Biogeosciences Discuss., 11, 11569–11596, 2014
www.biogeosciences-discuss.net/11/11569/2014/
doi:10.5194/bgd-11-11569-2014

Biogeosciences Discussions
Open Access

Probing the fate of soil-derived core and intact polar GDGTs in aquatic environments

F. Peterse[1,*], **C. M. Moy**[2], **and T. I. Eglinton**[1]

[1]ETH Zürich, Geological Institute, Sonneggstrasse 5, 8092 Zürich, Switzerland
[2]University of Otago, Geology Department, Dunedin, New Zealand
[*]now at: Utrecht University, Department of Earth Sciences, Utrecht, the Netherlands

Received: 15 July 2014 – Accepted: 21 July 2014 – Published: 29 July 2014

Correspondence to: F. Peterse (f.peterse@uu.nl)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

We have performed incubation experiments in order to examine the fate of branched glycerol dialkyl glycerol tetraether (brGDGT) membrane lipids upon entering an aquatic environment and to asses the suitability of brGDGTs as tracers for fluvial land-sea transport of soil organic carbon. We incubated a soil from the Rakaia River catchment on the South Island of New Zealand using Rakaia River water and ocean water collected near the river mouth as inocula for a period of up to 152 days. The concentrations of brGDGTs derived from intact polar ("living"; IPL) lipids and core ("fossil"; CL) lipids remained stable over the course of the experiment, suggesting an absence of significant brGDGT production or degradation. Moreover, the lack of change in brGDGT distribution during the experiment implies that the initial soil signature remains unaltered during transport through the aquatic environment, at least over the time frame of the experiment. In contrast, the total pool of isoprenoid GDGTs (isoGDGTs), currently attributed to soil *Thaumachaeota*, increased substantially (27–72 %) in all incubation setups by the end of the experiment. As a consequence, a decrease in Branched and Isoprenoid Tetraether (BIT) index values – a proxy for the relative input of fluvially discharged soil material into a marine system – became evident after an incubation period of 30 days, with a maximum final decrease of 0.88 to 0.74 in the experiment with river water. The relative distribution within the isoGDGT pool shows changes with time, suggesting different membrane adaptation rates to the aquatic environment, or a shift in source organism(s). While the stability of soil brGDGTs in aquatic environments reinforces their potential as tracers for land-sea transport of soil organic carbon and their use in paleoclimate reconstructions, the distributional differences between GDGTs in river water and nearby soil indicate that further research is needed to pinpoint the sources of GDGTs that are ultimately discharged to the oceans and are subsequently archived in continental margin sediments.

BGD
11, 11569–11596, 2014

1 Introduction

The global carbon cycle encompasses a myriad of biogeochemical processes that influence our climate and link all carbon reservoirs on the Earth surface. Soils are considered to play a very active and fundamental role in this cycle, as their mobilization from land and subsequent deposition in marine sediments serves as a long-term sink of atmospheric CO_2. However, the exact magnitude and mechanisms of soil organic carbon (OC) transfer from terrestrial source to marine sink remain elusive (e.g. Cole et al., 2007; Weyhenmeyer et al., 2012), which partly stems from the lack of a suitable tracer of the soil OC pool. Our current insights in land-sea soil OC transport dynamics are primarily based on bulk properties of river particulate suspended matter (SPM). However, next to soil OC, river SPM also comprises carbon derived from aquatic production and "fossil" carbon from rock erosion, each of which influences the bulk properties of SPM (Blair et al., 2010).

Analytical advances in the field of organic biogeochemistry have yielded a growing number of powerful tools with the potential to exclusively target components of specific pools, including soil OC. In this context, branched glycerol dialkyl glycerol tetraethers (brGDGTs; Fig. 1) have been put forward as tracers for soil-derived OC in carbon transport studies (Hopmans et al., 2004; Kim et al., 2006). Since their discovery (Sinninghe Damsté et al., 2000; Schouten et al., 2000), brGDGTs have been found in soils and peats worldwide (Weijers et al., 2007b; Peterse et al., 2012). The exact organism(s) that produce(s) these compounds have yet to be identified, but current evidence points towards an origin from heterotrophic soil bacteria (Pancost and Sinninghe Damsté, 2003; Oppermann et al., 2010; Weijers et al., 2010) from the phylum of *Acidobacteria* (Weijers et al., 2009; Peterse et al., 2010; Sinninghe Damsté et al., 2011). BrGDGTs have been used as a proxy for the relative input of fluvially transported soil OC in marine systems based on their abundance in coastal marine sediments relative to that of crenarchaeol (Fig. 1), an isoprenoid GDGT (isoGDGTs) produced by marine *Thaumarchaeota* (Sinninghe Damsté et al., 2002), parameterized as the Branched and Isoprenoid Tetraether

BGD
11, 11569–11596, 2014

(BIT) index (Hopmans et al., 2004). Moreover, subtle variations in the molecular distribution of the brGDGTs have been found to relate to mean annual air temperature and soil pH (Weijers et al., 2007b), indicating their potential for utility in paleoclimate studies. Indeed, using a combination of the Methylation of Branched Tetraethers (MBT) and Cyclisation of Branched Tetraether (CBT) indices (the so-called "MBT-CBT" proxy; Weijers et al., 2007b, recently revised as MBT'-CBT by Peterse et al., 2012), down-core variations in brGDGT distribution in fluvially-dominated continental margin sediments have been used to obtain an integrated climate history of the adjacent drainage basin (e.g. Weijers et al., 2007a).

Although GDGT-based proxies are finding increase use, our understanding of mobilization and transfer of soil OC and associated GDGT signals to fluvial environments, and the processes acting upon these components during transport are still poorly understood. There is emerging evidence, for example, for in situ production of brGDGTs in aquatic environments including high-latitude fjord systems (Peterse et al., 2009), open shelf sediments (Zhu et al., 2011), lakes (e.g. Sinninghe Damsté et al., 2009; Tierney and Russell, 2009), and most recently, rivers (De Jonge et al., 2014; Kim et al., 2012; Zell et al., 2013b; Zhang et al., 2012). The presence of intact polar lipid (IPL) precursors of brGDGTs in SPM from the Amazon (Zell et al., 2013b), Pearl (Zhang et al., 2012), and Yenisei rivers (De Jonge et al., 2014) provides strong evidence for aquatic brGDGT production, as the IPL head groups are thought to be rapidly lost upon cell death (Harvey et al., 1986; White et al., 1979). The core lipids (CLs) that are released after IPL degradation are considered to represent "dead", or fossil material – the fraction that is considered to be stored in sedimentary archives – and targeted for paleoclimate reconstruction. Hence, during fluvial transport from land to sea, the initial soil-derived brGDGT distribution entering a river may be modified by the addition of aquatic produced brGDGTs with a potentially different signature, but also by microbial degradation and transformation of soil brGDGTs.

In order to explore the fate of soil brGDGTs in aquatic systems, we performed a laboratory experiment in which we incubated soil using river water or ocean water from

BGD
11, 11569–11596, 2014

near the mouth of the same river as microbial inocula. In the frame of a larger study on fluvial transport of soil organic carbon from land to sea on the South Island of New Zealand, we used soil and river water from the Rakaia River catchment for the experiment. In addition, the braided character of the Rakaia River likely reduces the potential contribution of in situ produced brGDGTs, as the generally harsh and unstable conditions limits primary production in such river systems, thus enabling the monitoring of what should be a primarily soil derived signal. For that matter, concentration and distributional changes in IPL-derived and CL-brGDGTs were determined at different time intervals during the incubation experiment. Although isoGDGTs (Fig. 1) are primarily associated with marine archaea, they are also produced by soil *Thaumarchaeota* (Sinninghe Damsté et al., 2012), albeit in small amounts relative to the brGDGTs (Weijers et al., 2006b). In the marine realm, changes in isoGDGT distributions form the basis for the TEX_{86} index, which is used as a proxy for sea surface temperature (SST; Schouten et al., 2002; Kim et al., 2010). Large contributions from soil isoGDGTs to the total isoGDGTs pool in marine sediments may consequently complicate the interpretation of TEX_{86}-derived SST records from near continental margins (Weijers et al., 2006b). Therefore, all soil-derived GDGTs, i.e. both branched and isoprenoidal, were monitored during the experiment.

