JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 115, G01015, doi:10.1029/2009JG001109, 2010

Click Here for Full Article

# Assessing past temperature and soil pH estimates from bacterial tetraether membrane lipids: Evidence from the recent lake sediments of Lochnagar, Scotland

Jonathan J. Tyler,[1,2] Alexandra J. Nederbragt,[3] Vivienne J. Jones,[1] and Jürgen W. Thurow[3]

Received 5 August 2009; revised 20 October 2009; accepted 2 November 2009; published 24 March 2010.

[1] Past variation in soil pH and air temperature can potentially be reconstructed from the relative abundance in sediments of branched glycerol dialkyl glycerol tetraethers (GDGTs), synthesized by anaerobic bacteria. Specifically, the cyclization of branched tetraethers (CBT) is believed to be a function of pH, whereas temperature can be estimated from a combination of the extent of both the CBT and methylation of branched tetraethers. Here we explore this potential by comparing a recent sedimentary GDGT profile from Lochnagar, Scotland, with reconstructed air temperature (statistically extrapolated from regional instrumental data sets) and diatom-inferred lake water pH for the past ~200 years. Branched glycerol dialkyl glycerol tetratether and diatom-inferred pH generally agree throughout the core, supporting the use of cyclization of branched tetraethers to reconstruct pH. During the period of rapid industrial acidification (~1860–1970 A.D.), changes in diatom-inferred pH lag behind those inferred using branched tetraethers by between 10 and 50 years, possibly due to differing nonlinear responses to acid deposition within soil and lake water environments. However, branched-GDGT-derived temperatures are both lower than extrapolated mean annual air temperature estimates (by ~5°C) and exhibit at least double the rate of reconstructed warming (~2.5°C in 200 years). At Lochnagar, methylation and cyclization of branched tetraethers are closely correlated ($r^2$ = 0.96) suggesting that in this setting the underlying controls over the two indices may not significantly differ. Therefore the validity of branched-GDGT-derived temperature is uncertain and further research is required to address the environmental controls over branched glycerol dialkyl glycerol tetratether synthesis and thus their value as palaeoclimate proxies.

**Citation:** Tyler, J. J., A. J. Nederbragt, V. J. Jones, and J. W. Thurow (2010), Assessing past temperature and soil pH estimates from bacterial tetraether membrane lipids: Evidence from the recent lake sediments of Lochnagar, Scotland, *J. Geophys. Res.*, *115*, G01015, doi:10.1029/2009JG001109.

## 1. Introduction

[2] The relative abundance of soil-derived branched glycerol dialkyl glycerol tetraethers (GDGTs) within marine and lacustrine sediments is rapidly gaining interest as a proxy for past air temperature and soil pH of continental regions [*Peterse et al.*, 2009a, 2009b; *Rueda et al.*, 2009; *Sinninghe Damstè et al.*, 2008; *Weijers et al.*, 2007a, 2007b, 2007c]. Branched GDGTs are probably produced in soils by anaerobic bacteria and are globally abundant [*Sinninghe Damstè et al.*, 2000; *Weijers et al.*, 2006a, 2006b, 2007c]. *Weijers et al.* [2007c] proposed two indices concerning branched GDGTs: the relative abundance of cyclopentyl moieties (cyclization of branched tetraethers (CBT)) and the relative abundance of methyl branches (methylation of branched tetraethers (MBT)) [*Weijers et al.*, 2007c]. A study of 134 soil samples demonstrated an empirical relationship between CBT and pH ($r^2$ = 0.7), whereas the MBT ratio was correlated with temperature ($r^2$ = 0.62) and pH ($r^2$ = 0.37). Together, temperature and pH explained most of the variance in MBT ($r^2$ = 0.82), presenting the opportunity to estimate temperature as a function of CBT and MBT combined ($r^2$ = 0.77) [*Weijers et al.*, 2007a, 2007b, 2007c]. Further support was obtained by *Peterse et al.* [2009b], who observed similar effects of in situ soil temperature and pH on MBT and CBT in geothermally heated soils. In addition, *Rueda et al.* [2009] reconstructed air temperatures from coastal marine sediments off southern Norway and Sweden for the last 200 years before

[1]Environmental Change Research Centre, Department of Geography, University College London, London, UK.

[2]Now at Department of Earth Sciences, University of Oxford, Oxford, UK.

[3]Department of Earth Sciences, University College London, London, UK.


0148-0227/10/2009JG001109

present, which compare favorably with regional instrumental summer air temperatures for this period. However, *Sinninghe Damstè et al.* [2008], in a study of branched GDGTs in soils across an altitudinal gradient at Mount Kilimanjaro, Kenya, observed a temperature dependence over the MBT ratio which was inconsistent with previous calibration efforts. They concluded that localized calibration studies are required in order to achieve accurate palaeotemperature estimates using this method [*Sinninghe Damstè et al.*, 2008]. Additional concerns were raised by *Peterse et al.* [2009a] whose data suggest substantial in situ production of branched GDGTs in coastal sediments off Svalbard, thus highlighting the need to focus on sediments with a high soil-derived organic content. Branched GDGTs have been used to reconstruct continental temperature and soil pH over the last glacial-interglacial transition in the Congo Basin, Africa [*Weijers et al.*, 2007a], during the Palaeocene-Eocene Thermal Maximum (PETM) from Arctic Ocean sediments [*Weijers et al.*, 2007b] and at the Oligocene-Eocene boundary in Greenland [*Schouten et al.*, 2008], all using marine sediments. To our knowledge, there have been no applications to date using lake sediments, despite obvious potential in settings where soil-derived organic matter represents a major contribution to the sedimentary record.

[3] Calibration of complex palaeoclimatic proxies using geographically arranged data sets can be problematic because the nature and extent of the forcing environmental gradient quite often differs between spatial and temporal contexts. Consequently, although spatial data sets are pivotal in the development of a new method, the ability of that method to accurately replicate recorded temporal changes is also a necessary prerequisite. Therefore, we analyzed MBT and CBT ratios from recent lake sediments at Lochnagar, Scotland (spanning the past ~200 years) for comparison with geographically extrapolated instrumental temperature and independently derived pH estimated from diatom assemblages. Lochnagar has been the site of extensive palaeo- and neolimnological research since the early 1980s and therefore provides a wealth of evidence against which to test the validity of the branched GDGT method for reconstructing past pH and temperature.

## 2. Site

[4] Lochnagar (Latitude 56.959°N; Longitude 3.231°W; National Grid Reference 325200 785900) is a corrie loch (lake) lying at an altitude of 788 m above sea level (asl) in the eastern Highlands of Scotland (Figure 1). The history of research at Lochnagar, including the lake morphology, catchment and biota have been described in detail elsewhere [*Dalton et al.*, 2005; *Rose et al.*, 2004; *Rose*, 2007; *Tyler et al.*, 2007; *Yang et al.*, 2002a]. Briefly, the catchment consists of biotite granite, overlain in places by shallow blanket peats, extensive boulder fields and scree with very little evidence of human alteration. The lake lies above the potential tree line (~650 m asl) and has a sparse catchment vegetation consisting of *Calluna*, *Vaccinium* and a number of mosses and lichens [*Birks*, 2007]. The lake has an average depth of 8.4 m, with a steep bathymetry and a maximum depth of 26 m [*Hughes*, 2007]. It has a surface area of 9.8 ha, with a catchment to lake ratio of 9.4 [*Hughes*, 2007]. The spatial variability of sediment accumulation rate within Lochnagar during the last 140 years was studied by *Yang et al.* [2002a, 2002b], who revealed that the depth of sediment deposited between 1860–1997 varied between 3 and 30 cm. Higher sediment accumulation rates were estimated within the northern and eastern margins of the lake, contrasting with lower sediment accumulation in deeper water to the south and west, where a steep corrie wall rises from the lake edge [*Yang et al.*, 2002a].

