brGDGT record captures variability that is representative of, but not necessarily in-phase with, the Northern Hemisphere at large. One possible mechanism to explain this is the North Atlantic Oscillation (NAO), which exhibits a quasi-periodic oscillation of ~60 yr (Sun et al., 2015). While the NAO has some regionally coherent climatic effects, the signature of positive and negative NAO modes is spatially heterogeneous and complex; this could explain the phase offset in the ~60 yr band between the Basin Pond record and the other Northern Hemisphere reconstructions.

Another possible driver of the MBT'$_{5ME}$ changes we see is the Atlantic Multidecadal Oscillation (AMO). The AMO, which is based on sea surface temperature anomalies in the North Atlantic and shows variability in quasi-periodic 60–80 yr cycles (Trenberth et al.., 2017). An AMO reconstruction spanning the last 400 years shows some similarities to the MBT'$_{5ME}$ reconstruction from Basin Pond. Although the records do not show a strong cross correlation, (r=0.08, p=0.53), they feature apparently synchronous cool and warm periods (i.e. 1550 to- 1650 AD and 1780 to– 1830 AD) (Fig. 810). This suggests that climate at Basin Pond is coupled to Atlantic sea surface temperatures on multi-decadal timescales. Thus, the record presented here may prove useful in the future for reconstructing changes in the AMO earlier in the paleorecord.

5.75 20th century Meteorological station and Maine statewide temperature data

Daily temperature measurementsaverages from meteorological stations located within 32 kilometersin the state of Basin PondMaine were accessed and obtained through the National Climatic Data Center (NOAA, 2014). To ensure maximum temporal coverage, daily records from two stations (Farmington and Livermore Falls) were compiled, with Farmington covering 1893–2002, and Livermore Falls covering 2002–2014. These data formed a nearly continuous and complete 121 year record of observational data from October of 1893 to December 2014 from 1895 – present day (NOAA, 2014) (Fig. 9). Furthermore, statewide and regional average temperatures for Maine were obtained from 1895–present day and compared to the local temperature station data (NOAA, 2014) (Fig. 11). 9).

Average temperatures in Maine have warmed by ~1.5ºC since 1895 (Fig. 9). Although this trend is apparent in all seasons, it is smallest during the spring.AD (Fig. 11). The temperature increase is dominated by changes from 1895-1945 AD and 1985-present; for the forty intervening years mean temperatures were more stable, with a slight cooling observed during fall (Fig. 911). Interannual variability of +/- 1ºC is observed throughout the record, with the most pronounced variability during the winter (NOAA, 2014). Local meteorological observations from Farmington, ME show similar structure to the statewide trends, but differ substantially enough, especially in the last fifty years, that we consider them inaccurate and use the state averages for further comparison.

5.86 20th Century brGDGT Reconstructions

VariationsInterestingly, variations in MBT'_{5ME} values for the last 100 years do not agree with instrumental observations. The brGDGT-based reconstruction shows stable values from 1900-1950 AD, followed by an abrupt increase (warming) in MBT'_{5ME} of 0.1 over two decadesuntil approximately 1975 AD (three data points), which decreases again over the and a subsequent two decades (threecontinual decrease since then (five data points) (Fig. 9). This produces a prominent spike that is irreconcilable with instrumental records.11). In factcontrast, instrumental records indicate a slight cooling, or at least a stabilization of warming, starting at the same time (1960s-70s) when the MBT'_{5ME} values begin to increaseare increasing (Fig. 9).11). We note decreasing MBT'_{5ME} values in the upper 3.5 cm (Fig. 11). Low MBT'_{5ME} values in surface and core top sediments have been noted in other studies as well (Sinnighee.g. Sinninghe Damsté et al., 2012; Tierney et al., 2012), suggestingindicating that this trend is reproduciblefeature occurs in different regions and environments, and may be driven by mechanisms associated with brGDGT production or preservation. Tierney et al. (2012) note a similar pattern in the brGDGT distributions of Salt Pond (RI) surface sediments that we observe at Basin Pond where the shallow surface sediments are characterized by more methylated brGDGTs. These authors suggest that more methylated brGDGTs present in shallow lake sediments do not survive diagenesis and they also note that deeper sediments yielded reasonable brGDGT reconstructed temperatures (Tierney et al., 2012). This hypothesis requires further testing and additionally, other influences such as changes in brGDGT producer, post-depositional mobility and/or overprinting of the brGDGT signal, biotic and abiotic compound diagenesis, and anthropogenic impacts to lake ecosystems should be examined as well. Despite the uncertainties about the MBT'_{5ME} record during the last 100 years, we believe that the Basin Pond brGDGT record is useful for describing regional climate evolution over the last millennium in the NE US.

It is possible that land-use change and other anthropogenic impacts have had an impact onaffected the brGDGT record over the last 100 years. However, known land use change in the Basin Pond catchment is minimal over the past century (Gajewski, 1988). A complicating factor is the addition of the piscicide rotenone to the lake in 1955 to remove fish species in competition with trout (USGS, 1996). While the estimated lifetime of rotenone in the water column is short (days to weeks), it has been shown to have lasting long-term (years) effects on zooplankton communities and lake productivity (Kiser, 1963; Andersen, 1970; Sanni and Waervagen, 1990).

In lacustrine environments, some classes of lipid biomarkers, specifically sterols and stanols, can give valuable insight into variability of lake productivity of certain types of algae throughout time. Many sterols (and their saturated counterparts, stanols) ~~can be~~are indicative of certain groups of source organisms, in particular, specific phytoplankton groups (~~Castañeda and Schouten, 2011; Volkman, 2003;~~e.g. Volkman et al., 1998; Volkman, 2003). For example, dinosterol and dinostanol are found in dinoflagellates and are not produced in higher plants, and are therefore used as a biomarker for dinoflagellate species (Volkman et al., 1998). ~~The phytosterol class, including β-sitosterol/stanol and campesterol/stanol, has been linked to terrestrially-derived higher plant sources (Fernholz and MacPhillamy, 1941; Segura et al., 2006; Volkman, 2003, 1986).~~ The compounds isololiolide and loliolide are known to be anoxic degradation products of ~~diatoms, and have been used as a biomarker for diatom species~~diatom pigments (Klok et al., 1984; Repeta, 1989~~). Long~~) while long-chain alkyl diols are produced by eustigmatophyte ~~or~~ (yellow-green) algae~~, and can be indicative of this algal class~~ (Volkman et al., 1998). At Basin Pond, several algal ~~community~~ biomarker concentrations, including isololiolide/loliolide, dinosterol/stanol, and C_{30} 1,13 *n*-alkyl diol, decrease following the rotenone treatment in 1955 AD while ~~B~~β-sitosterol increases (Fig~~9~~. 11) suggesting a shift in the overall algal community structure. Additionally, after 1955 contributions of the different algal biomarkers are remarkably stable in comparison to earlier times (Fig~~.~~. 11). Due to the widespread shift in algal community structure and productivity, we posit that bacterial communities and therefore brGDGT production may also have been impacted. However, brGDGT concentrations do not clearly respond to the rotenone treatment (See Supplementary data) and additional knowledge of brGDGT producers would be required to further investigate this idea.

~~**9). Thus, we believe that while the Basin Pond record may be useful for describing regional climate evolution over the last millennium in the NE US, it may have been compromised over the 20th century by anthropogenic influences, a fate that is not uncommon for lakes in developed regions (Itkonen & Salonen 1994, Köster et al., 2005, Myrbo, 2008).**~~

6 Conclusions

We find evidence for seasonally-biased, *in situ* production of branched gylcerol dialkyl glycerol tetraethers (brGDGTs) in a lake in central Maine, NE US. BrGDGTs are mostly produced in September at Basin Pond, and their downward fluxes in the water column peak at ~~24~~30 m water depth. A downcore brGDGT-based reconstruction reveals both gradual and transient climate changes over the last 900 years and records cooling and warming events correlated with other Northern Hemisphere records and the NAO and AMO indices. This suggests inland Maine climate is sensitive to hemispheric climate forcing as well as changes in regional atmospheric pressure patterns and North Atlantic sea surface temperatures. ~~Along with~~Our new MBT'_{5ME} temperature reconstruction, supported by a pollen record from the same site, ~~our reconstruction~~ reveals a prominent cooling trend from ~~AD~~ 1100–1900 AD in this area. Comparison with regional hydroclimate records suggests that despite increasingly cool and wet conditions persisting at Basin Pond over the last 900 years, fire activity has increased. Although recent fire activity is likely anthropogenically triggered (i.e. via land-use change), our results imply ~~a distinct~~an independent relationship between climate and NE US fire occurrence over the ~~last 900 years in the NE US~~study interval. Thus, the paleotemperature reconstruction presented here alongside site-specific knowledge from Basin Pond informs our understanding of climatic variability in NE US beyond the era of human influence.