2 Materials and methods

2.1 Sample collection and incubation setup

The Rakaia River is one of the largest braided rivers on the South Island of New Zealand and has a mean annual discharge of $203\,m^3\,s^{-1}$. The Rakaia is estimated to contribute 4.15 Mt of sediment a year, accounting for approximately 5 % of the total South Island sediment yield to the adjacent continental shelf (Hicks et al., 2011). The river originates in the Southern Alps and flows through the Canterbury Plains before reaching the Pacific Ocean approximately 150 km from its source. Fresh water

BGD
11, 11569–11596, 2014

from the river was sampled in jerry cans close to the town Rakaia (43°44′57.9″ S, 172°01′52.9″ E), about 20 km upstream from the river mouth and outside of the tidal influence. The ocean water used as inoculum was collected from the shoreline (43°54′15.1″ S, 172°11′41.9″ E), close to the river mouth. Based on pH measurements, this water (pH 7.6) was strongly fluvially influenced (pH 7.5). Surface soil (0–10 cm; pH 5.8) was collected on the Canterbury Plains within the Rakaia River catchment (43°52′00.8″ S, 172°09′10.8″ E). All soil material and incubation water was collected in January 2012 and directly transported to the University of Otago, where the incubation experiment was set up the next day. SPM in the river and ocean water was collected by filtration (10–100 L) onto pre-combusted 0.7 µm GF/F or polyethersulfone membranes in the field, after which they were stored frozen.

In the laboratory at the University of Otago, the soil was sieved over a 2 mm mesh to remove roots and homogenize the sample, after which two 10 g subsamples of the soil were directly frozen at −20 °C for subsequent determination of initial GDGT composition. For the incubations, twenty-eight 250 mL bottles were filled with 10 g soil subsamples, after which 100 mL of river water or ocean water, untreated to preserve the natural microbial community, was added to twelve bottles each. Distilled water was added to the remaining four bottles to serve as control setup. The incubation bottles were loosely plugged with cotton wool, creating quasi-aerobic conditions, and placed on a shaker table from January to June 2012. Based on IPL degradation rates observed in previous studies (Harvey et al., 1986; Logemann et al., 2011), two bottles with river water and two bottles with ocean water were taken from the shaker table and immediately placed into a freezer (−20 °C) at 1, 7, 14, 30, 91, and 152 days after the start of the experiment. Duplicate control samples were frozen after 91 and 152 days. At the end of the experiment all bottles were shipped on ice to ETH Zürich, Switzerland, where the supernatant was pipetted off, the soils freeze dried, and stored frozen at −20 °C until subsequent sample work-up and analysis.

BGD
11, 11569–11596, 2014

2.2 GDGT extraction and analysis

Freeze-dried soil samples (3–4 g) were solvent-extracted three times using a Bligh and Dyer technique modified from Sturt et al. (2004). In short, a solvent mixture of MeOH : dichloromethane (DCM) : phosphate buffer at pH 7.4 (2 : 1 : 0.8, $v/v/v$) was added to the soils and ultrasonically extracted for 10 min. The extract was collected each time after centrifuging at 1000 rpm for 5 min. DCM and phosphate buffer were added to the combined extracts to a volume ratio of 1 : 1 : 0.9 to obtain phase separation. The DCM phase, containing the GDGTs, was collected after centrifuging, and the remaining solvent was rinsed twice with DCM. The combined DCM phases were dried under N_2 and passed over a silica column (deactivated with 1 weight % water) to separate CLs and IPLs according to (Pitcher et al., 2009), with the exception that hexane : ethyl acetate 1 : 1 (v/v) was used to elute the CLs. An aliquot of the IPL fraction was analyzed directly for CLs in order to assess potential carry over. The remainder of IPL fraction was dissolved in 6N HCl in MeOH and heated at 100 °C for at least 3 h to release IPL-bound CLs. A known amount of C_{46} GDGT standard (Huguet et al., 2006) was added to all fractions prior to analysis.

The filters were freeze dried and extracted with a MARS Xpress microwave extraction system, using DCM : MeOH 9 : 1 (v/v). After centrifugation (5 min at 400 rpm), the total lipid extract (TLE) was pipetted off and the residues were rinsed twice with DCM : MeOH 9 : 1 (v/v). The combined extracts were dried under N_2 with a known amount of C_{46} GDGT standard, after which the TLEs were separated into an apolar and a polar (GDGT) fraction by passing them over a silica (1 % water deactivated) column using hexane : DCM 9 : 1 (v/v) and DCM : MeOH 1 : 1 (v/v), respectively.

All GDGT-fractions were dissolved in hexane : isopropanol 99 : 1 (v/v), filtered over a 0.45 µm PTFE filter, and analyzed using high performance liquid chromatography/atmospheric pressure chemical ionization – mass spectrometry (HPLC/APCI-MS) with an Agilent 1260 Infinity series LC/MS at ETH Zürich according to Schouten et al. (2007a). Separation of the GDGTs was achieved with a Grace Prevail Cyano

BGD
11, 11569–11596, 2014

column (3 µm, 150 mm × 2.1 mm) after passing through a guard column of the same material (5 µm, 7.5 mm × 2,1 mm) with hexane : isopropanol (99 : 1, *v*/*v*) as an eluent at a flow rate of 0.2 mL min^{-1}. The GDGT-fractions eluted isocratically with 90 % A and 10 % B for 5 min, and then with a linear gradient to 18 % B for 34 min, where A = hexane and B = hexane : isopropanol 9 : 1 (*v*/*v*). Selective ion monitoring of the $[M+H]^+$ was used to detect the different GDGTs. Although brGDGTs appear to have a higher response factor than isoGDGTs (Schouten et al., 2013a), quantification was done assuming similar response factors for all GDGTs and the internal standard. Hence, reported brGDGT concentrations are likely overestimated compared to those of the isoGDGTs. The amounts of all GDGTs are given as the average and standard deviation of the duplicate incubation samples.

2.3 GDGT-based index calculations

The CBT and MBT′ indices based on brGDGTs were calculated according to (Weijers et al., 2007b):

$$\mathrm{CBT} = -\log((\mathrm{Ib} + \mathrm{IIb})/(\mathrm{Ia} + \mathrm{IIa})) \quad (1)$$

and (Peterse et al., 2012):

$$\mathrm{MBT'} = (\mathrm{Ia} + \mathrm{Ib} + \mathrm{Ic})/(\mathrm{Ia} + \mathrm{Ib} + \mathrm{Ic} + \mathrm{IIa} + \mathrm{IIb} + \mathrm{IIc} + \mathrm{IIIa}) \quad (2)$$

The BIT index was calculated following (Hopmans et al., 2004):

$$\mathrm{BIT} = (\mathrm{Ia} + \mathrm{IIa} + \mathrm{IIIa})/(\mathrm{cren} + \mathrm{Ia} + \mathrm{IIa} + \mathrm{IIIa}) \quad (3)$$

and for the TEX_{86} index based on isoGDGTs the equation of (Schouten et al., 2002) was used:

$$\mathrm{TEX}_{86} = (\mathrm{GDGT\text{-}2} + \mathrm{GDGT\text{-}3} + \mathrm{cren'})/(\mathrm{GDGT\text{-}1} + \mathrm{GDGT\text{-}2} + \mathrm{GDGT\text{-}3} + \mathrm{cren'}) \quad (4)$$

Roman numerals and GDGT names refer to the molecular structures in Fig. 1.