[5] Lake water monitoring has been ongoing at Lochnagar since 1980, with an increase in frequency since the inception of the UK Acid Waters Monitoring Network (AWMN, 1988 to present), and more recently the EU funded research projects MOLAR (1996–1999), EMERGE (2000–2003) and Eurolimpacs (2004–2009). These projects have provided extensive background information on lakewater major ion chemistry, aquatic biology, meteorology and lake water temperature [*Rose*, 2007]. Lochnagar has a sedimentary sequence, which spans the Holocene [*Dalton et al.*, 2005], and a number of palaeolimnological projects have been carried out focusing on recent deposition of atmospherically transported pollutants [*Battarbee et al.*, 1996; *Jones et al.*, 1993; *Rose et al.*, 2004; *Yang et al.*, 2002a]. Mean contemporary lake water pH is 5.5, having decreased markedly since the beginning of the industrial revolution ~1860 [*Battarbee et al.*, 1996; *Jones et al.*, 1993; *Monteith et al.*, 2007]. The extent of the recovery of Lochnagar to recent declines in industrial emissions and acid rain is a matter of continued debate [*Monteith et al.*, 2007; *Rose et al.*, 2004], hence the potential value of an alternative means of reconstructing catchment soil pH.

## 3. Methods

### 3.1. Sediment Cores

[6] Sediment cores were taken from the Environmental Change Research Centre (ECRC) archive, having been collected, sliced (into subsamples of 0.2 to 1 cm thickness) and air-dried during previous research projects. Dry sediments were stored in airtight, sterile polythene bags in a dark, cool environment. Material from three cores, NAG21, NAG27 and NAG29 was analyzed (Figure 1). NAG21 (30 cm) was recovered using a gravity corer [*Glew*, 1991; *Yang et al.*, 2002a], while the longer (170 cm) NAG27 and NAG29 cores were collected using a percussion piston corer [*Chambers and Cameron*, 2001; *Dalton et al.*, 2005; *Yang et al.*, 2007]. Sediment chronologies were based on previously published calculations whereby two cores were dated using $^{210}$Pb, and the distinctive first occurrence of spheroidal carbonaceous particles (SCP), representing the onset of industrial emissions from 1860, was used to link subsequent cores to this chronology [*Dalton et al.*, 2005; *Jones et al.*, 1993; *Rose et al.*, 2004; *Yang et al.*, 2002a, 2007]. Cross correlation between cores was achieved by matching the core tops, representing the coring date (1997) and the 1860 SCP horizon. A composite depth and estimated age was fitted by linear interpolation between these tie points assuming constant sedimentation rate [*Yang et al.*, 2002b, 2007].

### 3.2. GDGT Analysis

[7] For analysis of GDGT composition, samples were ultrasonically extracted once with methanol, three times with dichloromethane (DCM)/methanol (1:1, v/v), and three times with DCM. The extracts were split into apolar and

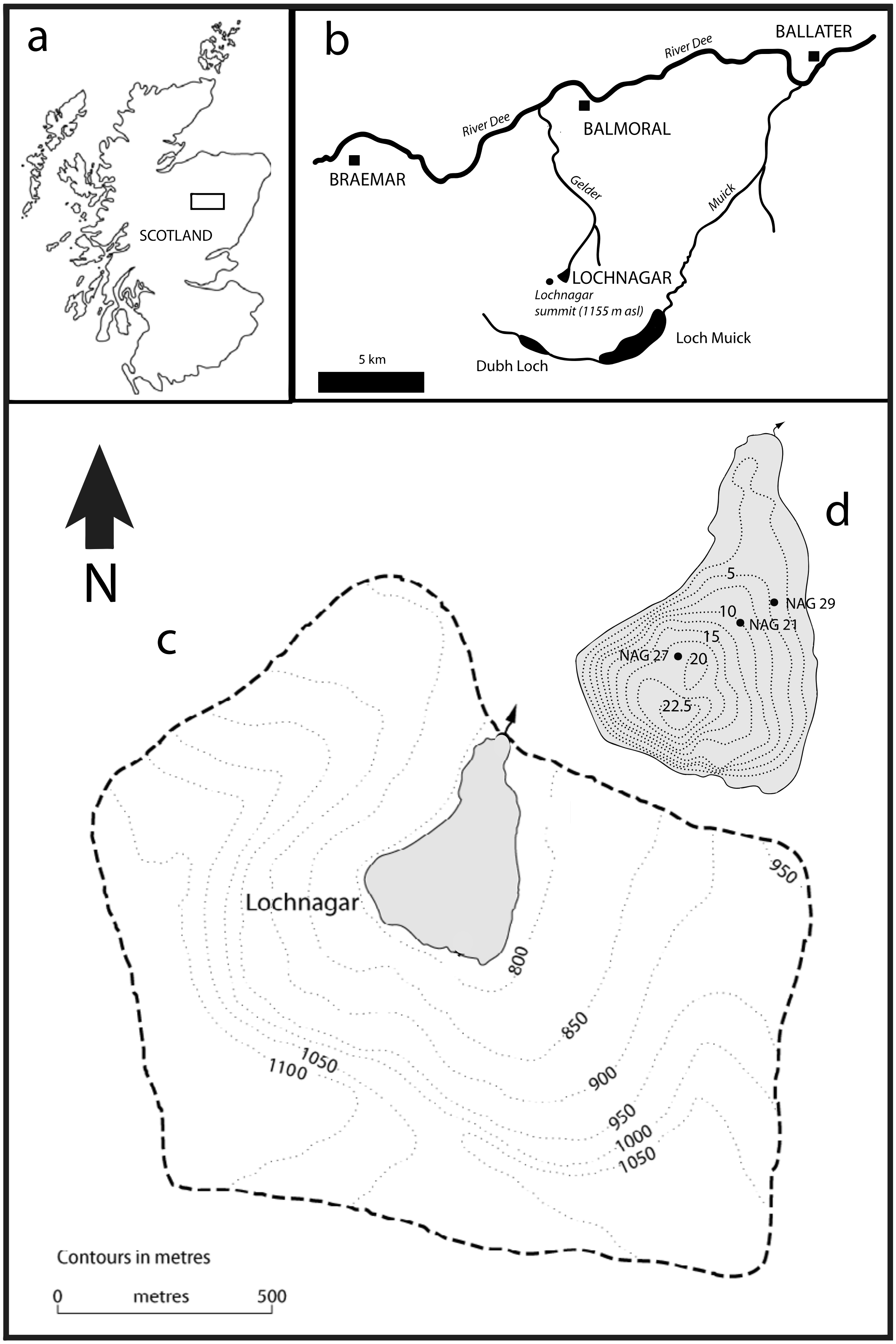


**Figure 1.** Lochnagar (a) site location, (b) regional hydrology, (c) catchment topography, and (d) bathymetry with coring locations.

polar fractions by column chromatography using activated $Al_2O_3$ as the stationary phase and a hexane/DCM (9:1, v/v) and DCM/methanol (1:1, v/v) mixture, respectively, as the eluent. Extracts were dried under a continuous $N_2$ flow at 40°C. The separated fraction was then dissolved in hexane/propa-2-nol (99:1, v/v) and filtered through a 0.45 $\mu$m PTFE filter. GDGT abundances were analyzed in the department of Earth Sciences at University College London on an Agilent 1200 series high-performance liquid chromatography (HPLC) attached to a G6130A single quadrupole mass spectrometer. The analytical protocol followed is as described by *Schouten et al.* [2007a]. The abundance of both isoprenoid and branched GDGTs were measured in single ion scanning mode. Due to limited sample amounts, few replicate analyses were possible from Lochnagar sediments. Eight duplicate analyses gave errors of 0.012 for MBT and 0.011 for CBT (1 standard deviation, n = 8). More frequent repeat calculation of the GDGT-derived $Tex_{86}$ and BIT indices [*Weijers et al.*, 2006b] from two in-house standards (marine sediment and mixed marine/terrestrial sediment) yielded standard deviations of 0.007 (n = 39) and 0.01 (n = 8), respectively. Further, in an interlaboratory comparison experiment, results from our laboratory were found to compare favorably with data from other laboratories [*Schouten et al.*, 2009].