Data Availability

BrGDGT data, including fractional abundances of 5- and 6-methyl isomers, BIT Index values, MBT'_{5Me} values, CBT'_{5Me} values, 5-methyl isomer ratio (IR), total brGDGT concentrations, and temperature calibrations (Dang et al., 2018; Russell et al., 2018) from Basin Pond watershed soils, SPM, and sediment samples are available at the National Oceanic and Atmospheric Administration National Centers for Environmental Information (NOAA NCEI) Paleoclimate Database. Concentrations of isololiolide/loliolide, C30 1,13 Diol, sitosterol/sitostanol, and dinosterol/dinostanol from the Basin Pond sediment core are also provided where measured. To access these data, please visit: https://www.ncdc.noaa.gov/data-access/paleoclimatology-data/datasets.

Author Contribution

DRM, MHH, and BAK designed the sediment traps, carried out field work, processed samples through all stages of laboratory prep and analysis, and prepared the manuscript for publication. ISC and RSB provided advice throughout the experiment and writing process, aided with field work, contributed to data interpretation, and covered costs of sample analysis. Manuscript revisions were made through contributions from all co-authors.

Competing Interests

The authors declare that they have no conflict of interest.

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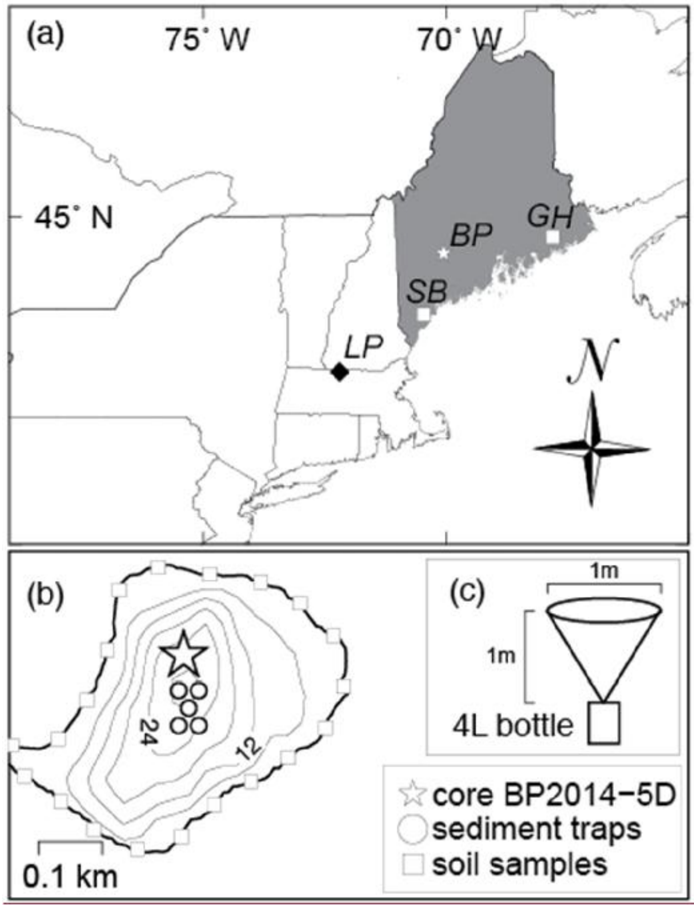
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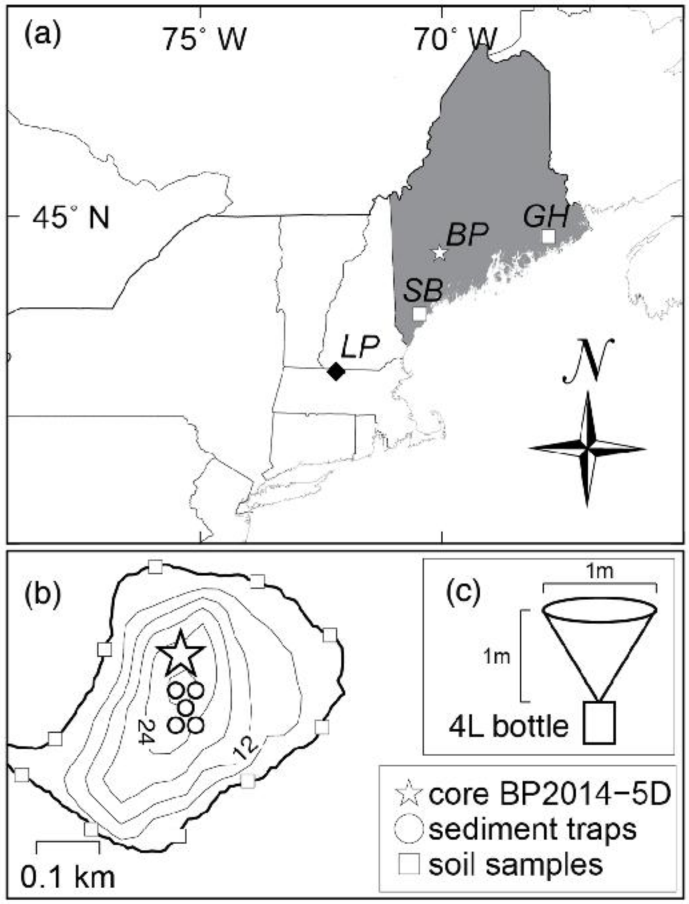
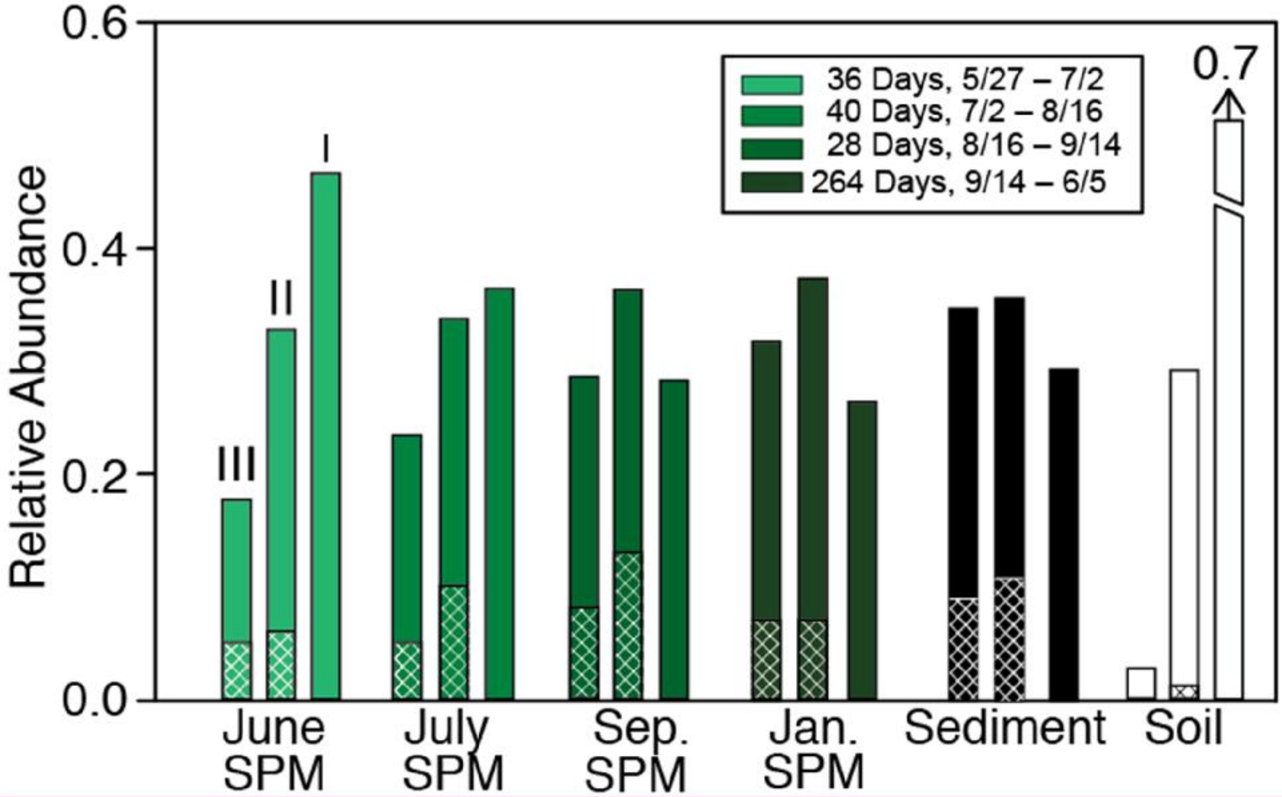