BGD
11, 11569–11596, 2014

3 Results and discussion

3.1 BrGDGT concentrations over time

The total brGDGT pool (IPLs + CLs) initially present in the soil is $239 \pm 13\,\mathrm{ng\,g^{-1}}$. In the different incubation experiments these concentrations varied between 187–325 $\mathrm{ng\,g^{-1}}$ (river water), 186–322 $\mathrm{ng\,g^{-1}}$ (ocean water), and 252–407 $\mathrm{ng\,g^{-1}}$ (distilled water control) (Fig. 2). Although the abundance of CL-brGDGTs seems to increase with time in the control setup, the trend is only weak and not significant ($r^2 = 0.34$, $p = 0.122$) due to the large spread in concentration between the two replicate samples at $t = 152$ days (Fig. 2). Overall both IPL-derived and CL brGDGT concentrations in all experimental setups are within the same range and remain essentially constant through time. Since the soils were incubated under natural light conditions, this indicates that soil-derived brGDGTs are not sensitive to photodegradation during their presence in an aquatic environment.

The contribution of IPLs to the total amount of brGDGTs in the soil at $t = 0$ is 12.4 ± 0.3 %, which is in the same range as has previously been reported for temperate soils from the Netherlands, Scotland, and the UK (Peterse et al., 2010; Weijers et al., 2011). The contribution of IPL-derived brGDGTs to the total pool varies mostly within the same range in the river water (7–16 %), ocean water (9–15 %), and control (9–17 %) setups, and like the total amount of CL-brGDGTs shows no significant trends or changes over time. This suggests that brGDGTs are either produced at the same rate that they are degraded, or that production and/or degradation of brGDGTs occurs at such low rates that these processes are not detected within the timeframe of this experiment. The apparent stability of the IPL-derived, or "living" brGDGT signature (Fig. 2) during the experiment is surprising, given the perceived lability of IPLs in general and their susceptibility to loss of their headgroups within a few days after cell lysis (Harvey et al., 1986; White et al., 1979). However, previous studies have indicated that the type of headgroup and the bond through which it is attached to a core lipid may influence the rate of degradation, offering a potential explanation for the absence of

BGD
11, 11569–11596, 2014

changes in IPL-brGDGT concentration in our experiment. For example, after a 96 h aerobic incubation of a mixture of IPLs with different headgroups in beach sediment, 70 % of the phospholipids had degraded, compared to only 3 % of the glycolipids (Harvey et al., 1986). Extrapolating these experimental data in a modeling study, Schouten et al. (2010) showed that in a marine water column, glycolipids are more persistent against degradation than IPLs with a phospho headgroup during settling from suspension. Although a primarily glycosidic headgroup composition would be expected based on these former results, the majority of IPL-brGDGTs in soils, peat, and lake sediments are thus far identified as phospholipids (Weijers et al., 2011; Peterse et al., 2011; Tierney et al., 2012), implying that they should be very sensitive to degradation, counter to our observations. Interestingly, Logemann et al. (2011) recently showed that the bond type within the CL, rather than the type of headgroup and its connection to that CL, determines IPL sensitivity to degradation. In their experiment, membrane lipids in which the side chains were ester-bound, as is common for bacteria, started to rapidly degrade within the first 5 days of the incubation period, whereas the abundance of lipids with ether-bound chains remained invariant during the entire 97 day experiment. BrGDGTs are thought to be produced by bacteria, but they also possess archaeal traits, including their tetraether structure (Weijers et al., 2006a). As a consequence, the presence of at least four ether bonds in each brGDGT may thus not only protect the IPL, but also the CL-brGDGTs from degradation during our experiment, even when the IPLs possess a phospho head group.

On the other hand, Weijers et al. (2010) determined a turnover rate for the total pool of CL brGDGTs in a soil of about two decades, which implies that any changes in brGDGT concentration or distribution are not yet detectable after 152 days of incubation. However, a recent study by Huguet et al. (2013) indicated that the brGDGT signature in a French peat bog had completely adapted to the 2 °C maximal daytime temperature increase induced by the placement of open top mini-greenhouses within a period of less than 26 months. Although these results suggest that brGDGTs are turned over at a substantially faster rate, significant changes were only observed in

BGD
11, 11569–11596, 2014

the latter phase of the warming experiment (Huguet et al., 2013). This finding is thus also consistent with the absence of any trends in our incubation setup, and suggests that longer incubation periods (> 1 year) with different temperature regimes may be necessary to reveal changes in brGDGT abundances.

While nutrient conditions in the river and ocean water added to the soil are presumably different, but this does not seem to have had any affect on brGDGT concentrations. Moreover, given the soil : water ratio (10 g in 100 mL) used in this experiment, the amounts of nutrients that are released from the soil after the addition of water is likely substantially higher than the concentrations initially present in the river and ocean. Nevertheless, the effect of nutrient availability on brGDGTs in soils has not yet received much attention, although recently was shown that variations in the amount and distribution of brGDGTs in lake sediments did not relate to water column nutrient concentrations (Loomis et al., 2014).

3.2 IsoGDGT concentrations over time

Crenarchaeol is the most abundant isoGDGT in the New Zealand soil at the start of the incubation, although its amount ($63 \pm 7\,ng\,g^{-1}$), as well as that of all other isoGDGTs ($50 \pm 5\,ng\,g^{-1}$) is low compared to the pool of brGDGTs ($239 \pm 13\,ng\,g^{-1}$). In contrast, the average fraction of isoGDGTs initially present in the soil as IPL is 54 % for crenarchaeol to 76 % for isoGDGT-2, substantially higher than proportion of brGDGTs occurring as IPLs (12 %) at the commencement of the experiment. Similar proportions of IPL-derived crenarchaeol have been found in soils from the Amazon (~ 50 %; Zell et al., 2013b). The total concentration (IPLs + CLs) of all isoGDGTs increases substantially during the experiment (Fig. 2), and that of isoGDGT-0 in the ocean water setup has even doubled by the end of the incubation.

The concentrations of the individual IPL-derived isoGDGTs vary between the different incubation setups, but are overall highest in ocean water (Fig. 2). The difference in isoGDGT concentration between incubations cannot be explained simply by the addition of aquatic isoGDGTs to the soil derived isoGDGT pool, as 100 mL of ocean water

BGD
11, 11569–11596, 2014

only contained ~0.5 ng isoGDGTs, which is < 1 % of their initial concentration in the soil. Because *Thaumarchaeota* play an important role in the nitrogen cycle in soils and the marine environment (Leininger et al., 2006; Wuchter et al., 2006; Zhang et al., 2010), nutrient availability may explain the concentration differences between experiments. So far, crenarchaeol has been found in all (enrichment) cultures of ammonia-oxidizing *Thaumarchaeota*, and is considered as a biomarker lipid for this group (de la Torre et al., 2008; Pitcher et al., 2010, 2011; Sinninghe Damsté et al., 2012). Its high concentration in the incubation setup using ocean water suggests that more ammonium is released in this experiment, likely due to the higher abundance of exchangeable cations (e.g. Na^+, Mg^+) in ocean water compared to fresh water. This is in agreement with the common method to determine available NH_4^+ in soils, which involves shaking soil in a KCl or Na_2SO_4 solution to extract ammonium from the soil matrix (e.g. Mehlich, 1953). The concentration profiles of the other isoGDGTs are comparable to that of crenarchaeol (Fig. 2), implying that they are also primarily derived from soil *Thaumarchaeota*. Although isoGDGTs are known to also commonly occur in the membranes of several other archaea (Schouten et al., 2013b, and references therein), the trace amounts of aquatic isoGDGTs added to the initial pool of soil isoGDGTs implies that production by soil archaea must be responsible for the isoGDGT increase during the experiment.