[8] Empirical models for CBT and MBT as a function of soil pH and mean annual air temperature (MAT) were formulated by *Weijers et al.* [2007c] by analysis of 137 globally distributed soils

$$MBT = 0.867 - 0.096 * pH + 0.021 * MAT, \quad (1)$$

$$CBT = 3.33 - 0.38 * pH, \quad (2)$$

$$MBT = 0.122 + (0.187 * CBT) + (0.020 * MAT). \quad (3)$$

In order to reconstruct pH ($pH_{CBT}$) and MAT ($T_{MBT}$) from Lochnagar sediments equations (2) and (3) were inverted to derive

$$pH_{CBT} = (CBT - 3.33)/-0.38 \quad (4)$$

$$T_{MBT} = (MBT - 0.122 - (0.187 * CBT))/0.020. \quad (5)$$

### 3.3. Diatom Analysis

[12] Using the same samples as those analyzed for GDGTs, an independent reconstruction of lake water pH was achieved by analysis of diatom microfossils following standard methods [*Battarbee et al.*, 2001]. Samples were heated (70°C) in hydrogen peroxide for removal of organic matter, followed by 10% HCl for removal of trace carbonates with rinsing three times in deionized water and concentration by centrifugation (1500 rpm) between chemical treatments [*Battarbee et al.*, 2001]. The residual diatom material was mounted upon microscope slides using Naphrax® optical adhesive and a minimum of 300 diatoms were counted per sample using phase contrast light microscopy at 1200 times (oil immersion) magnification, with identification following Krammer and Lange-Bertalot [*Krammer and Lange-Bertalot*, 1986, 1988, 1991a, 1991b]. Diatom-inferred pH ($pH_{diat}$) was achieved using four methods: classical and inverse weighted average (WA) and weighted average partial least squares (WA-PLS) regression based on the Surface Waters Acidification Project (SWAP) calibration training set [*Battarbee and Renberg*, 1990; *Birks et al.*, 1990; *ter Braak and Juggins*, 1993].

## 4. Supporting Data

[13] Long-term air temperature records exist for a number of stations in the United Kingdom, most notably the Central England Temperature record [*Folland et al.*, 2001; *Manley*, 1953, 1974; *Parker et al.*, 1992]. However, due to marked climatic differences with altitude, a linear relationship between lowland monitoring data and the upland climate of Lochnagar cannot be assumed. *Agusti-Panareda and Thompson* [2002] addressed this issue by developing empirical temperature extrapolation models for a number of European high elevation lakes, including Lochnagar, which accounted for seasonal variability in altitudinal lapse rate. These model estimates were validated against 13 monthly mean temperatures, measured on site, to enable hindcasts of Lochnagar air temperature for the period 1781–1995 [*Agusti-Panareda and Thompson*, 2002].

## 5. Results: Branched GDGTs in Lochnagar Sediments

[14] Glycerol dialkyl glycerol tetraethers (GDGTs) were abundant in all samples (for chemical structures see Appendix A of *Weijers et al.* [2007c]). In agreement with previous research [*Weijers et al.*, 2006b, 2007c], branched GDGTs containing one or more cyclopentyl moieties (Ib–IIIb and Ic–IIIc) are less abundant than those containing none (I–III) (Table 1 and Figure 2). GDGTs with two additional methyl branches at sites C-5 and C-5′ and one or more cyclopentyl moieties were not detected. Throughout the sediment profile, GDGT II was most abundant, with GDGT III second most abundant above 9.5 cm, and GDGT I second most abundant below 13.5 cm (Table 1). Downcore MBT and CBT indices exhibit limited between sample variability and coherent long-term trends (Figures 3a and 3b). Between 50 and 15 cm depth, both ratios are relatively constant, whereas both show increases between 15 and 0 cm. MBT values increase from 0.28 at 50 cm depth to 0.38 at the surface, while CBT values increase from 1.2 to 1.4. MBT and CBT are highly correlated ($r^2$ = 0.96, Figure 3c).

[15] The validity of GDGT-inferred pH ($pH_{CBT}$) and temperature ($T_{MBT}$) can be assessed through comparison with independent diatom-inferred pH and extrapolated instrumental climate data (Figure 4). In the Lochnagar sediment profile, $pH_{CBT}$ is correlated with diatom-inferred pH ($pH_{diat}$) with an $r^2$ of 0.84 (Figure 4 (top)). Reconstructed pH values using the two methods are very similar, within a range of ~0.2 pH units prior to 1860 (between 50 and 15 cm), and within 0.4 pH units between 1860 and 1997 (15–0 cm), and both follow similar trajectories, with values declining since 1860 (i.e., with decreasing depth above the 15 cm/1860 SCP marker horizon, Figure 4 (top)). However, during the period of pH decline post 1860, $pH_{diat}$ appears to lag $pH_{CBT}$, whereby $pH_{CBT}$ decreases more gradually, beginning at

**Table 1.** Sample Information, Relative Peak Intensity for GDGTs, and Calculated MBT and CBT Values From Lochnagar Sediment Cores

| | | GDGT Relative Peak Intensity (× 105) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Core | Depth (cm) | III | IIIb | IIIc | II | IIb | IIc | I | Ib | Ic | MBT | CBT |
| NAG21 | 0.25 | 6.65 | – | – | 13.14 | 0.48 | 0.17 | 11.90 | 0.42 | 0.21 | 0.38 | 1.45 |
| NAG27 | 0.5 | 33.19 | – | – | 63.22 | 2.26 | 0.76 | 56.41 | 2.13 | 0.81 | 0.37 | 1.44 |
| NAG27 | 0.7 | 47.24 | – | – | 97.55 | 3.08 | 1.51 | 82.96 | 3.09 | 1.19 | 0.37 | 1.47 |
| NAG27 | 1.1 | 32.53 | – | – | 70.51 | 2.21 | 0.74 | 61.14 | 2.22 | 0.71 | 0.38 | 1.47 |
| NAG27 | 1.5 | 27.35 | – | – | 55.58 | 1.87 | 0.69 | 50.70 | 1.85 | 0.77 | 0.38 | 1.46 |
| NAG27 | 1.9 | 28.09 | – | – | 59.91 | 1.81 | 0.76 | 52.25 | 1.96 | 0.76 | 0.38 | 1.47 |
| NAG21 | 2.25 | 9.42 | – | – | 16.53 | 0.73 | 0.21 | 14.33 | 0.56 | 0.20 | 0.36 | 1.38 |
| NAG27 | 2.3 | 34.36 | – | – | 68.35 | 2.38 | 0.83 | 63.31 | 2.43 | 0.87 | 0.39 | 1.44 |
| NAG21 | 3.25 | 36.91 | – | – | 60.87 | 2.56 | 1.02 | 52.60 | 2.03 | 0.81 | 0.35 | 1.39 |
| NAG21 | 4.25 | 57.25 | – | – | 97.43 | 4.00 | 1.35 | 85.62 | 3.20 | 1.23 | 0.36 | 1.40 |
| NAG21 | 5.25 | 41.79 | – | – | 73.78 | 2.68 | 0.92 | 61.58 | 2.39 | 0.81 | 0.35 | 1.43 |
| NAG21 | 6.25 | 26.65 | – | – | 49.19 | 1.96 | 0.70 | 41.91 | 1.65 | 0.58 | 0.36 | 1.40 |
| NAG21 | 7.5 | 43.49 | – | – | 72.08 | 2.90 | 0.94 | 59.82 | 2.53 | 0.84 | 0.35 | 1.39 |
| NAG21 | 8.5 | 61.06 | – | – | 86.37 | 4.49 | 1.36 | 70.90 | 3.28 | 1.05 | 0.33 | 1.31 |
| NAG21 | 9.5 | 41.57 | – | – | 51.04 | 2.96 | 0.66 | 42.98 | 2.04 | 0.58 | 0.32 | 1.27 |
| NAG21 | 10.5 | 52.27 | – | – | 66.37 | 3.49 | 0.74 | 55.22 | 2.52 | 0.67 | 0.32 | 1.31 |
| NAG21 | 11.5 | 31.46 | – | – | 40.54 | 2.21 | 0.48 | 35.25 | 1.60 | 0.50 | 0.33 | 1.30 |
| NAG21 | 12.5 | 40.42 | – | – | 47.58 | 2.82 | 0.77 | 41.20 | 2.00 | 0.60 | 0.32 | 1.27 |
| NAG21 | 13.5 | 42.02 | – | – | 45.26 | 2.65 | 0.60 | 36.57 | 1.85 | 0.51 | 0.30 | 1.26 |
| NAG21 | 14.5 | 72.33 | – | – | 74.26 | 4.97 | 0.85 | 54.89 | 3.08 | 0.81 | 0.28 | 1.21 |
| NAG29 | 15.25 | 32.94 | – | – | 36.42 | 2.39 | 0.48 | 23.93 | 1.66 | 0.37 | 0.26 | 1.17 |
| NAG21 | 15.5 | 50.83 | – | – | 50.56 | 3.60 | 0.75 | 38.03 | 2.39 | 0.56 | 0.28 | 1.17 |
| NAG21 | 16.5 | 48.38 | – | – | 55.52 | 4.12 | 0.92 | 40.97 | 2.48 | 0.62 | 0.29 | 1.16 |
| NAG21 | 17.5 | 45.49 | – | – | 51.17 | 3.80 | 1.03 | 34.83 | 2.30 | 0.55 | 0.27 | 1.15 |
| NAG21 | 18.5 | 45.33 | – | – | 48.99 | 3.44 | 0.98 | 33.59 | 2.08 | 0.55 | 0.27 | 1.17 |
| NAG29 | 21.25 | 32.05 | – | – | 37.20 | 2.55 | 0.56 | 27.02 | 1.65 | 0.44 | 0.29 | 1.18 |
| NAG29 | 25.75 | 31.57 | – | – | 35.11 | 2.63 | 0.63 | 23.78 | 1.78 | 0.47 | 0.27 | 1.13 |
| NAG29 | 30.75 | 48.70 | – | – | 51.74 | 3.90 | 0.82 | 35.76 | 2.53 | 0.59 | 0.27 | 1.13 |
| NAG29 | 35.75 | 59.05 | – | – | 65.17 | 4.62 | 0.99 | 45.57 | 3.03 | 0.66 | 0.28 | 1.16 |
| NAG29 | 40.75 | 34.59 | – | – | 38.44 | 2.76 | 0.64 | 23.92 | 1.78 | 0.41 | 0.25 | 1.14 |
| NAG29 | 45.75 | 84.26 | – | – | 90.93 | 7.12 | 2.04 | 63.18 | 4.68 | 1.08 | 0.27 | 1.12 |
| NAG29 | 50.75 | 40.33 | – | – | 46.63 | 3.41 | 0.85 | 33.95 | 2.37 | 0.62 | 0.29 | 1.14 |