Figure 1. Map of Basin Pond. (a) The location of Basin Pond (BP) (white star) in Maine, USA. Locations of three other sites are labelled: Little Pond (LP; Gao et al. 2017), Great Heath Lake (GH; Nichols and Huang, 2012; Clifford and Booth, 2013), and Saco Bog (SB; Clifford and Booth, 2013). ~~For more information regarding these sites, see Supplementary Information.~~ **(b) Bathymetric profile (6 m contours) of Basin Pond with position of floating sediment traps (circles), surface soil samples (squares), and core BD-2014-5D used for the downcore temperature reconstruction in this study (star). The pond has an area of approximately 0.14 km^2. (c) Schematic of sediment traps utilized in this study.**



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0.0
Relative Abundance
36 Days, 5/27 – 7/2
40 Days, 7/2 – 8/16
28 Days, 8/16 – 9/14
264 Days, 9/14 – 6/5
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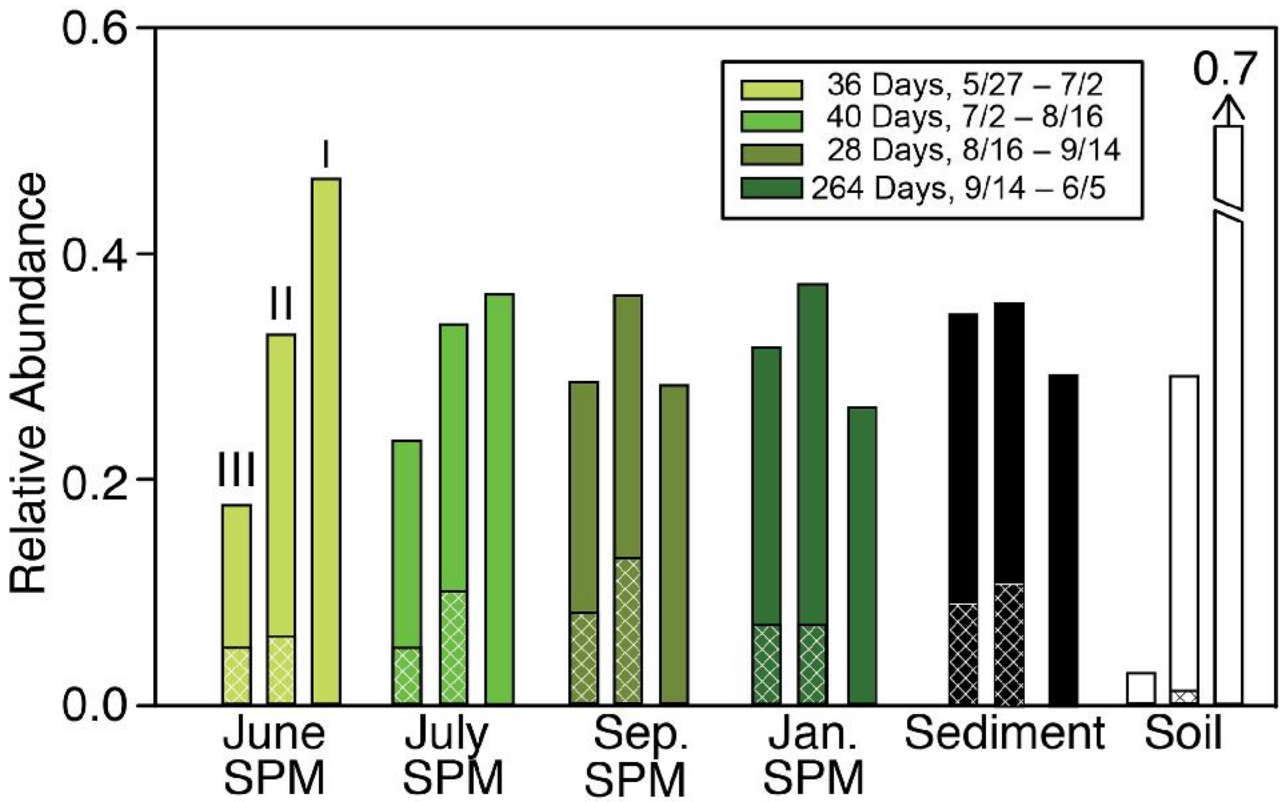
I
II
III
June SPM
July SPM
Sep. SPM
Jan. SPM
Sediment
Soil



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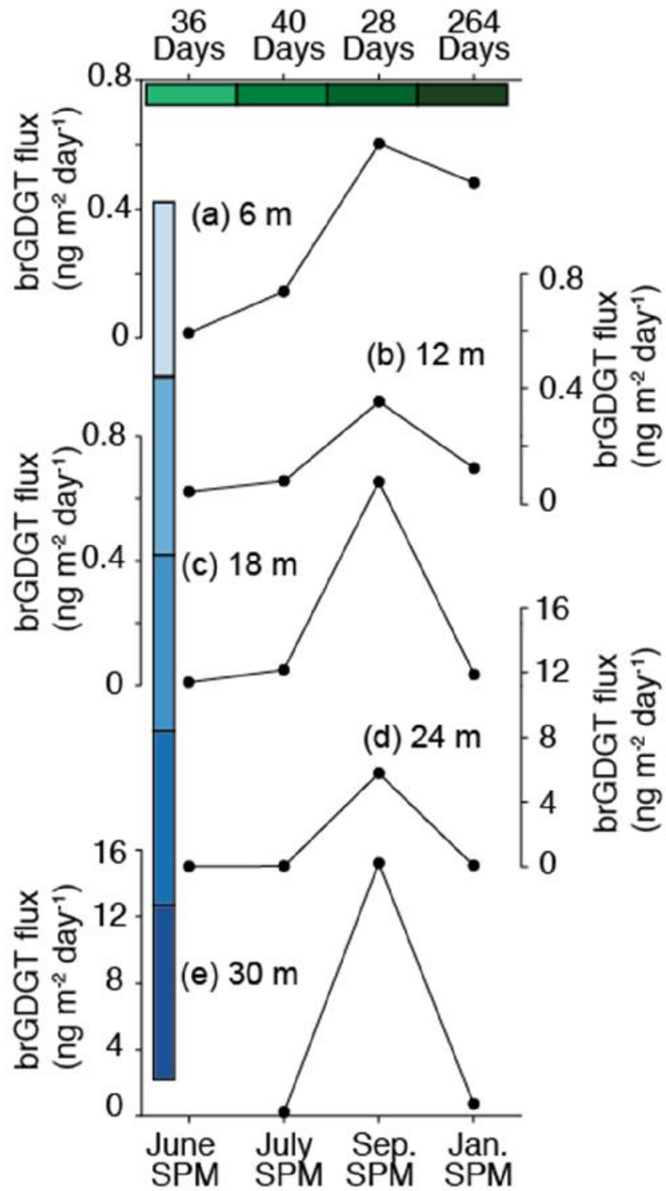
0.7
I
II
III
June SPM
July SPM
Sep. SPM
Jan. SPM
Sediment
Soil

Figure 2. Temporal variation of the relative abundance of ~~groups~~group I, II and III brGDGTs in SPM (green shaded bars), sediment (black bars), and catchment soil samples (white bars). As in the plot of June SPM, the brGDGT groups III, II, and I, are displayed from left to right for each collection period and sediment and soil samples. Sediment and soil samples were collected in Spring of 2014. Green shaded bars for SPM samples reflect averages for each date samples were collected, measured in July 2014 (lightest green), August 2014, September 2014 and June 2015 (darkest green). For each category, brGDGT groups III, II, and I are shown in that order (left to right). Lines in each bar represent the relative abundance of 5- and 6- methyl brGDGTs, with cross hatching representing 6- methyl abundances.