Despite the increase of the total isoGDGT pool, there is no statistically significant increase in the concentration of IPL-derived isoGDGTs during the course of the incubation experiment (e.g. max. $r^2 = 0.18$ for IPL-derived crenarchaeol in ocean water; Fig. 2). We assume therefore that the production rate of IPL-isoGDGTs is approximately constant. The proportional decrease of IPL-isoGDGTs with time (Fig. 3) subsequently indicates that the increase in the overall isoGDGT pool is a result of CL accumulation. This in turn implies that the turnover of the IPL pool, and thus the release of CL-isoGDGTs, is faster than the degradation of these CLs. The rapid IPL degradation rate may indicate that the isoGDGTs contain a phospho headgroup (cf. Harvey et al., 1986; Lengger et al., 2012), consistent with a recent survey of GDGTs in soil *Thaumar-*

BGD
11, 11569–11596, 2014

chaeota enrichment cultures (Sinninghe Damsté et al., 2012) and with a molecular and genomic study of the archaeal community in the water column of Lake Challa in Africa (Buckles et al., 2013). Thus, in contrast to the apparent stability of IPL-brGDGTs, the likely predominance of isoGDGTs with phospho headgroups in our experiment supports the use of these specific IPLs as indicators for their living precursor organisms.

3.3 GDGT distribution changes

To evaluate if and how soil GDGT signatures are modified in aquatic systems, we calculated brGDGT and isoGDGT-based indices commonly used in paleoclimate and carbon cycle studies (i.e. the MBT', CBT, BIT, TEX_{86}, and isoGDGT-0/cren).

The apparent absence of brGDGT production/degradation already suggest that no distribution changes are expected. Indeed, the values for the MBT' and CBT indices for the ocean and river water experiments exhibit minimal variation over time, remaining within a range of 0.04 for the MBT' index, and 0.02 for the CBT (Fig. 4). Surprisingly, the largest changes are observed in the control experiment using distilled water. The MBT' index for the IPL-derived brGDGT fraction in the control setup increases from 0.23 ± 0.00 to 0.29 ± 0.04 ($r^2 = 0.57$, $p = 0.023$; Fig. 4), and is primarily caused by an increase in the concentration of brGDGT-Ia (from 23 ± 0.3 to 29 ± 3.9 %). A closer look at the relative distributions of each of the brGDGT types at $t = 0$ and $t = 152$ days reveals a subtle shift in the contribution of IPL-derived brGDGT-III (decreasing from 23 ± 1.3 to 19 ± 0.1 %) to brGDGT-II (increasing from 54 ± 0.4 to 58 ± 0.4 %) in river water (data not shown). Since both brGDGTs-II and III in the denominator of the MBT′ index (Eq. 2), and the fraction of IPL-derived brGDGT-I remains stable, this change is not reflected by the index values. Given that the absolute amounts of IPL-derived brGDGTs do not significantly change with time, it is hard to determine the exact processes that cause the distributional changes, as in situ production or preferential degradation of specific brGDGTs could both influence the total concentration. Due to the absence of brGDGTs with cyclopentane moieties in the IPL-derived fraction it was not possible to calculate CBT index values for any of the incubation experiments, suggesting that if

BGD
11, 11569–11596, 2014

any brGDGT production is taking place in rivers and the marine environment, brGDGTs with one or more cyclopentane moieties are produced at an even lower rate than those without.

The BIT index is clearly influenced by the substantial production of crenarchaeol during the experiment, and starts to decrease between $t = 30$ and $t = 91$ days in all water types (Fig. 4). Due to the large percentage of crenarchaeol that is present as IPL compared to that of the brGDGTs, the BIT index of the IPL-derived fraction is much (0.48) lower than that of the CL fraction (0.88) at $t = 0$. The lowest BIT index value for the IPL-derived fraction is 0.35 at $t = 152$ days in ocean water (Fig. 4), and stems from relatively high production of crenarchaeol (and isoGDGTs in general) in this experiment. The trend of a lower BIT value for the IPL vs. the CL fraction has also been found for river SPM from the Yenisei (De Jonge et al., 2014) and Amazon (Zell et al., 2013b), where the difference was explained by a lower degradation rate of soil-derived crenarchaeol IPLs compared to brGDGTs and/or a contribution of in situ produced crenarchaeol IPLs in the river (Zell et al., 2013b). Our incubation results show that the degradation of IPLs from soil-derived crenarchaeol is faster than that of brGDGTs, and that the difference in BIT index between the IPL-derived and CL fractions is thus mainly caused by the higher production rate of crenarchaeol. This is in agreement with the recent finding that the BIT index of river SPM primarily tracks the seasonal aquatic production of crenarchaeol rather than that of soil input (Yang et al., 2013; Zell et al., 2013a). Our results furthermore indicate that care should be taken with using the BIT index to constrain the input of fluvially transported soil OC into a marine system. However, the stability of the soil brGDGT pool supports earlier observations that tracing the absolute amount (as opposed to the relative abundance) of brGDGTs in rivers during land-sea transport may provide a more reliable tracer of soil OC (e.g. Smith et al., 2012; Zell et al., 2013b). Moreover, the spread in GDGT response factors between laboratories resulting in a range of BIT values for the same sample provides another, independent argument to use absolute concentration measurements (Schouten et al., 2013a).

BGD
11, 11569–11596, 2014

TEX_{86} index values start to change between 30 and 91 days of incubation for the IPL-fraction in river water and the CL-fraction in ocean water experiments (Fig. 4). We find no clear explanation for the diverging trends for the different water types or IPL vs. CL fractions. Although the major part of the community producing the isoGDGTs seems to be soil-derived, the different trends may be caused by preferential growth of specific organisms. Alternatively, the relative distribution of isoGDGTs may differ per type of headgroup in both marine (Schouten et al., 2008; Pitcher et al., 2011; Lengger et al., 2012) and soil *Thaumarchaeota* (Sinninghe Damsté et al., 2012), so that the deviation in TEX_{86} values may be explained by different turnover rates per headgroup. However, even though the total variation in TEX_{86} corresponds with a 4 °C SST change in the experiment, given the low absolute amounts of terrestrial isoGDGTs that are finally discharged to the ocean in this case, this will have a minor impact on TEX_{86} records from the marine environment where their abundances are much higher.

The ratio of isoGDGT-0/crenarchaeol is on average 0.26 ± 0.05 for the CL, and 0.51 ± 0.06 for the IPL-derived fraction (Fig. 4). Blaga et al. (2009) suggested that the ratio of isoGDGT-0/crenarchaeol could be used to detect methanogenic activity, as a high concentration of isoGDGT-0 is often associated with the presence of methanogens (Schouten et al., 2013b, and references therein). The ratio values below 2 indicate that the contribution of isoGDGT-0 produced by methanogenic archaea can be considered low, and that all isoGDGTs in our experiments are primarily produced by *Thaumarchaeota*.

3.4 Comparing brGDGT distributions in river SPM and catchment soil

Despite prior evidence for in situ production of brGDGTs in rivers (Kim et al., 2012; Zhang et al., 2012; Zell et al., 2013b; Yang et al., 2013; De Jonge et al., 2014), we have not observed this in our experiment. However, we can see that the distribution of brGDGTs in SPM of the Rakaia River does not precisely reflect that in the soil sample (Fig. 4), which does support the idea that brGDGTs in soils and river SPM have different sources. The absence of an in situ production signal in our data can be explained

BGD
11, 11569–11596, 2014

by the soil : water ratio of 1 : 10 that we used in our experimental setup, which is likely more concentrated than in most natural systems, so that the relatively large amount of soil-brGDGTs may have overprinted any indication of aquatic brGDGT production during the experiment. Note that soil-SPM offset we observe is based on a single sample location in the entire river basin. Although using soil from just one location served the aim of the experiment, it is unlikely to represent the upstream part of the catchment reflected by the SPM. Moreover, the distribution of brGDGTs can show substantial variation within a small area due to soil heterogeneity (e.g. Weijers et al., 2007; Naeher et al., 2014). Finally, the Rakaia River is a relatively short and braided river system, which makes it different from the large rivers with well-developed floodplains like the Amazon and Yangtze that have been studied so far. This likely results in a shorter residence time of soil material in the river, and thus decreases the exposure to degradation, as well as the opportunity for additional in situ production in the Rakaia River. Nonetheless, the occurrence, rate, and exact implications of in situ aquatic brGDGT production during fluvial land-sea transport require further investigation.