1860 (15 cm), and $pH_{diat}$ decreases more sharply, between 1900 and 1930 (10–6 cm; Figure 4 (top)). The two reconstructions converge once more after 1930 (6–0 cm), however $pH_{diat}$ remains ~0.2 pH units higher than $pH_{CBT}$ (Figure 4 (top)). There is a slight indication that $pH_{diat}$ stabilizes in the most recent sediments, possibly as a result of reduced pollution emissions since the 1970s, however such a pattern is less clear in $pH_{CBT}$, which decreases continually toward the surface sediments except for two small increases around 10 cm and 4 cm (Figure 4 (top)).

[16] Because MBT and CBT correlate, MBT also correlates with $pH_{diat}$. Consequently, MBT/CBT-inferred temperature is inversely correlated with reconstructed $pH_{CBT}$ and $pH_{diat}$. Reconstructed temperatures ($T_{MBT}$) are relatively constant before 1860 (50–15 cm, ~−3°C) and increase by ~2.5°C between 1860 and 1997 (15–0 cm; from −3.5°C to −1°C, Figure 4 (bottom)). Although calibrated against mean annual air temperature [*Weijers et al.*, 2007c] $T_{MBT}$ estimates are consistently lower than instrumentally derived mean annual air temperature ($T_{mod}$) by ~5°C, instead corresponding more closely with mean winter (DJF) air temperatures. The rate of reconstructed warming according to $T_{MBT}$ is more than double that estimated by $T_{mod}$. During the same period, $T_{mod}$ (mean annual temperature) exhibits linear warming trends of 0.16°C between 1781 and 1860 (i.e., equivalent to 23–15 cm sediment depth) and 0.52°C between 1860 and 1995 (15–0 cm) [*Agusti-Panareda and Thompson*, 2002]. The mean annual warming trend is set against a shift in the balance of seasonal temperature trajectories: winter (DJF) temperatures increase by 0.66°C between 1781 and 1860 but decrease by 0.21 between 1860 and 1995 whereas summer (JJA) temperatures decrease by 0.58°C between 1781 and 1860 but increase by 0.69°C 1860–1995 (Figure 4 (bottom)) [*Agusti-Panareda and Thompson*, 2002]. Although the trends before and after 1860 differ, there is no indication that 1860 or thereabouts was a significant change point, as is suggested by $T_{MBT}$ (Figure 4). Irrespective of season, $T_{mod}$ is characterized by a gradual long-term trend and short-term fluctuations about a mean of 4°C, with a notable temperature minimum between 1815 and 1820 (~19 cm, Figure 4 (bottom)). Due to the poorer resolution of the sediment data, it is unclear whether or not some of the short-term variability in $T_{MBT}$ corresponds with $T_{mod}$.

## 6. Discussion

### 6.1. CBT-pH Relationship

[17] It is well established that lake water acidification occurred across Europe and North America in the 19th and 20th centuries as a result of industrially derived acid rain [*Battarbee*, 1990; *Flower and Battarbee*, 1983]. Empirical pH-diatom relationships have been observed in a variety of settings, across both spatial and temporal gradients, supporting the use of diatom-based pH transfer functions [*Battarbee*, 1994; *Battarbee et al.*, 2001; *Birks et al.*, 1990; *Cameron et al.*, 1999; *Dixit et al.*, 1992; *Korhola et al.*, 1999].

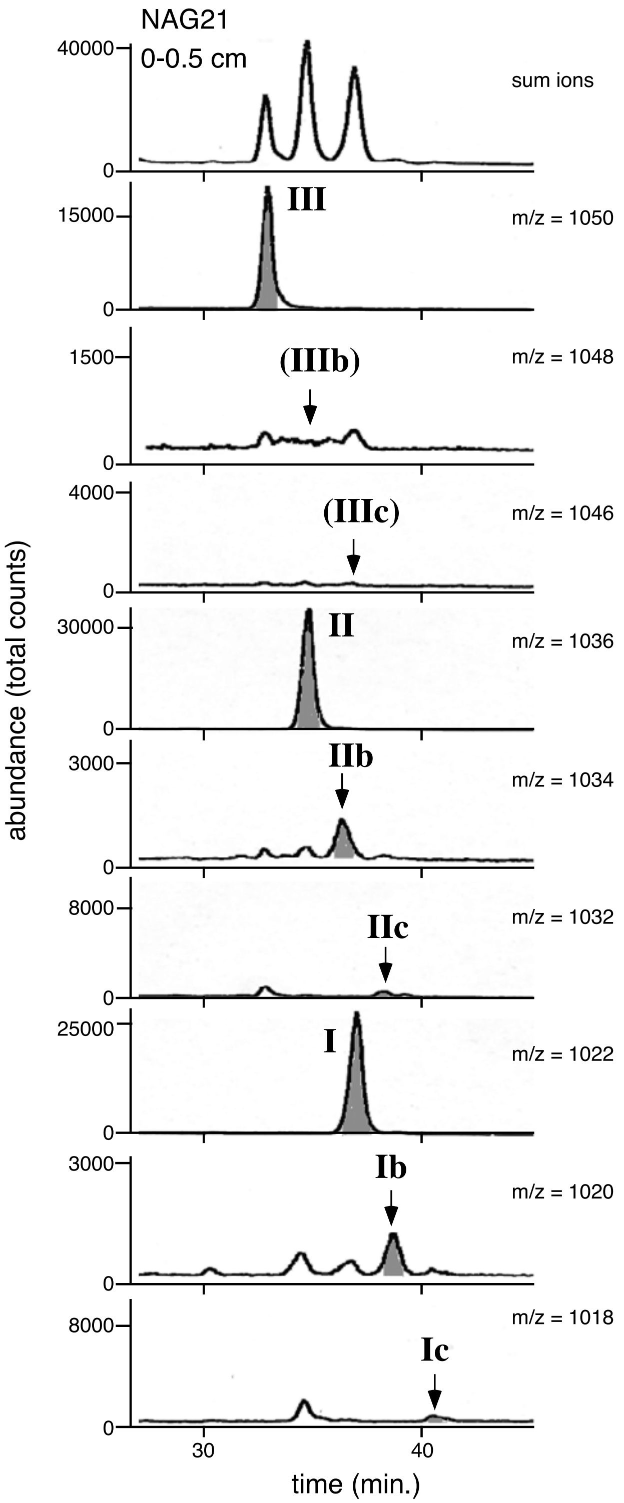


**Figure 2.** HPLC/mass spectrometry base peak chromatogram illustrating the branched GDGTs found in core NAG21 sample 0–0.5 cm. Roman numerals identify GDGTs given in Table 1.