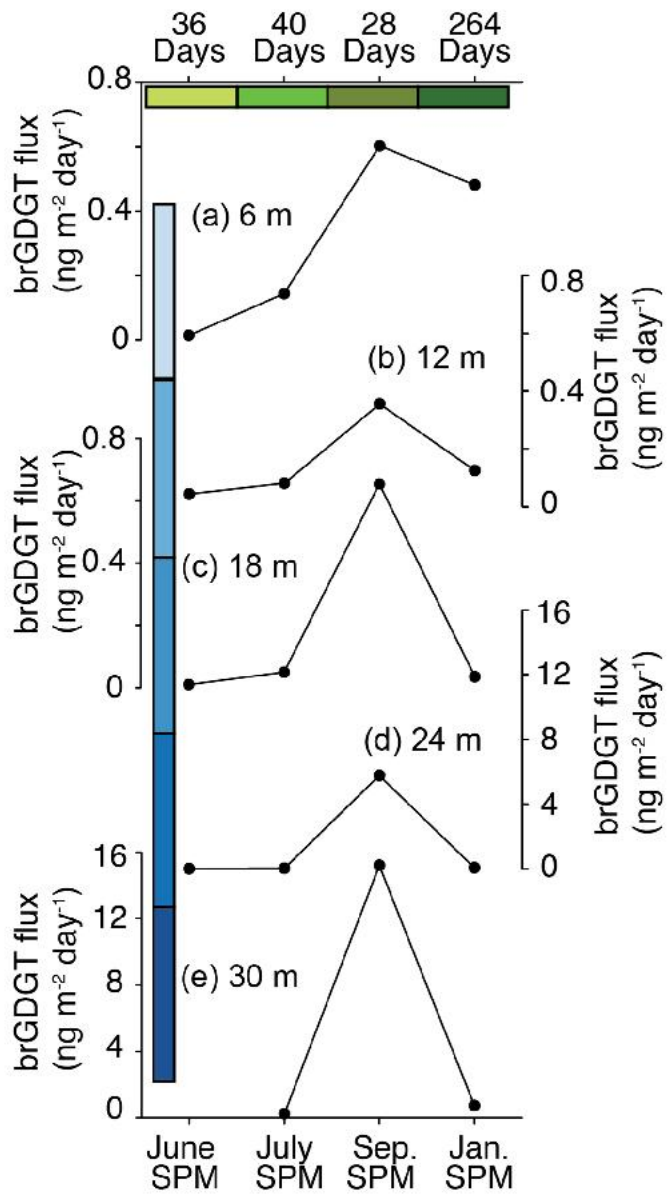


Figure 3. Time series of brGDGT fluxes for each of the sediment traps in Basin Pond. brGDGT fluxes at 6m (a), 12m (b), 18m (c), 24m (d), and 30m (e) are shown. There is no data for trap (e) in July 2014. Note the change of scale for (d) and (e), indicating fluxes an order of magnitude higher for the lowermost traps. Green bars correspond to the time periods in Figure 2. Blue bars correspond to the depth ranges in Figure 5.

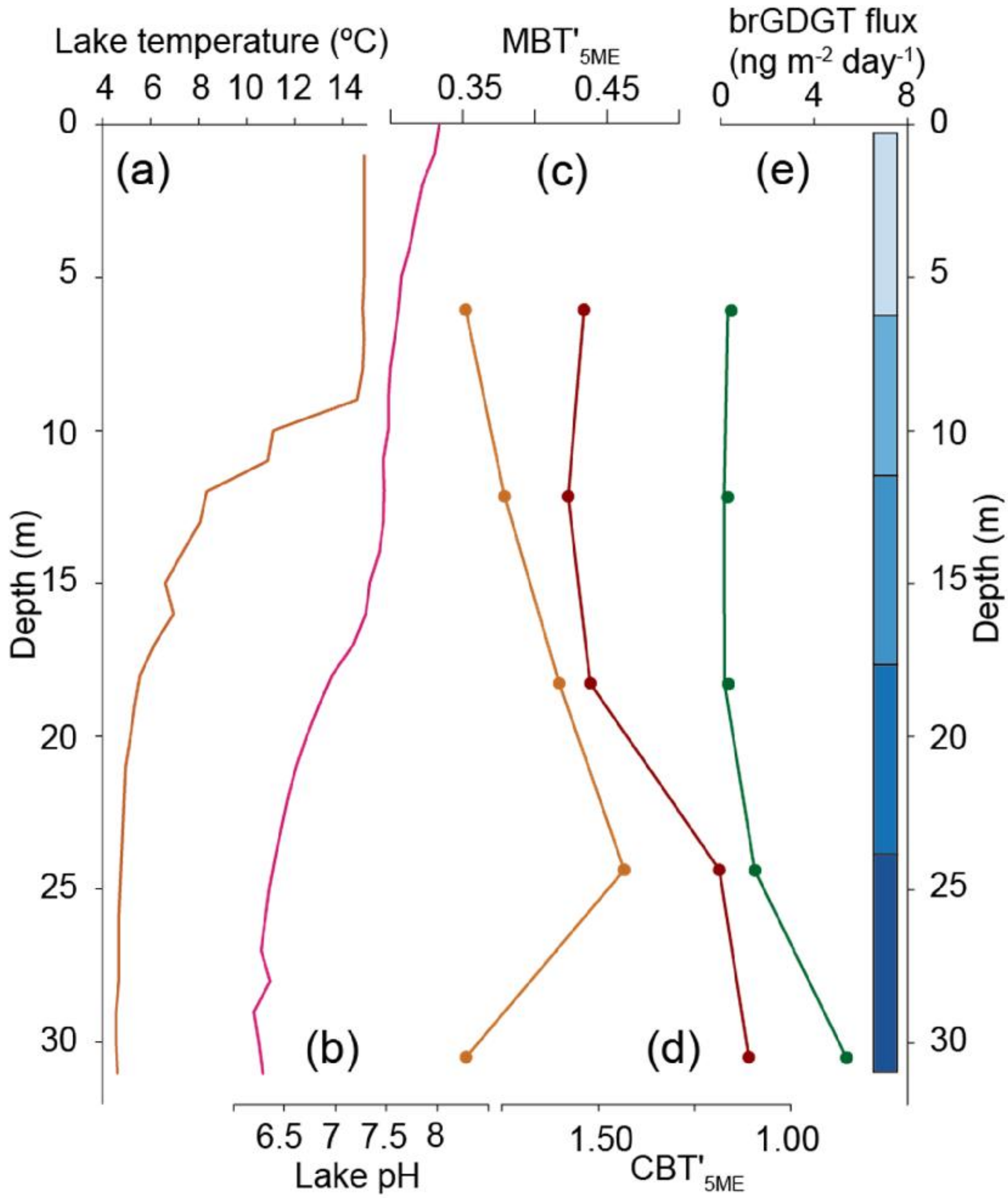
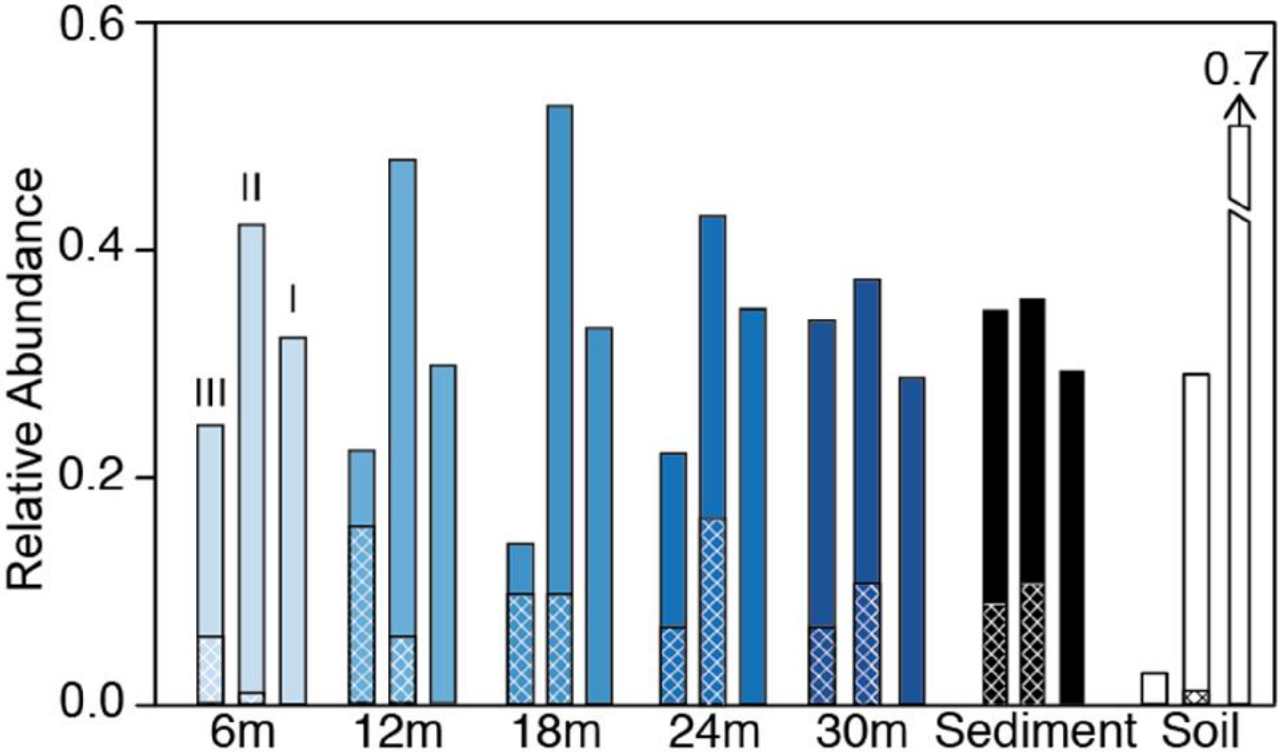