4 Conclusions

Laboratory incubation experiments involving admixture of soil and fresh/ocean water indicate that soil-derived brGDGTs appear to be surprisingly stable in aquatic environments in both IPL- and CL-configurations. Our observations suggest an absence of significant brGDGT production or degradation, at least over the duration of the incubation experiments, and imply that soil brGDGT signatures delivered to the oceans will echo those entering the corresponding fluvial network. However, distributional offsets between brGDGTs in river SPM and catchment soil indicate that the sources of brGDGTs in a river system need to be well constrained before these compounds can be used as tracers for land-sea transport of soil organic carbon, as well as for paleoclimate reconstructions.

BGD
11, 11569–11596, 2014

As opposed to brGDGTs, significant production of isoGDGT took place during the incubation experiments, altering their initial relative distribution. Although the changes in TEX_{86} index values correspond with a maximum change of about 4 °C in reconstructed SSTs in the ocean water setup, the low abundance of isoGDGTs in soils relative to in marine settings suggests that their land-sea transport would have minimal impact on TEX_{86} recorded in the marine sedimentary record. Nevertheless, isoGDGT production after more than 30 days was sufficient to affect BIT index values, with potential consequences for the interpretation of TEX_{86}-based SST records with a BIT index close to the cutoff value of 0.3 (Weijers et al., 2006b), as the actual input of soil-derived GDGTs may be larger than anticipated

The Supplement related to this article is available online at doi:10.5194/bgd-11-11569-2014-supplement.

Acknowledgements. This study received funding from ETH Fellowship (FEL-36 11-1), ESF-MOLTER Exchange Grant (nr. 3695), and NWO Veni grant (863.13.016) awarded to FP. We thank John Williams (University of Otago) for monitoring the incubation experiment, Daniel Montluçon (ETH) for laboratory support, and Lukas Jonkers (Universidad Autònoma de Barcelona/Cardiff University) for help in the field.

References

Blaga, C. I., Reichart, G. J., Heiri, O., Sinninghe Damsté, J. S.: Tetraether membrane lipid distributions in lake particulate matter and sediments: a study of 47 European lakes along a north–south transect, J. Paleolimnol., 41, 523–540, 2009.

Blair, N. E., Leithold, E. L., Brackley, H., Trustrum, N., Page, M., and Childress, L.: Terrestrial sources and export of particulate organic carbon in the Waipaoa sedimentary system: problems, progress and processes, Mar. Geol., 270, 108–118, 2010.

BGD
11, 11569–11596, 2014

Buckles, L. K., Villanueva, L., Weijers, J. W. H., Verschuren, D., and Sinninghe Damsté, J. S.: Linking isoprenoidal GDGT membrane lipid distributions with gene abundances of ammonia-oxidizing *Thaumarchaeota* and uncultured crenarchaeotal groups in the water column of a tropical lake (Lake Challa, East Africa), Environ. Microbiol., 15, 2445–2462, 2013.

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J., and Melack, J.: Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget, Ecosystems, 10, 171–184, 2007.

De Jonge, C., Stadnitskaia, A., Hopmans, E. C., Cherkashov, G., Fedotov, A., and Sinninghe Damsté, J. S.: In-situ produced branched glycerol dialkyl glycerol tetraethers in suspended particulate matter from the Yenisei River, Eastern Siberia, Geochim. Cosmochim. Ac., 125, 476–491, 2014.

De la Torre, J. R., Walker, C. B., Ingalls, A. E., Könneke, M., and Stahl, D. A.: Cultivation of a thermophilic ammonia oxidizing archaeon synthesizing crenarchaeol, Environ. Microbiol., 10, 810–818, 2008.

Goñi, M. A., Ruttenberg, K. C., and Eglinton, T. I.: A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico, Geochim. Cosmochim. Ac., 62, 3055–3075, 1998.

Harvey, H. R., Fallon, R. D., and Patton, J. S.: The effect of organic matter and oxygen on the degradation of bacterial membrane lipids in marine sediments, Geochim. Cosmochim. Ac., 50, 795–804, 1986.

Hopmans, E. C., Weijers, J. W. H., Schefuss, E., Herfort, L., Sinninghe Damsté, J. S., and Schouten, S.: A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid tetraether lipids, Earth Planet. Sc. Lett., 224, 107–116, 2004.

Huguet, A., Fosse, C., Laggoun-Défarge, F., Delarue, F., and Derenne, S.: Effects of a short-term experimental microclimate warming on the abundance and distribution of branched GDGTs in a French peatland, Geochim. Cosmochim. Ac., 105, 294–315, 2013.

Huguet, C., Hopmans, E. C., Febo-Ayala, W., Thompson, D. H., Sinninghe Damsté, J. S., and Schouten, S.: An improved method to determine the absolute abundance of glycerol dibiphytanyl glycerol tetraether lipids, Org. Geochem., 37, 1036–1041, 2006.

Kim, J.-H., Schouten, S., Buscail, R., Ludwig, W., Bonnin, J., Sinninghe Damsté, J. S., and Bourrin, F.: Origin and distribution of terrestrial organic matter in the NW Mediterranean (Gulf

BGD
11, 11569–11596, 2014

of Lions): exploring the newly developed BIT index, Geochem. Geophy. Geosy., 7, Q11017, doi:10.1029/2006GC001306, 2006.

Kim, J.-H., van der Meer, J., Schouten, S., Helmke, P., Willmott, V., Sangiorgi, F., Koç, N., Hopmans, E. C., and Sinninghe Damsté, J. S.: New indices and calibrations derived from the distribution of crenarchaeol isoprenoid tetraether lipids: implications for past sea surface temperature reconstructions, Geochim. Cosmochim. Ac., 74, 4639–4654, 2010.

Kim, J.-H., Zell, C., Moreira-Turcq, P., Pérez, M. A. P., Abril, G., Mortillaro, J.-M., Weijers, J. W. H., Meziane, T., and Sinninghe Damsté, J. S.: Tracing soil organic carbon in the lower Amazon River and its tributaries using GDGT distributions and bulk organic matter properties, Geochim. Cosmochim. Ac., 90, 163–180, 2012.

Leininger, S., Urich, T., Schloter, M., Schwark, L., Qi, J., Nicol, G. W., Prosser, J. I., Schuster, S. C., and Schleper, C.: Archaea predominate among ammonia-oxidizing prokaryotes in soils, Nature, 442, 806–809, 2006.

Lengger, S. K., Hopmans, E. C., Reichart, G.-J., Nierop, K. G. J., Sinninghe Damsté, J. S., and Schouten, S.: Distribution of core and intact polar glycerol dibiphytanyl glycerol tetraether lipids in the Arabian Sea Oxygen Minimum Zone. II: Evidence for selective preservation and degradation in sediments and consequences for the TEX_{86}, Geochim. Cosmochim. Ac., 98, 244–258, 2012.

Logemann, J., Graue, J., Köster, J., Engelen, B., Rullkötter, J., and Cypionka, H.: A laboratory experiment of intact polar lipid degradation in sandy sediments, Biogeosciences, 8, 2547–2560, doi:10.5194/bg-8-2547-2011, 2011.