The correlation between CBT and diatom-inferred pH from the Lochnagar sediments suggests that both reflect a response to acid rain deposition, supporting the concept that CBT also varies as a function of pH (Figure 4 (top)). However, a firm conclusion based on these data is restricted due to differences in the site of production. While diatoms grow within the lake, branched GDGTs are probably synthesized by anaerobic bacteria within the surrounding catchment soils [*Weijers et al.*, 2006a, 2006b], although recent research has suggested in situ production of branched GDGTs within either coastal marine water or marine sediments [*Peterse et al.*, 2009a]. In contemporary catchments, soil and lake water pH do not necessarily correlate, so an exact correlation between $pH_{diat}$ and $pH_{CBT}$ was not expected. However, due to the acidic soils, limited groundwater input and short water residence time of the Lochnagar catchment [*Jenkins et al.*, 2001; *Monteith et al.*, 2007; *Tyler et al.*, 2007], both soil pore water and lake water pH are likely to be heavily influenced by the chemistry of precipitation. Therefore, considering the small area, sparse vegetation and shallow soils of the Lochnagar catchment, it is not surprising that soil and lake water pH both decreased as a result of acid deposition.

[18] At Lochnagar, downcore changes in $pH_{diat}$ and $pH_{CBT}$ exhibit similar patterns and absolute values, suggesting that they both responded to the same external forcing (acid deposition). However, changes in $pH_{diat}$ lag behind $pH_{CBT}$, and a number of explanations can be proposed for this. Because diatoms are authocthonous, the diatom signal would be expected to respond more immediately to change than the branched GDGTs, which are catchment derived and thus dependent on transport processes. Therefore, it is unlikely that preferential transport and sedimentation of GDGTs explains the lagged response of $pH_{diat}$. More likely, the observed pattern indicates differential responses within soil and lake water to acid deposition, due to different buffering capacity. The peaty nature and base-poor bedrock of the Lochnagar catchment indicate that the soils were probably poorly buffered prior to acid deposition. In addition, the proportionately higher surface area to water volume of the catchment soils compared to the lake would have led to concentration of atmospheric pollutants within the soil, which acts as a filter during throughflow. Consequently, it is possible that soil bacteria will have been exposed to lower pH conditions for a period during which lake water chemistry underwent a more gradual change. A third explanation invokes a more complex response within the diatom community to external acidification. Although a relationship between diatom species assemblage and water pH has been demonstrated a number of times, there is no detailed ecophysiological understanding of how pH influences the growth and competitive abilities of individual taxa [*Battarbee et al.*, 2001]. Changes in the species composition of photoautotropic communities, including diatoms, are a function of a number of factors, including water chemistry, climate and inherent biological interactions [*Battarbee*, 2000; *Battarbee et al.*, 2001; *Reynolds*, 2006]. It is therefore possible that the response of the diatom community to acidification was nonlinear, and may have required the breach of a particular ecological threshold prior to a response within the species composition. Overall, the comparison between $pH_{diat}$ and $pH_{CBT}$ in the Lochnagar sediments supports the use of either proxy and suggests (1) that CBT is indeed a function of soil water pH and (2) that lake water acidification over the past two centuries at Lochnagar occurred alongside deposition of acid pollutants, as indicated by SCP accumulation, and acidification of surrounding catchment soils.

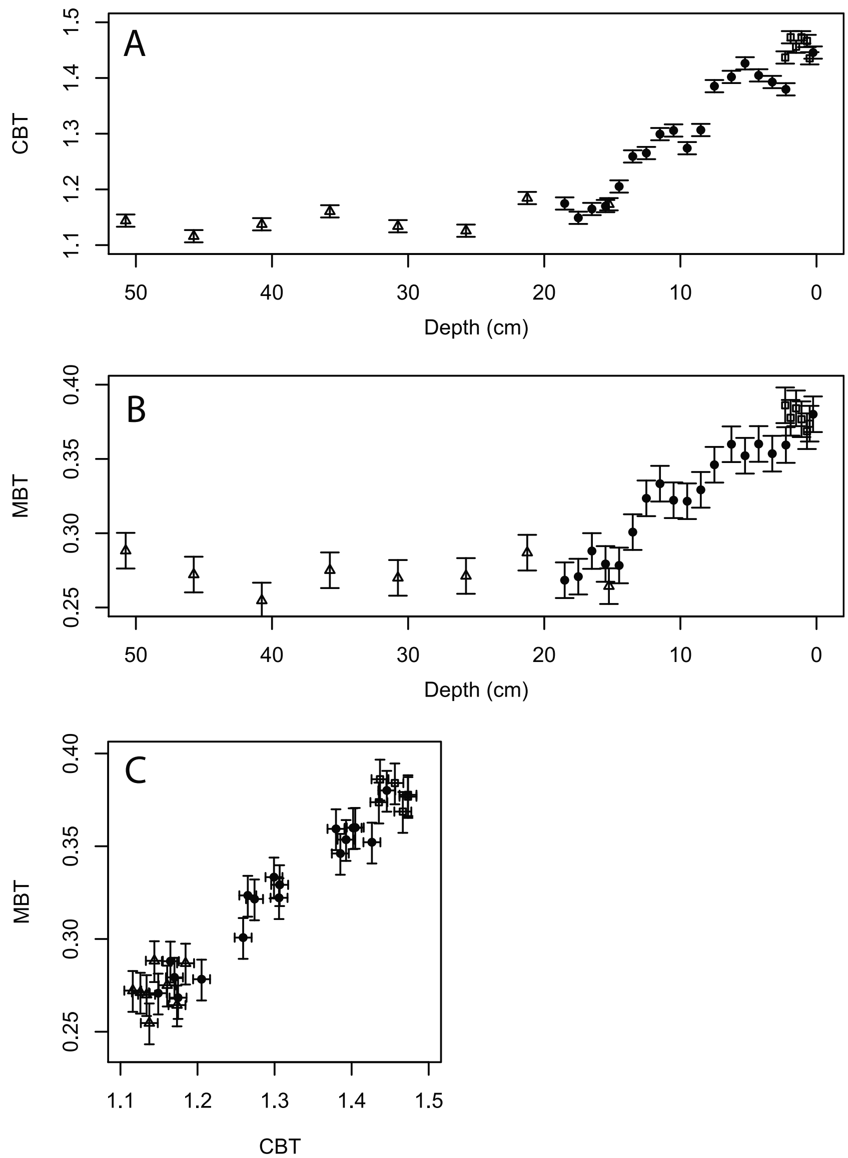


**Figure 3.** Down core variability in (a) CBT and (b) MBT in Lochnagar sediments versus depth from sediment-water interface (cm); (c) scatterplot of CBT versus MBT. Point types represent which core was analyzed: solid circles are NAG21, open squares are NAG27, and open triangles are NAG29. Error bars represent 1 standard deviation from duplicate measurements (n = 8).

### 6.2. MBT-pH/Temperature Relationship

[19] The potential use of the CBT and MBT indices to reconstruct past air temperature is rapidly gaining interest in palaeoclimatology. To date, this approach has only been applied to cores collected from marine sediments off arctic Siberia, tropical Africa, Greenland and Norway [*Rueda et al.*, 2009; *Schouten et al.*, 2008; *Weijers et al.*, 2007a, 2007b]. In particular, such studies enable an assessment of the changing ocean-land temperature gradient, with implications for past regional atmospheric circulation and precipitation [*Weijers et al.*, 2007a]. However, studies of branched GDGTs in contemporary environments indicate that uncertainties remain concerning the validity of palaeoclimate reconstructions using this method [*Peterse et al.*, 2009a; *Rueda et al.*, 2009].