Figure 4. Hydrolab-measured temperature and pH profiles for Basin Pond compared with flux weighted average brGDGT-based reconstructions. (a) Fall lake temperature profile, showing the mixed layer extending to ~9 m water depth, followed by the thermocline (9-15 m) and a cold deep layer (15-32 m). (b) Fall pH profile. the pH ranges from ~7.5 at the surface to ~6.2 at depth. (c) ~~Average~~Flux weighted average MBT values measured at sediment traps. (d) ~~Average~~Flux weighted average CBT values measured at sediment traps. (e) brGDGT fluxes measured at sediment traps.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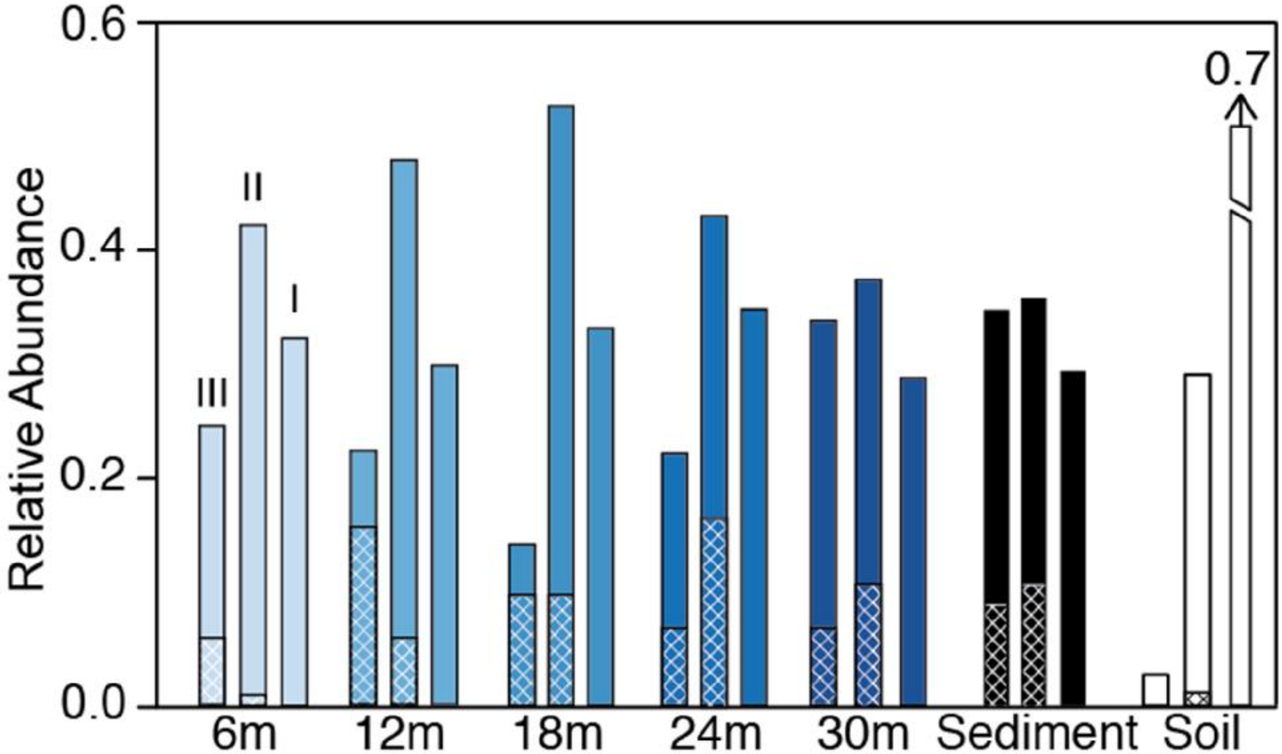
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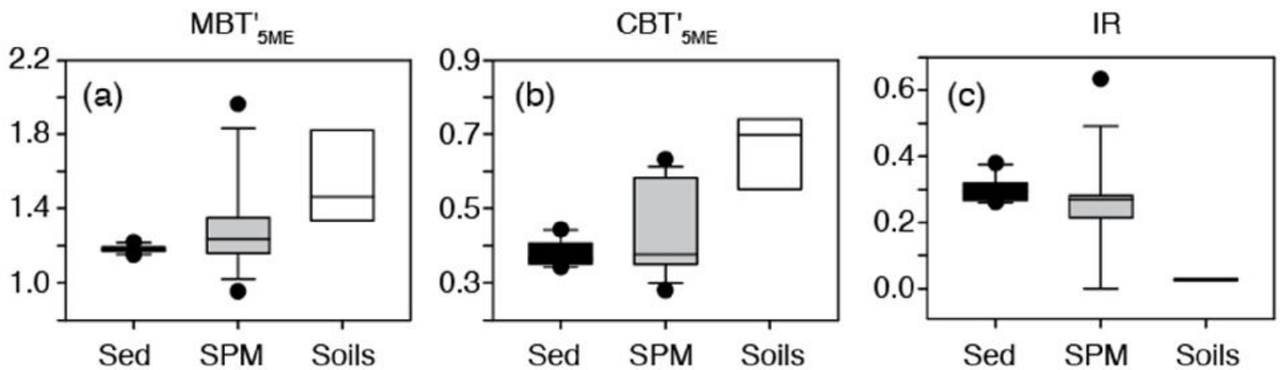
Sediment
Soil

Figure 5. Spatial variation in the water column of the relative abundance of groups I, II and III brGDGTs in SPM as a function of water depth. As in the plot of June SPM, the brGDGT groups III, II, and I, are displayed from left to right for each collection period and sediment and soil samples. For each group, the relative abundance at depths of 6 m (lightest blue), 12 m, 18 m, 24 m, and 30 m (darkest blue) is plotted next to the average surface sediment (black) and catchment soil (white). For each category, brGDGT groups III, II, and I are shown in that order (left to right). Lines in each bar represent the relative abundance of 5- and 6-methyl brGDGTs, with cross hatching representing 6- methyl abundances.