Loomis, S. E., Russell, J. M., Eggermont, H., Verschuren, D., and Sinninghe Damsté, J. S.: Effects of temperature, pH, and nutrient concentration on branched GDGT distributions in East African lakes: implications for paleoenvironmental reconstruction, Org. Geochem., 66, 25–37, 2014.

Mehlich, A.: Determination of P, Ca, Mg, K, Na, and NH_4, Pub. No. 1-53, NC Soil Testing Division, Raleigh, NC, 1953.

Naeher, S., Peterse, F., Smittenberg, R. H., Niemann, H., Zigah, P. K., and Schubert, C. J.: Sources of glycerol dialkyl glycerol tetraethers (GDGTs) in catchment soils, water column and sediments of Lake Rotsee (Switzerland) – implications for the application of GDGT-based proxies for lakes, Org. Geochem., 66, 164–173, 2014.

BGD
11, 11569–11596, 2014

Oppermann, B. I., Michaelis, W., Blumenberg, M., Frerichs, J., Schulz, H. M., Schippers, A., Beaubien, S. E., and Krüger, M.: Soil microbial community changes as a result of long-term exposure to a natural CO_2 vent, Geochim. Cosmochim. Ac., 74, 2697–2716, 2010.

Pancost, R. D. and Sinninghe Damsté, J. S.: Carbon isotopic compositions of prokaryotic lipids as tracers of carbon cycling in diverse settings, Chem. Geol., 195, 29–58, 2003.

Peterse, F., Kim, J.-H., Schouten, S., Klitgaard Kristensen, D., Koç, N., and Sinninghe Damsté, J. S.: Constraints on the application of the MBT/CBT palaeothermometer at high latitude environments (Svalbard, Norway), Org. Geochem., 40, 692–699, 2009.

Peterse, F., Nicol, G. W., Schouten, S., and Sinninghe Damsté, J. S.: Influence of soil pH on the abundance and distribution of core and intact polar lipid-derived branched GDGTs in soil, Org. Geochem., 41, 1171–1175, 2010.

Peterse, F., Hopmans, E. C., Schouten, S., Mets, A., Rijpstra, W. I. C., and Sinninghe Damsté, J. S.: Identification and distribution of intact polar branched tetraether lipids in peat and soil, Org. Geochem., 42, 1007–1015, 2011.

Peterse, F., van der Meer, J., Schouten, S., Weijers, J. W. H., Fierer, N., Jackson, R. B., Kim, J.-H., and Sinninghe Damsté, J. S.: Revised calibration of the MBT-CBT paleotemperature proxy based on branched tetraether membrane lipids in surface soils, Geochim. Cosmochim. Ac., 96, 215–229, 2012.

Pitcher, A., Hopmans, E. C., Schouten, S., and Sinninghe Damsté, J. S.: Separation of core and intact polar archaeal tetraether lipids using silica columns: insights into living and fossil biomass contributions, Org. Geochem., 40, 12–19, 2009.

Pitcher, A., Rychlik, N., Hopmans, E. C., Spieck, E., Rijpstra, W. I. C., Ossebaar, J., Schouten, S., Wagner, M., and Sinninghe Damsté, J. S.: Crenarchaeol and its regioisomer dominate the membrane lipids of "*Candidatus Nitrososphaera gargensis*", a thermophilic Group I.1b Crenarchaeote, ISME J., 4, 542–552, 2010.

Pitcher, A., Hopmans, E. C., Mosier, A. C., Francis, C. A., Reese, S. K., Schouten, S., and Sinninghe Damsté, J. S.: Distribution of core and intact polar tetraether lipids in enrichment cultures of *Thaumarchaeota* from marine sediments, Appl. Environ. Microb., 77, 3468–3477, 2011.

Schouten, S., Hopmans, E. C., Pancost, R. D., and Sinninghe Damsté, J. S.: Widespread occurrence of structurally diverse tetraether membrane lipids: evidence for the ubiquitous presence of low-temperature relatives of hyperthermophiles, P. Natl. Acad. Sci. USA, 97, 14421–14426, 2000.

BGD
11, 11569–11596, 2014

Schouten, S., Hopmans, E. C., Schefuss, E., and Sinninghe Damsté, J. S.: Distributional variations in marine crenarchaeotal membrane lipids: a new tool for reconstructing ancient sea water temperatures?, Earth Planet. Sc. Lett., 204, 265–274, 2002.

Schouten, S., Huguet, C., Hopmans, E. C., Kienhuis, M. V. M., and Sinninghe Damsté, J. S.: Analytical methodology for TEX86 paleothermometry by high-performance liquid chromatography/atmospheric pressure chemical ionization-mass spectrometry, Anal. Chem., 79, 2940–2944, 2007.

Schouten, S., Middelburg, J. J., Hopmans, E. C., and Sinninghe Damsté, J. S.: Fossilization and degradation of intact polar lipids in deep subsurface sediments: a theoretical approach, Geochim. Cosmochim. Ac., 74, 3806–3814, 2010.

Schouten, S., Hopmans, E. C., Rosell-Melé, A., Pearson, A., Adam, P., Bauersachs, T., Bard, E., Bernasconi, S. M., Bianchi, T. S., Brocks, J. J., Carlson, L. T., Castañeda, I. S., Derenne, S., Selver, A. D., Dutta, K., Eglinton, T., Fosse, C., Galy, V., Grice, K., Hinrichs, K. U., Huang, Y., Huguet, A., Huguet, C., Hurley, S., Ingalls, A., Jia, G., Keely, B., Knappy, C., Kondo, M., Krishnan, S., Lincoln, S., Lipp, J., Mangelsdorf, K., Martínez-García, A., Ménot, G., Mets, A., Mollenhauer, G., Ohkouchi, N., Ossebaar, J., Pagani, M., Pancost, R. D., Pearson, E. J., Peterse, F., Reichart, G.-J., Schaeffer, P., Schmitt, G., Schwark, L., Shah, S. R., Smith, R. W., Smittenberg, R. H., Summons, R. E., Takano, Y., Talbot, H. M., Taylor, K. W. R., Tarozo, R., Uchida, M., Dongen, B. E. van, Van Mooy, B. A. S., Wang, J., Warren, C., Weijers, J. W. H., Werne, J. P., Woltering, M., Xie, S., Yamamoto, M., Zhang, C. L., Zhang, Y., Zhao, M., and Sinninghe Damsté, J. S.: An interlaboratory study of TEX_{86} and BIT analysis of sediments, extracts, and standard mixtures, Geochem. Geophy. Geosy., 14, 5263–5285, 2013a.

Schouten, S., Hopmans, E. C., and Sinninghe Damsté, J. S.: The organic geochemistry of glycerol dialkyl glycerol tetraether lipids: a review, Org. Geochem., 54, 19–61, 2013b.

Sinninghe Damsté, J. S., Hopmans, E. C., Pancost, R. D., Schouten, S., and Geenevasen, J. A. J.: Newly discovered non-isoprenoid glycerol dialkyl glycerol tetraether lipids in sediments, Chem. Commun., 17, 1683–1684, 2000.

Sinninghe Damsté, J. S., Rijpstra, W. I. C., Hopmans, E. C., Prahl, F. G., Wakeham, S. G., and Schouten, S.: Distribution of membrane lipids of planktonic Crenarchaeota in the Arabian Sea, Appl. Environ. Microb., 68, 2997–3002, 2002.

Sinninghe Damsté, J. S., Ossebaar, J., Abbas, B., Schouten, S., and Verschuren, D.: Fluxes and distribution of tetraether lipids in an equatorial African lake: constraints on the application of

BGD
11, 11569–11596, 2014

the TEX(86) palaeothermometer and BIT index in lacustrine settings, Geochim. Cosmochim. Ac., 73, 4232–4249, 2009.