[20] There is good evidence that global air temperature has increased significantly over the past 200 years [*Intergovernmental Panel on Climate Change*, 2007], and that these changes are reflected in the regional climate data for the United Kingdom [*Manley*, 1974; *Parker et al.*, 1992]. Reconstructed air temperature at Lochnagar suggests that these changes were manifest at the study site [*Agusti-Panareda and Thompson*, 2002], supported by anecdotal evidence for marked reductions in duration of lake ice cover and catchment snow depth over the past century [*Rose*, 2007]. It is important to note that the reconstructed mean annual air temperatures ($T_{mod}$) are also subject to error, being derived from multiple regression using lowland instrumental weather data [*Agusti-Panareda and Thompson*, 2002]. Based on

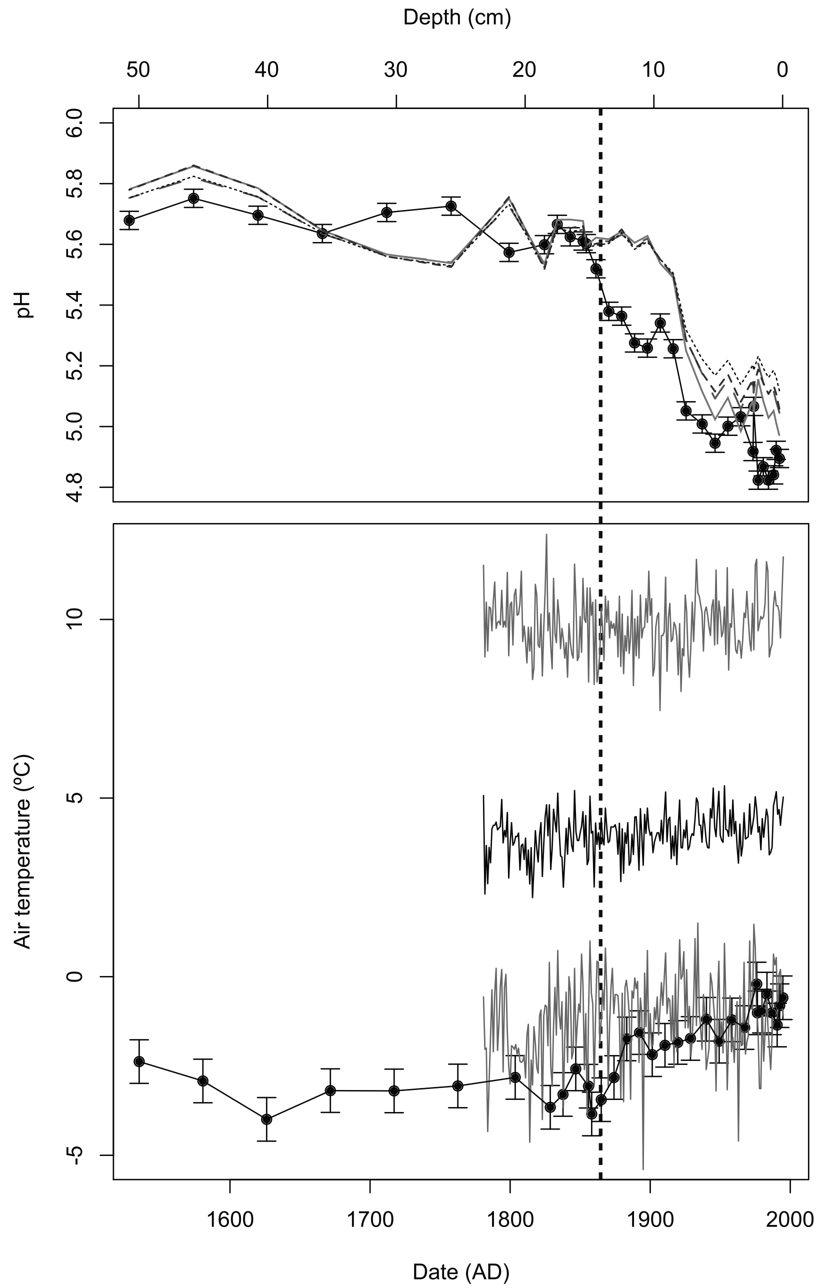


**Figure 4.** (top) Comparison of CBT-inferred pH (solid black line and circles) with diatom-inferred pH (four models, gray solid and dashed lines). (bottom) Comparison of CBT/MBT-inferred temperature using equation (5) (black line and circles) with estimated mean annual air temperature (solid black line) and mean winter (DJF) and summer (JJA) temperatures (gray lines, from *Agusti-Panareda and Thompson* [2002]). Error bars represent 1 standard deviation analytical error from duplicate analyses (n = 8). Vertical dashed line indicates 1860 sphaeroidal carbonaceous particle marker horizon at 14.0 cm.

comparison between reconstructed Lochnagar air temperature and 13 on site (automatic weather station) monthly mean temperature measurements, *Agusti-Panareda and Thompson* [2002] noted a bias between observed and predicted temperatures within a range of +1.3 to −1.5°C, with a mean bias of −0.6°C. In particular, the largest biases occurred during spring and autumn months, however, *Agusti-Panareda and Thompson* [2002] estimate that these monthly biases translate to prediction errors of ±0.3°C for mean annual air temperature. Nevertheless, it is possible that $T_{mod}$ values are slightly lower than true air temperatures at Lochnagar, but not to the degree of difference between $T_{mod}$ and $T_{MBT}$. $T_{MBT}$ estimates fall consistently ~5°C lower than $T_{mod}$ and are more comparable with estimated winter temperatures for Lochnagar (Figure 4 (bottom)). To date, very little is known concerning the synthesis of branched GDGTs in soils,

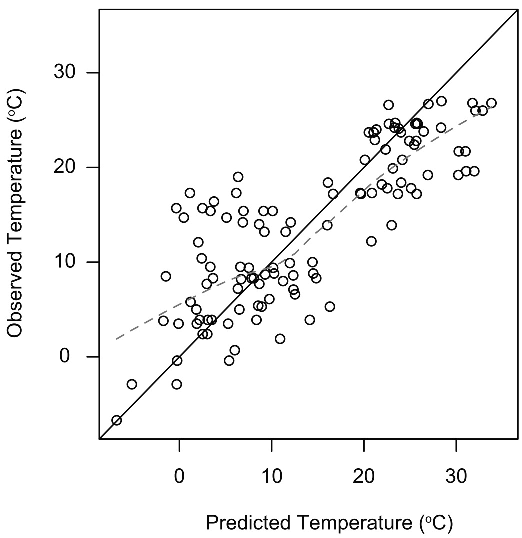


**Figure 5.** The relationship between predicted and observed air temperature from the *Weijers et al.* [2007c] calibration data, derived using equation (5) ($T_{MBT}$) by inversion of equation (3). Solid line is 1:1, and gray dashed line is Lowess-smoothed response.

including the nature of the bacteria and the environmental and seasonal controls over their activity. However, because the Lochnagar catchment is snow covered during much of the winter and temperatures are generally at or below freezing, we would not expect branched GDGTs to be preferentially synthesized during the winter [*Peterse et al.*, 2009a]. Our data from Lochnagar also contrast with observations by *Rueda et al.* [2009] who noted a correlation between $T_{MBT}$ and regional summer air temperatures from recent marine sediments off the Norwegian coast. Comparison of the winter and summer trends in $T_{mod}$ provides further evidence against potential winter synthesis of branched GDGTs. Winter reconstructed temperatures increase between 1781 and 1860 and show a moderate decrease between 1860 and 1995, whereas summer reconstructed temperatures decrease prior to 1860 and increase thereafter. Therefore, in terms of the direction of change (but not magnitude), $T_{MBT}$ is more comparable with summer rather than winter changes at Lochnagar. In addition, the onset of a period of marked MBT/CBT-inferred warming, which begins shortly after the 1860 SCP marker horizon, does not resemble extrapolated air temperatures ($T_{mod}$) or regional instrumental data for this period (Figure 4 (bottom)). Furthermore, the magnitude of warming in $T_{MBT}$ is greater than double that of $T_{mod}$, either for mean annual or mean summer (JJA) temperatures. Clearly, further research is required into the seasonal patterns of branched GDGT synthesis in soils, however the early indication is that $T_{MBT}$ markedly underestimates air temperatures for Lochnagar and exaggerates the magnitude of postindustrial warming (Figure 4 (bottom)). The low temporal resolution of the Lochnagar sediment record restricts a comparison with the finer details of the extrapolated instrumental data and independent effects of temperature change over MBT at Lochnagar are difficult to identify since, to some extent, the effects of increasing temperature will have been partially masked by concurrent decreases in pH. Nevertheless, $T_{MBT}$ values from Lochnagar indicate that uncertainties exist with regards the validity of MBT-inferred air temperature estimates at sub-centennial timescales.