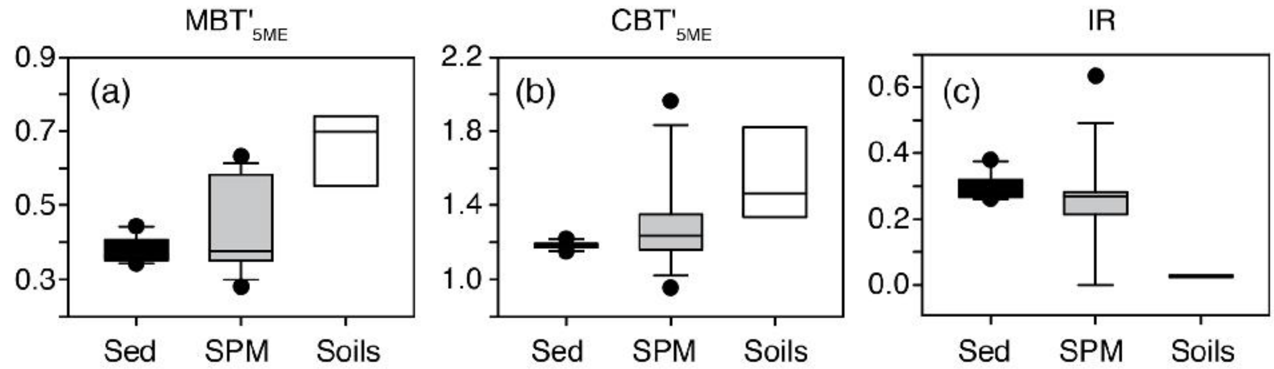
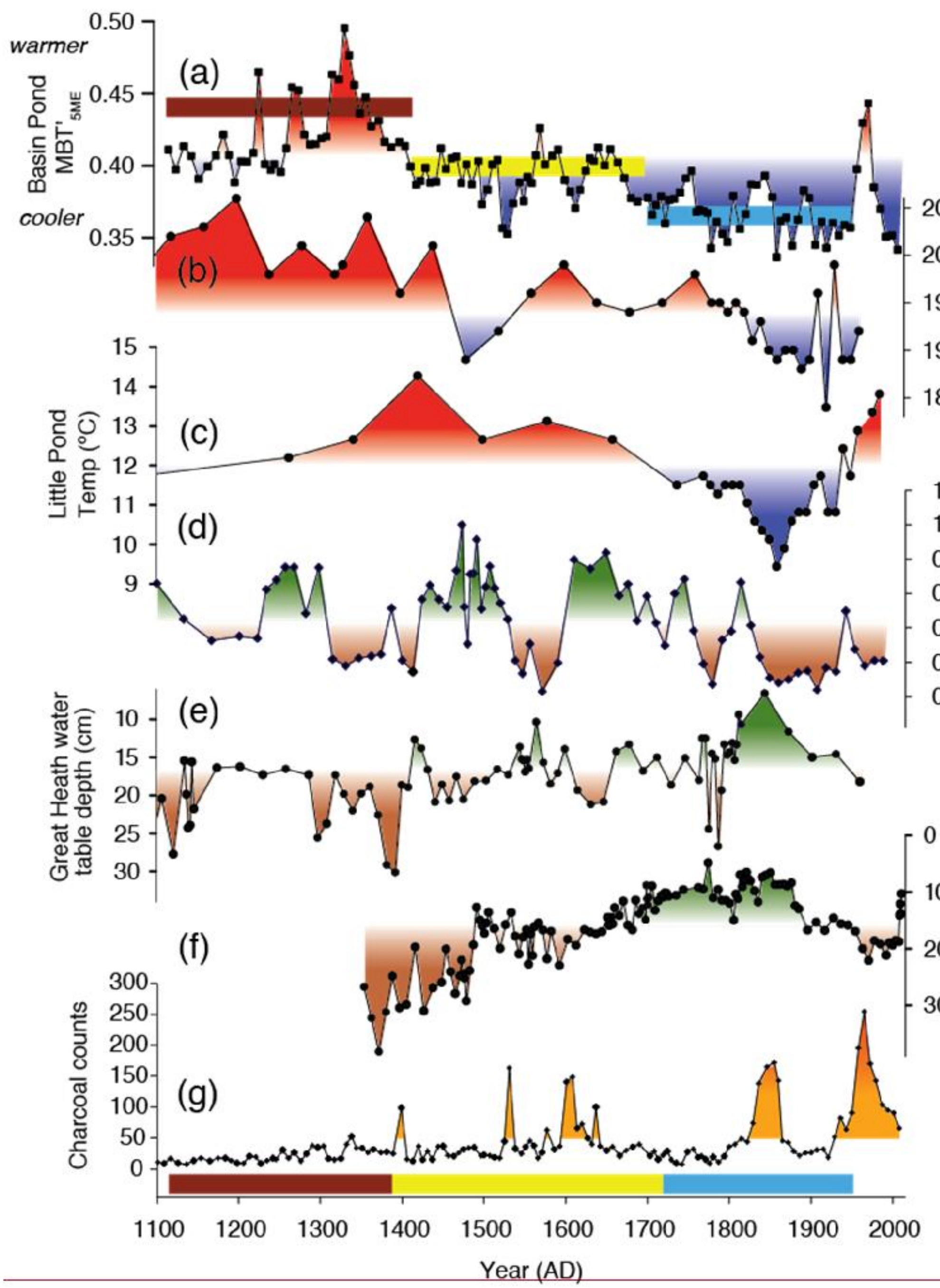


Figure 6. BrGDGT-based proxies measured on surface sediments (black), SPM (gray), and catchment soils (white). (a) Cyclization of Branched Tetraethers (CBT), (b) Methylation of branched tetraethers (MBT'$_{5ME}$), and (c) the Isomer Ratio (IR).



warmer
cooler
Basin Pond MBT'5ME
(a)
(b)
Basin Pond Pollen Temp (ºC)
(c)
Little Pond Temp (ºC)
(d)
wetter
drier
Great Heath SVR
(e)
Great Heath water table depth (cm)
(f)
Saco water table depth (cm)
(g)
Charcoal counts
Year (AD)

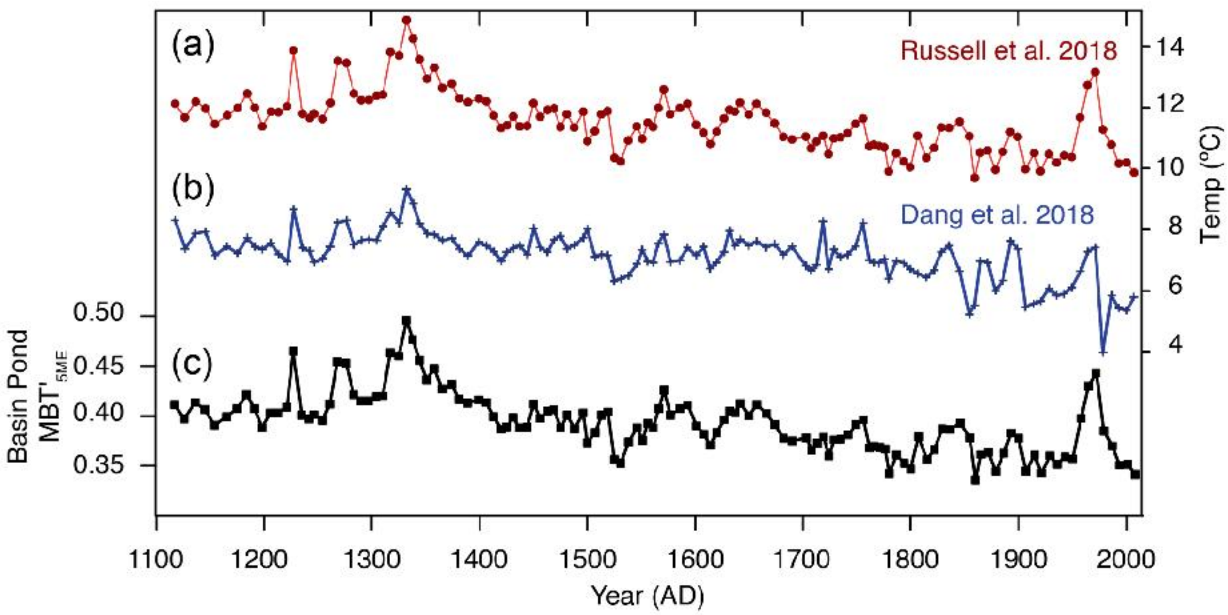


Figure 7. **Comparison of Basin Pond MBT'$_{5ME}$ with newly published temperature calibrations. (a) Core BP2014-5D plotted using the African Lakes calibration (Russell et al., 2018), and the (b) Chinese lakes calibration (Dang et al., 2018). (c) Basin Pond MBT'$_{5ME}$ values.**

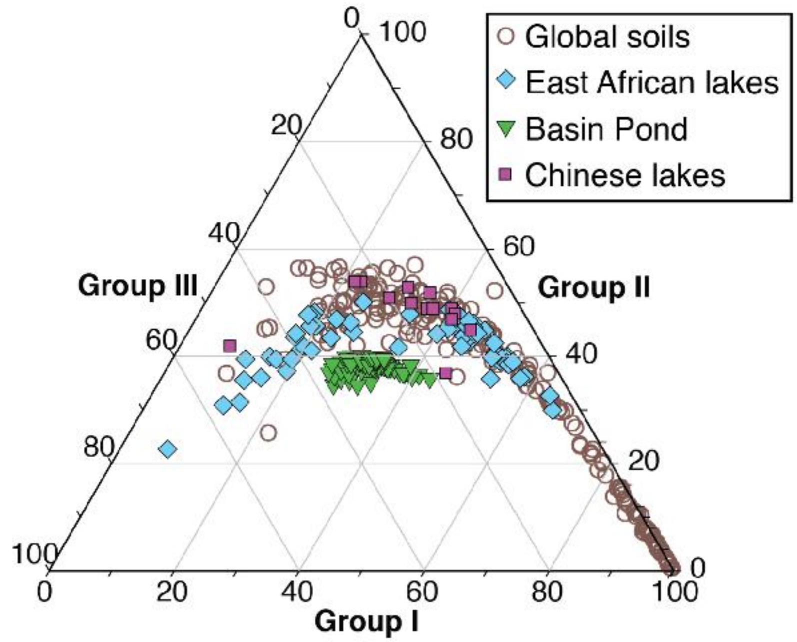


Figure 8. Ternary diagram of brGDGT distributions of lake sediments (Dang et al., 2018; Russell et al., 2018) and global soils (Peterse et al., 2012) and Basin Pond sediments.