Sinninghe Damsté, J. S., Rijpstra, W. I. C., Hopmans, E. C., Weijers, J. W. H., Foesel, B. U., Overmann, J., and Dedysh, S. N.: 13,16-dimethyl octacosanedioic acid (iso-diabolic acid), a common membrane-spanning lipid of acidobacteria subdivisions 1 and 3, Appl. Environ. Microb., 77, 4147–4154, 2011.

Sinninghe Damsté, J. S., Rijpstra, W. I. C., Hopmans, E. C., Jung, M. Y., Kim, J. G., Rhee, S. K., Stieglmeier, M., and Schleper, C.: Intact polar and core glycerol dibiphytanyl glycerol tetraether lipids of group I.1a and I.1b *Thaumarchaeota* in soil, Appl. Environ. Microb., 78, 6866–6874, 2012.

Smith, R. W., Bianchi, T. S., and Li, X.: A re-evaluation of the use of branched GDGTs as terrestrial biomarkers: Implications for the BIT index, Geochim. Cosmochim. Ac., 80, 14–29, 2012.

Sturt, H. F., Summons, R. E., Smith, K., Elvert, M., and Hinrichs, K.-U.: Intact polar membrane lipids in prokaryotes and sediments deciphered by high-performance liquid chromatography/electrospray ionization multistage mass spectrometry – new biomarkers for biogeochemistry and microbial ecology, Rapid Commun. Mass Sp., 18, 617–628, 2004.

Tierney, J. E. and Russell, J. M.: Distributions of branched GDGTs in a tropical lake system: implications for lacustrine application of the MBT/CBT paleoproxy, Org. Geochem., 40, 1032–1036, 2009.

Tierney, J. E., Schouten, S., Pitcher, A., Hopmans, E. C., and Sinninghe Damsté, J. S.: Core and intact polar glycerol dialkyl glycerol tetraethers (GDGTs) in Sand Pond, Warwick, Rhode Island (USA): insights into the origin of lacustrine GDGTs, Geochim. Cosmochim. Ac., 77, 561–581, 2012.

Weijers, J. W. H., Schouten, S., Hopmans, E. C., Geenevasen, J. A. J., David, O. R. P., Coleman, J. M., Pancost, R. D., and Sinninghe Damsté, J. S.: Membrane lipids of mesophilic anaerobic bacteria thriving in peats have typical archaeal traits, Environ. Microbiol., 8, 648–657, 2006a.

Weijers, J. W. H., Schouten, S., Spaargaren, O. C., and Sinninghe Damsté, J. S.: Occurrence and distribution of tetraether membrane lipids in soils: implications for the use of the TEX(86) proxy and the BIT index, Org. Geochem., 37, 1680–1693, 2006b.

BGD
11, 11569–11596, 2014

Weijers, J. W. H., Schefuss, E., Schouten, S., and Sinninghe Damsté, J. S.: Coupled thermal and hydrological evolution of tropical Africa over the last deglaciation, Science, 315, 1701–1704, 2007a.
Weijers, J. W. H., Schouten, S., van den Donker, J. C., Hopmans, E. C., and Sinninghe Damsté, J. S.: Environmental controls on bacterial tetraether membrane lipid distribution in soils, Geochim. Cosmochim. Ac., 71, 703–713, 2007b.
Weijers, J. W. H., Panoto, E., van Bleijswijk, J., Schouten, S., Rijpstra, W. I. C., Balk, M., Stams, A. J. M., and Sinninghe Damsté, J. S.: Constraints on the biological source(s) of the orphan branched tetraether membrane lipids, Geomicrobiol. J., 26, 402–414, 2009.
Weijers, J. W. H., Wiesenberg, G. L. B., Bol, R., Hopmans, E. C., and Pancost, R. D.: Carbon isotopic composition of branched tetraether membrane lipids in soils suggest a rapid turnover and a heterotrophic life style of their source organism(s), Biogeosciences, 7, 2959–2973, doi:10.5194/bg-7-2959-2010, 2010.
Weijers, J. W. H., Bernhardt, B., Peterse, F., Werne, J. P., Dungait, J. A. J., Schouten, S., and Sinninghe Damsté, J. S.: Absence of seasonal patterns in MBT-CBT indices in mid-latitude soils, Geochim. Cosmochim. Ac., 75, 3179–3190, 2011.
Weyhenmeyer, G. A., Fröberg, M., Karltun, E., Khalili, M., Kothawala, D., Temnerud J., and Tranvik, L. J.: Selective decay of terrestrial organic carbon during transport from land to sea, Glob. Change Biol., 18, 349–355, 2012.
White, D. C., Davis, W. M., Nickels, J. S., King, J. D., and Bobbie, R. J.: Determination of the sedimentary microbial biomass by extractible lipid phosphate, Oecologia, 40, 51–62, 1979.
Wuchter, C., Abbas, B., Coolen, M. J. L., Herfort, L., Timmers, P., Strous, M., van Bleijswijk, J., Teira, E., Herndl, G. J., Middelburg, J. J., Schouten S., and Sinninghe Damsté, J. S.: Archaeal nitrification in the ocean, P. Natl. Acad. Sci. USA, 103, 12317–12322, 2006.
Yang, G., Zhang, C. L., Xie, S., Chen, Z., Gao, M., Ge, Z., and Yang, Z.: Microbial glycerol dialkyl glycerol tetraethers from river water and soil near the Three Gorges Dam on the Yangtze River, Org. Geochem., 56, 40–50, 2013.
Zell, C., Kim, J.-H., Abril, G., Lima Sobrinho, R., Dorhout, D., Moreira-Turcq, P., and Sinninghe Damsté, J. S.: Impact of seasonal hydrological variation on the distributions of tetraether lipids along the Amazon River in the central Amazon Basin: implications for the MBT/CBT paleothermometer and the BIT index, Front. Terr. Microbiol., 4, 228, doi:10.3389/fmicb.2013.00228, 2013a.

BGD
11, 11569–11596, 2014

Zell, C., Kim, J.-H., Moreira-Turcq, P., Abril, G., Hopmans, E. C., Bonnet, M.-P., Lima Sobrinho, R., and Sinninghe Damsté, J. S.: Disentangling the origins of branched tetraether lipids and crenarchaeol in the lower Amazon River: implications for GDGT-based proxies, Limnol. Oceanogr., 58, 343–353, 2013b.

Zhang, C. L., Wang, J., Wei, Y., Zhu, C., Huang, L., and Dong, H.: Production of branched tetraether lipids in the lower Pearl River and estuary: effects of extraction methods and impact on bGDGT proxies, Front. Terr. Microbiol., 2, 274, doi:10.3389/fmicb.2011.00274, 2012.

Zhang, L.-M., Offre, P. R., He, J.-Z., Verhamme, D. T., Nicol, G. W., and Prosser, J. I.: Autotrophic ammonia oxidation by soil *Thaumarchaeota*, P. Natl. Acad. Sci. USA, 107, 17240–17245, 2010.

Zhu, C., Weijers, J. W. H., Wagner, T., Pan, J.-M., Chen, J.-F., and Pancost, R. D.: Sources and distributions of tetraether lipids in surface sediments across a large river-dominated continental margin, Org. Geochem., 42, 376–386, 2011.