[21] The correlation between MBT and CBT suggests that short-term variability in MBT at Lochnagar is dominated by changes in pH, overriding the effects of temperature. This in turn raises questions concerning the validity of the global MBT-temperature correlation. Similar concerns are raised when examining the calibration data set of *Weijers et al.* [2007c] (Figure 5). In particular, a weaker influence of temperature at lower temperatures (higher latitudes, 0–15°C) is evident, with residual deviation between observed and predicted temperature in some cases >10°C at temperatures <15°C, compared with a more definite relationship at temperatures >20°C (Figure 5). It is therefore possible that the effect of temperature on high latitude, low temperature branched GDGTs has been overestimated, with additional factors explaining MBT variability in these soils. Support for such a hypothesis can be found in recent studies, whereby although a clear MBT-temperature relationship can be observed in low latitude and high temperature (geothermally heated) soils [*Peterse et al.*, 2009b; *Sinninghe Damstè et al.*, 2008], studies at higher latitudes have proved less conclusive [*Peterse et al.*, 2009a; *Rueda et al.*, 2009]. At Lochnagar, CBT and MBT (and $pH_{diat}$) correlate, which is not the case in the *Weijers et al.* [2007c] data set. If CBT is controlled by changes in catchment pH, then this suggests that MBT is affected by an additional factor which varies with latitude in the *Weijers et al.* [2007c] data set, but which remained constant at Lochnagar, i.e., independent of temperature change. Therefore, some of the latitudinal variability in MBT could be a function of other factors, including geographic variability in the organisms which produce branched GDGTs [*Schouten et al.*, 2007b; *Uda et al.*, 2001] or the influence of soil type, geology or thermally dependent diagenetic processes [*Peterse et al.*, 2009a]. Soil chemical data in the *Weijers et al.* [2007c] data set are limited to electrical conductivity, total cation and pH values and none demonstrate any marked trends with latitude, except that soils in very low latitudes typically have low total cations. However, soil type and chemistry are known to vary significantly with latitude, climatic regime, land use and geology [*Rowell*, 1994] and thus may warrant further attention with regards their influence over branched GDGT synthesis. Therefore, further efforts are needed to calibrate the effect of temperature over branched GDGT abundance, particularly on a local level [*Peterse et al.*, 2009a; *Sinninghe Damstè et al.*, 2008], with greater control over soil conditions and bioactivity [*Peterse et al.*, 2009b]. More investigations into the sources of GDGTs and their fate postdeposition are also required [*Peterse et al.*, 2009a].

## 7. Conclusion

[22] We compared pH and air temperature reconstructions derived from the MBT and CBT indices of branched GDGTs with independent evidence from diatom assemblages and instrumentally derived climate data, using the recent lake sediments of Lochnagar, Scotland. Diatom and CBT-inferred pH ($pH_{diat}$ and $pH_{CBT}$, respectively) correlate well in the Lochnagar sediments, with differences only in the rate of acidification suggested by the two different methods. Possibly, this indicates differences in the buffering capacity between

catchment soils and lake water together with a nonlinear response from the diatom communities. Nevertheless, the CBT ratio appears to be a promising method for reconstructing catchment pH. Uncertainties exist regarding branched GDGT-inferred air temperature ($T_{MBT}$). $T_{MBT}$ values are underestimated by ~5°C in comparison with extrapolated mean annual air temperature, while overestimating the rate of warming during the last ~200 years. MBT and CBT (and therefore $pH_{diat}$) are correlated at Lochnagar, a lack of independence which suggests that the existing calibration model insufficiently describes the environmental controls over MBT, possibly due to geographical variability in soil properties not accounted for previously. Consequently, the global applicability of MBT-inferred temperature remains uncertain. Therefore, despite obvious potential for the use of branched GDGTs to reconstruct past continental air temperature and pH, further efforts are required in understanding the role of source, environment and diagenesis on the relative abundance of these biomarkers on a local scale.

[23] **Acknowledgments.** Preparation of this manuscript was aided by postdoctoral funding to J.J.T. in the Department of Earth and Planetary Sciences and the Ocean Research Institute, Tokyo University, at the Japan Agency for Marine Earth Science (JAMSTEC; JSPS Fellowship PE07622) and in the Department of Botany, Natural History Museum, London (NERC Fellowship NE/F014708/1). J.J.T. also thanks Gavin Simpson and David Casenove for valuable statistical advice. We thank the editors and two anonymous reviewers for helpful comments and suggestions, which have improved the quality of this manuscript.

## References


Agusti-Panareda, A., and R. Thompson (2002), Reconstructing air temperature at eleven remote alpine and arctic lakes in Europe from 1781 to 1997 AD, *J. Paleolimnol.*, *28*(1), 7–23, doi:10.1023/A:1020363700397.

Battarbee, R. W. (1990), The causes of lake acidification, with special reference to the role of acid deposition, *Philos. Trans. R. Soc. Lond. Ser. B*, *327*(1240), 339–347.

Battarbee, R. W. (1994), Diatoms, lake acidification and the Surface-Water Acidification Program (SWAP): A review, *Hydrobiologia*, *274*(1–3), 1–7, doi:10.1007/BF00014621.

Battarbee, R. W. (2000), Palaeolimnological approaches to climate change, with special regard to the biological record, *Quat. Sci. Rev.*, *19*(1–5), 107–124.

Battarbee, R. W., and I. Renberg (1990), The Surface-Water Acidification Project (SWAP) paleolimnology program, *Philos. Trans. R. Soc. Lond. Ser. B*, *327*(1240), 227–232.

Battarbee, R. W., et al. (1996), Palaeolimnological evidence for the atmospheric contamination and acidification of high Cairngorm lochs, with special reference to Lochnagar, *Bot. J. Scotl.*, *48*, 79–87, doi:10.1080/03746609609480375.

Battarbee, R. W., et al. (2001), Diatoms, in *Tracking Environmental Change Using Lake Sediments—Volume 3: Terrestrial, Algal, and Siliceous Indicators*, edited by J. P. Smol, H. J. B. Birks, and W. M. Last, pp. 155–202, Kluwer Acad., Dordrecht, Netherlands.

Birks, H. J. B. (2007), Flora and vegetation of Lochnagar: Past, present and future, in *Lochnagar: The Natural History of a Mountain Lake*, edited by N. L. Rose, pp. 121–151, Springer, Dordrecht, Netherlands.

Birks, H. J. B., et al. (1990), Diatoms and pH reconstruction, *Philos. Trans. R. Soc. Lond. Ser. B*, *327*(1240), 263–278.

Cameron, N. G., et al. (1999), Surface-sediment and epilithic diatom pH calibration sets for remote European mountain lakes (AL:PE Project) and their comparison with the Surface Waters Acidification Programme (SWAP) calibration set, *J. Paleolimnol.*, *22*(3), 291–317, doi:10.1023/A:1008025928509.

Chambers, J. W., and N. G. Cameron (2001), A rod-less piston corer for lake sediments: An improved, rope-operated percussion corer, *J. Paleolimnol.*, *25*(1), 117–122, doi:10.1023/A:1008181406301.

Dalton, C., et al. (2005), A multi-proxy study of lake-development in response to catchment changes during the Holocene at Lochnagar, north-east Scotland, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *221*(3–4), 175–201, doi:10.1016/j.palaeo.2005.02.007.

Dixit, S. S., et al. (1992), Diatoms: Powerful indicators of environmental change, *Environ. Sci. Technol.*, *26*(1), 22–33, doi:10.1021/es00025a002.

Flower, R. J., and R. W. Battarbee (1983), Diatom evidence for recent acidification of two Scottish lochs, *Nature*, *305*(5930), 130–133, doi:10.1038/305130a0.

Folland, C. K., et al. (2001), Global temperature change and its uncertainties since 1861, *Geophys. Res. Lett.*, *28*(13), 2621–2624, doi:10.1029/2001GL012877.

Glew, J. R. (1991), Minature gravity corer for recovering short sediment cores, *J. Paleolimnol.*, *5*(3), 285–287, doi:10.1007/BF00200351.

Hughes, M. (2007), Physical characteristics of Lochnagar, in *Lochnagar: the Natural History of a Mountain Lake*, edited by N. L. Rose, pp. 27–35, Springer, Dordrecht, Netherlands.

Intergovernmental Panel on Climate Change (2007), *Climate Change 2007: The Physical Science Basis: Working Group I Contribution to the Fourth Assessment Report of the IPCC*, edited by S. Solomon et al., Cambridge Univ. Press, New York.