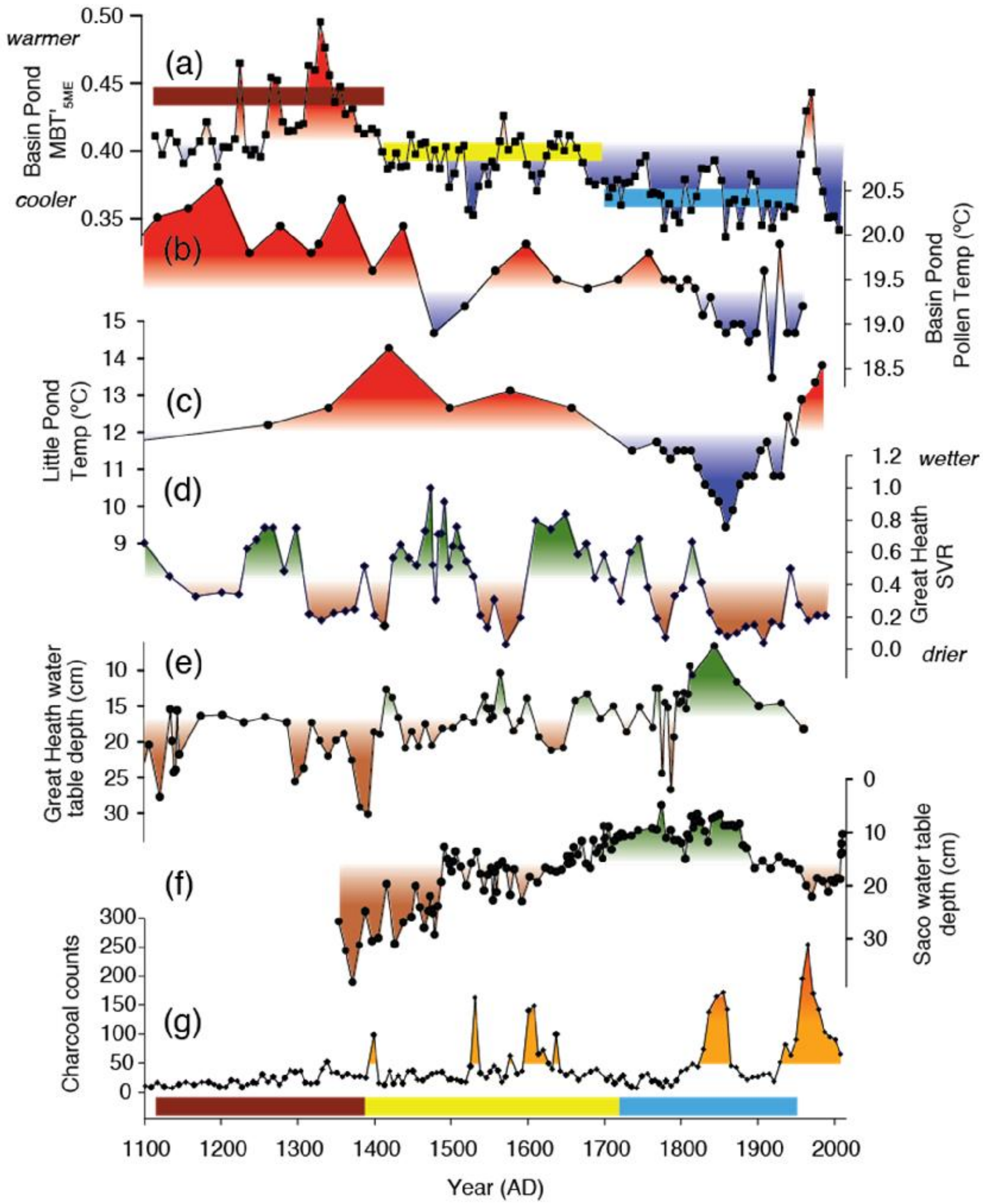


Figure 9. The Basin Pond ~~MBT~~MBT'5ME record compared with other paleoclimate records from the NE US. (a) ~~MBT~~MBT'5ME (this study). Colored bars indicate the three main periods discussed in the text. (b) Pollen-based reconstruction of temperature at Basin Pond (Gajewski, 1988). (c) Deuterium isotope ~~(□D~~(δD)-based temperature reconstruction ~~of temperature~~ at Little Pond (Gao et al., 2017). (d) Great Heath aridity reconstruction based on the *Sphagnum*/Vascular Ratio (SVR) (Nichols and Huang, 2012). (e) Water table reconstruction from Great Heath (Clifford and Booth, 2013). (f) Water table reconstruction from Saco Bog (Clifford and Booth, 2013). (g) Charcoal counts from Basin Pond (Miller et al., 2017).

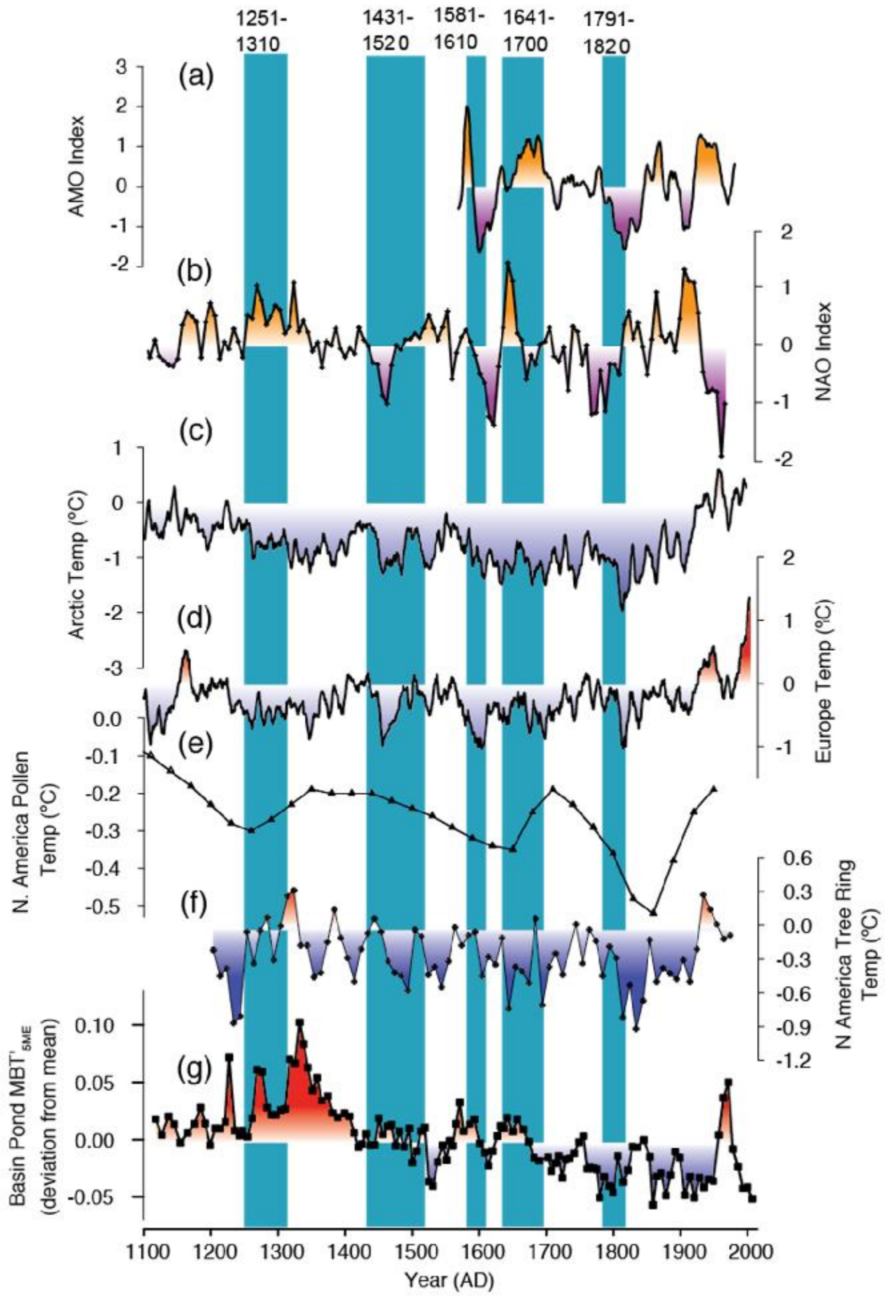
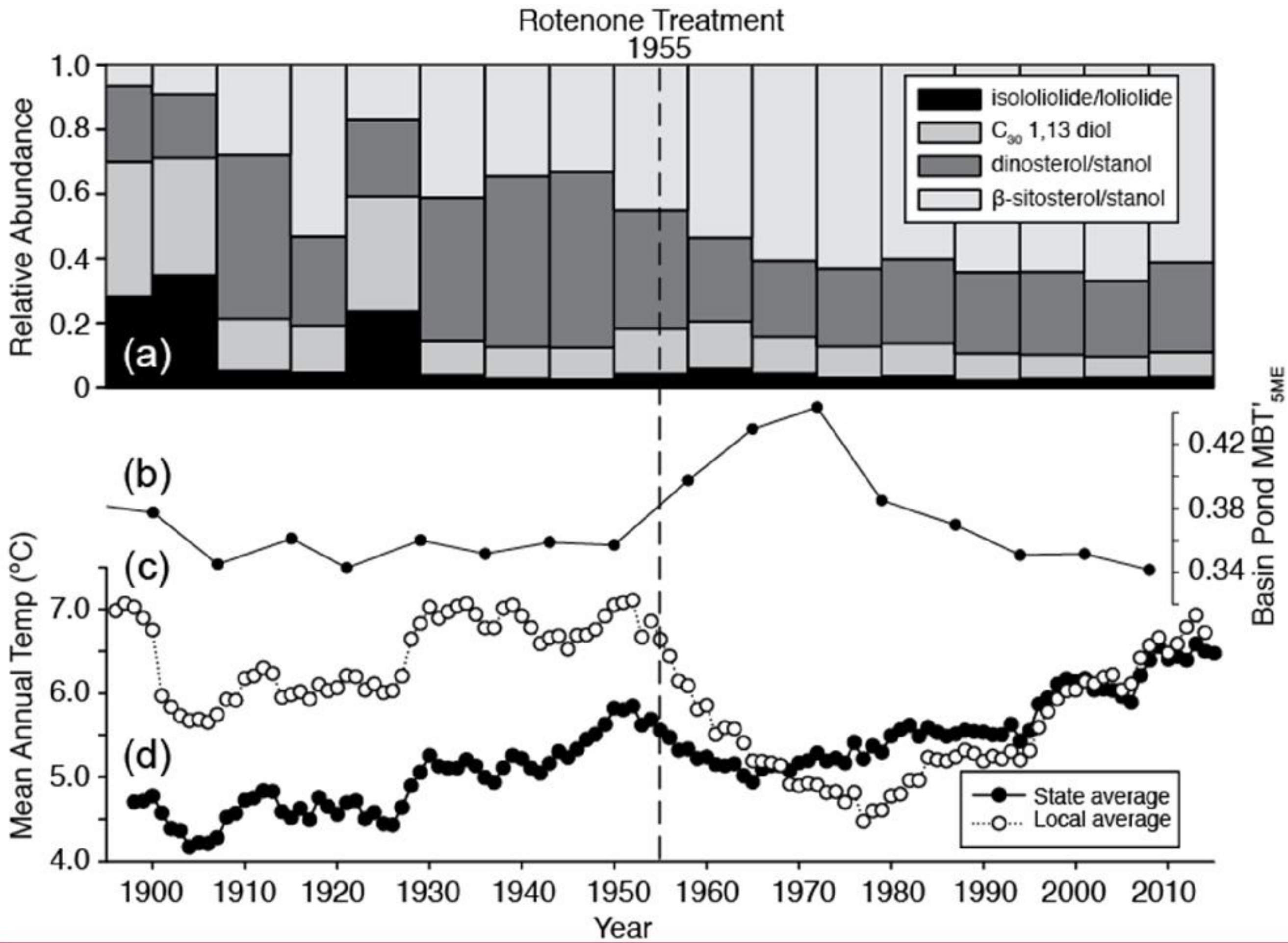