Jenkins, A., et al. (2001), Modelling nitrogen dynamics at Lochnagar, NE Scotland, *Hydrol. Earth Syst. Sci.*, *5*(3), 519–527.

Jones, V. J., et al. (1993), Paleolimnological evidence for the acidification and atmospheric contamination of lochs in the Cairngorm and Lochnagar areas of Scotland, *J. Ecol.*, *81*(1), 3–24, doi:10.2307/2261220.

Korhola, A., et al. (1999), Predicting the long-term acidification trends in small subarctic lakes using diatoms, *J. Appl. Ecol.*, *36*(6), 1021–1034, doi:10.1046/j.1365-2664.1999.00461.x.

Krammer, K., and H. Lange-Bertalot (1986), *Bacillariophyceae. 1. Teil: Naviculaceae*, Springer, Stuttgart, Germany.

Krammer, K., and H. Lange-Bertalot (1988), *Bacillariophyceae. 2. Teil: Bacillariaceae, Epithemiaceae, Surriellaceae*, Springer, Stuttgart, Germany.

Krammer, K., and H. Lange-Bertalot (1991a), *Bacillariophyceae. 3. Teil: Centrales, Fragilariaceae, Eunotiaceae*, Springer, Stuttgart, Germany.

Krammer, K., and H. Lange-Bertalot (1991b), *Bacillariophyceae. 4. Teil: Achnanthaceae, Kritische Erganzungen zu Navicula (Lineolatae) und Gomphonema, Gesamtliteraturverzeichnis Teil 1–4*, Springer, Stuttgart, Germany.

Manley, G. (1953), The mean temperature of central England, 1698–1952, *Q. J. R. Meteorol. Soc.*, *79*(340), 242–261, doi:10.1002/qj.49707934006.

Manley, G. (1974), Central England temperatures: Monthly means 1659 to 1973, *Q. J. R. Meteorol. Soc.*, *100*(425), 389–405, doi:10.1002/qj.49710042511.

Monteith, D. T., et al. (2007), Acidification of Lochnagar and prospects for recovery, in *Lochnagar: The Natural History of a Mountain Lake*, edited by N. L. Rose, pp. 317–344, Springer, Dordrecht, Netherlands.

Parker, D. E., et al. (1992), A new daily central England temperature series, 1772–1991, *Int. J. Climatol.*, *12*(4), 317–342, doi:10.1002/joc.3370120402.

Peterse, F., et al. (2009a), Constraints on the application of the MBT/CBT palaeothermometer in high latitude environments (Svalbard, Norway), *Org. Geochem.*, *40*(6), 692–699, doi:10.1016/j.orggeochem.2009.03.004.

Peterse, F., et al. (2009b), Distribution of branched tetraether lipids in geothermally heated soils: Implications for the MBT/CBT temperature proxy, *Org. Geochem.*, *40*(2), 201–205, doi:10.1016/j.orggeochem.2008.10.010.

Reynolds, C. S. (2006), *The Ecology of Phytoplankton (Ecology, Biodiversity and Conservation)*, Cambridge Univ. Press, Cambridge, U. K.

Rose, N. L. (2007), *Lochnagar: The Natural History of A Mountain Lake*, Springer, Dordrecht, Netherlands.

Rose, N. L., et al. (2004), A consideration of potential confounding factors limiting chemical and biological recovery to acidification at Lochnagar: A remote mountain loch in Scotland, *J. Limnol.*, *63*(1), 63–76.

Rowell, D. L. (1994), *Soil Science, Methods and Applications*, Longman, London.

Rueda, G., et al. (2009), Comparison of instrumental and GDGT-based estimates of sea surface and air temperatures from the Skagerrak, *Org. Geochem.*, *40*(2), 287–291, doi:10.1016/j.orggeochem.2008.10.012.

Schouten, S., et al. (2007a), Analytical methodology for TEX86 paleothermometry by high-performance liquid chromatography/atmospheric pressure chemical ionization-mass spectrometry, *Anal. Chem.*, *79*(7), 2940–2944, doi:10.1021/ac062339v.

Schouten, S., et al. (2007b), Archaeal and bacterial glycerol dialkyl glycerol tetraether lipids in hot springs of Yellowstone National Park, *Appl. Environ. Microbiol.*, *73*(19), 6181–6191, doi:10.1128/AEM.00630-07.

Schouten, S., et al. (2008), Onset of long-term cooling of Greenland near the Eocene-Oligocene boundary as revealed by branched tetraether lipids, *Geology*, *36*(2), 147–150, doi:10.1130/G24332A.1.

Schouten, S., et al. (2009), An interlaboratory study of TEX86 and BIT analysis using high-performance liquid chromatography-mass spectrometry, *Geochem. Geophys. Geosyst.*, *10*, Q03012, doi:10.1029/2008GC002221.

Sinninghe Damstè, J. S., et al. (2000), Newly discovered non-isoprenoid glycerol dialkyl glycerol tetraether lipids in sediments, *ChemComm*, 17, 1683–1684, doi:10.1039/b004517i.

Sinninghe Damstè, J. S., et al. (2008), Altitudinal shifts in the branched tetraether lipid distribution in soil from Mt. Kilimanjaro (Tanzania): Implications for the MBT/CBT continental palaeothermometer, *Org. Geochem.*, *39*(8), 1072–1076, doi:10.1016/j.orggeochem.2007.11.011.

ter Braak, C. J. F., and S. Juggins (1993), Weighted averaging partial least squares regression (WA-PLS): An improved method for reconstructing environmental variables from species assemblages, *Hydrobiologia*, *269–270*(1), 485–502, doi:10.1007/BF00028046.

Tyler, J. J., et al. (2007), Seasonality and the isotope hydrology of Lochnagar, a Scottish mountain lake: Implications for palaeoclimate research, *Holocene*, *17*, 717–727, doi:10.1177/0959683607080513.

Uda, I., et al. (2001), Variation in molecular species of polar lipids from Thermoplasma acidophilum depends on growth temperature, *Lipids*, *36*(1), 103–105, doi:10.1007/s11745-001-0914-2.

Weijers, J. W. H., et al. (2006a), Membrane lipids of mesophilic anaerobic bacteria thriving in peats have typical archaeal traits, *Environ. Microbiol.*, *8*, 648–657, doi:10.1111/j.1462-2920.2005.00941.x.

Weijers, J. W. H., et al. (2006b), Occurrence and distribution of tetraether membrane lipids in soils: Implications for the use of the TEX86 proxy and the BIT index, *Org. Geochem.*, *37*(12), 1680–1693, doi:10.1016/j.orggeochem.2006.07.018.

Weijers, J. W. H., et al. (2007a), Coupled thermal and hydrological evolution of tropical Africa over the last deglaciation, *Science*, *315*(5819), 1701–1704, doi:10.1126/science.1138131.

Weijers, J. W. H., et al. (2007b), Warm arctic continents during the Palaeocene-Eocene thermal maximum, *Earth Planet. Sci. Lett.*, *261*(1–2), 230–238, doi:10.1016/j.epsl.2007.06.033.

Weijers, J. W. H., et al. (2007c), Environmental controls on bacterial tetraether membrane lipid distribution in soils, *Geochim. Cosmochim. Acta*, *71*(3), 703–713, doi:10.1016/j.gca.2006.10.003.

Yang, H. D., et al. (2002a), Mercury and lead budgets for Lochnagar, a Scottish mountain lake and its catchment, *Environ. Sci. Technol.*, *36*(7), 1383–1388, doi:10.1021/es010120m.

Yang, H. D., et al. (2002b), Trace metal distribution in the sediments of the whole lake basin for Lochnagar, Scotland: A palaeolimnological assessment, *Hydrobiologia*, *479*(1–3), 51–61, doi:10.1023/A:1021054112496.

Yang, H. D., et al. (2007), The Pb pollution fingerprint at Lochnagar: The historical record and current status of Pb isotopes, *Environ. Pollut.*, *145*(3), 723–729, doi:10.1016/j.envpol.2006.06.026.

---

V. J. Jones, Environmental Change Research Centre, Department of Geography, University College London, Gower Street, London WC1E 6BT, UK.

A. J. Nederbragt and J. W. Thurow, Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, UK.

J. J. Tyler, Department of Earth Sciences, University of Oxford, Parks Road, Oxford OX1 3PR, UK. (jont@earth.ox.ac.uk)