Figure ~~8~~10. The Basin Pond MBT'$_{5ME}$ record compared with regional and global records of temperature change. (a) Tree-ring based reconstruction of the AMO Index (Gray et al., 2004). (b) NAO Index reconstruction (Sun et al., 2015). (c–f) Regional temperature stacks based on composite proxy reconstructions for the Arctic (c), Europe (d), and North America (pollen, (e); tree rings, (f). The records have been standardized to have the same mean (0) and standard deviation (1) from 1190–1970 AD (PAGES2k 2013). (g) MBT'$_{5ME}$ (this study).



Rotenone Treatment
1955
1.0
0.8
0.6
0.4
0.2
0
Relative Abundance
(a)
isololiolide/loliolide
C30 1,13 diol
dinosterol/stanol
β-sitosterol/stanol
(b)
0.42
0.38
0.34
Basin Pond MBT'5ME
(c)
7.0
6.0
5.0
4.0
Mean Annual Temp (°C)
(d)
State average
Local average
1900
1910
1920
1930
1940
1950
1960
1970
1980
1990
2000
2010
Year

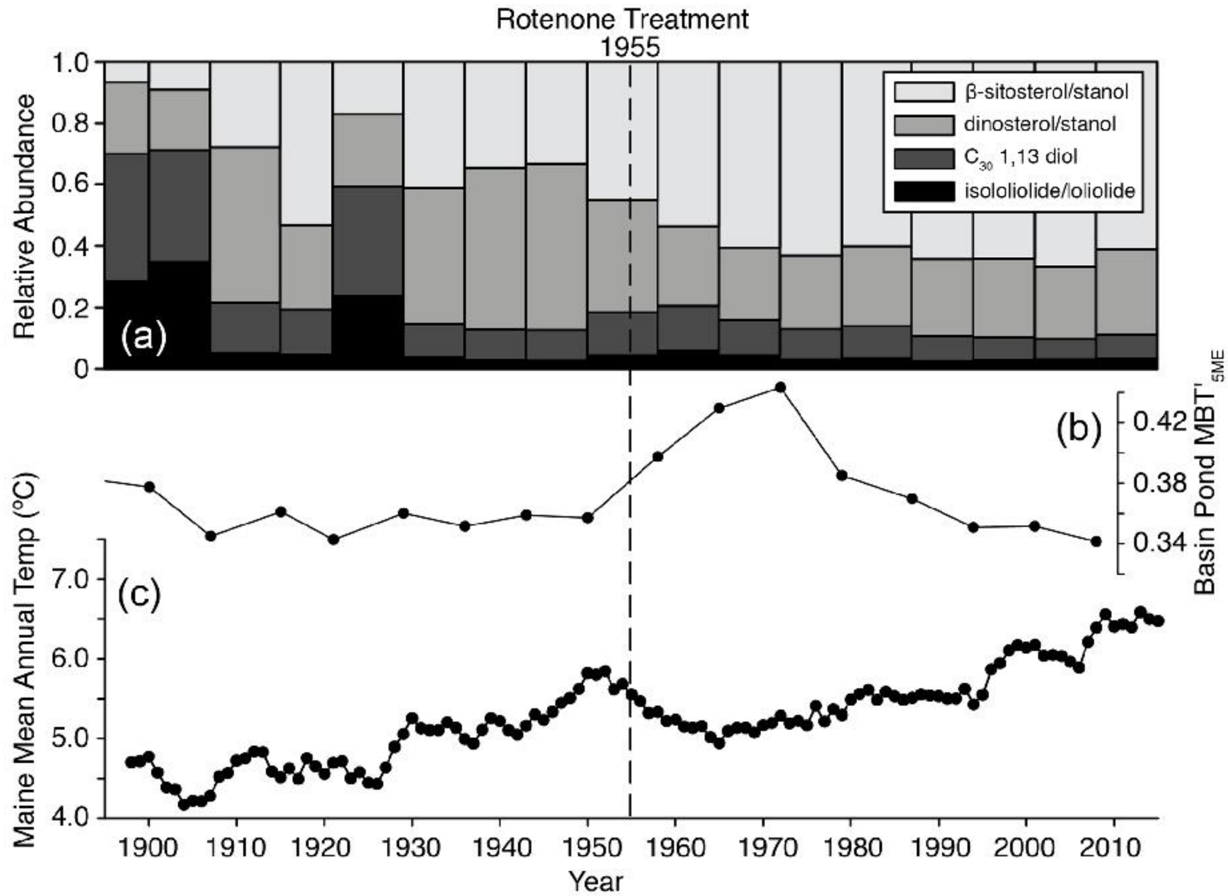


Figure ~~9~~11. Comparison of ~~regional~~ historical temperature records for ~~Maine (~~the state ~~and local temperature),~~of Maine, MBT'$_{5ME}$ reconstruction, and algal lipid biomarkers in Basin Pond. (a) Relative abundance of four major algal lipids. (b) MBT'$_{5ME}$ record. ~~(c) Local temperature measured at Farmington and Livermore Falls meteorological stations. (d) Maine statewide~~(c) Maine state-wide average temperature (NOAA, 2014). The black line indicates the rotenone treatment of the lake in 1955.