BGD
11, 11569–11596, 2014

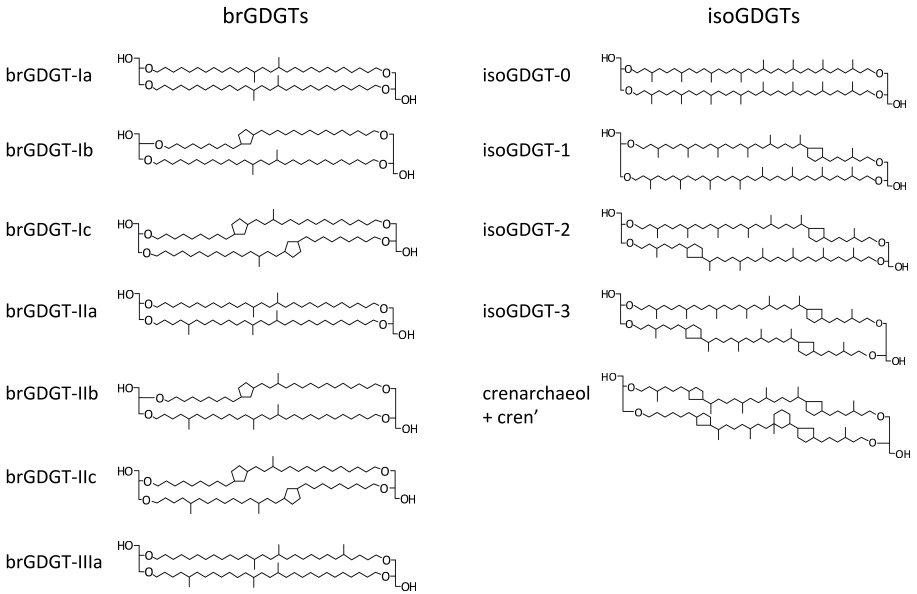

Figure 1. Molecular structures of the brGDGTs and isoGDGTs monitored during the incubation experiment.

BGD
11, 11569–11596, 2014

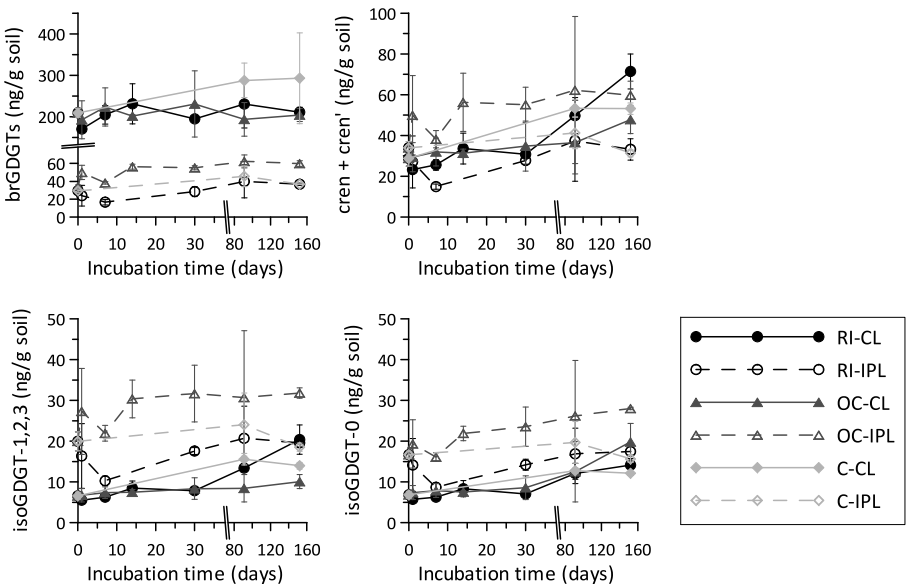

Figure 2. Average concentrations and standard deviation of core lipid (CL) and intact polar lipid (IPL)-derived **(a)** brGDGTs, **(b)** crenarchaeol + cren′, **(c)** isoGDGT-1,2,3, and **(d)** isoGDGT-0 in a sandy loam soil from the Raiaka River catchment, New Zealand, during incubation (t = 152 days) in river (RI), ocean (OC), and distilled (C) water under quasi-aerobic conditions.

BGD
11, 11569–11596, 2014

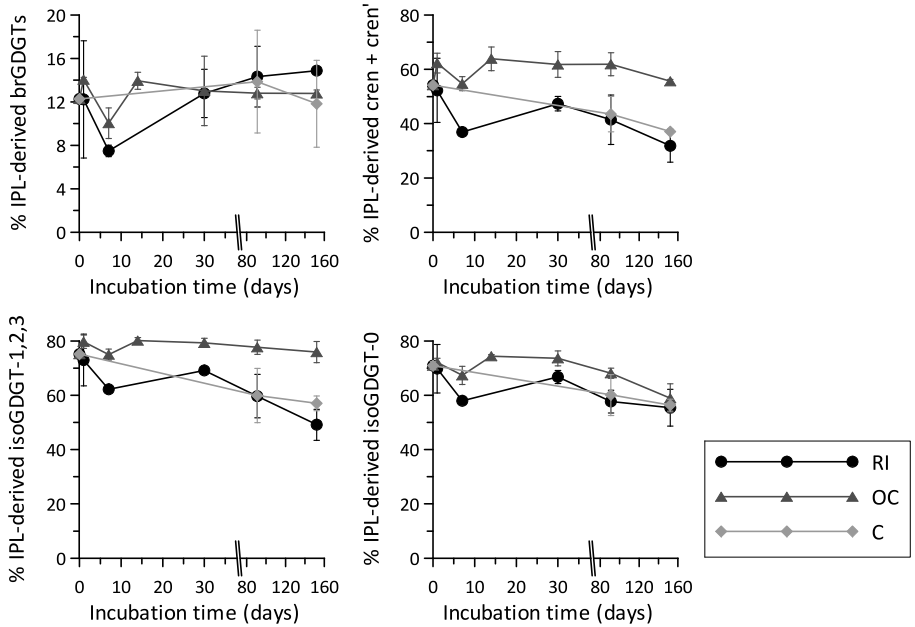

Figure 3. Average percentage of the total pool of **(a)** brGDGTs, **(b)** crenarchaeol + cren′, **(c)** isoGDGTs-1,2,3, and **(d)** isoGDGT-0 present in "living", or intact polar lipid (IPL)-derived form.

BGD
11, 11569–11596, 2014

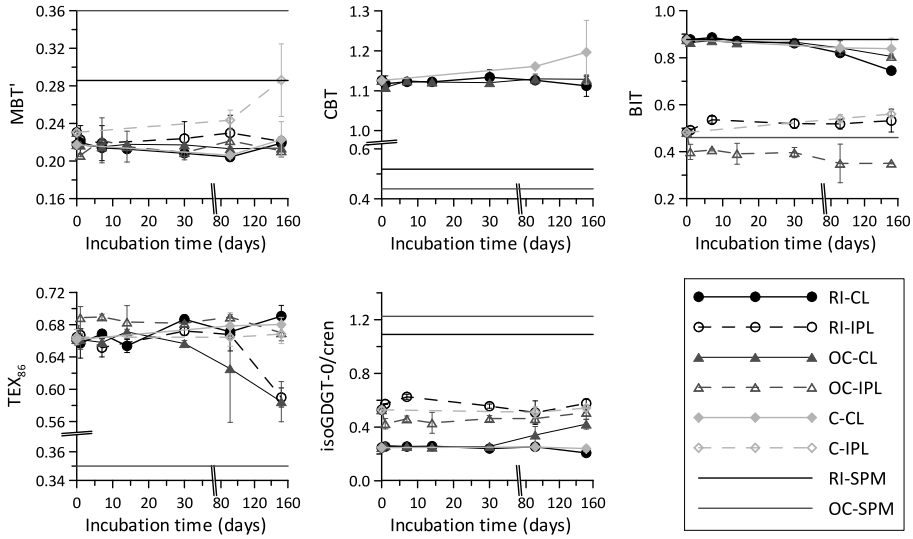

Figure 4. Average distribution and deviation of core lipid (CL) and intact polar lipid (IPL)-derived GDGTs in a sandy loam soil from the Rakaia River catchment, New Zealand, as reflected by the **(a)** MBT′ index, **(b)** CBT index, **(c)** BIT index, **(d)** TEX_{86} index, and **(e)** isoGDGT-0/crenarchaeol ratio during incubation (t = 152 days) in river (RI), ocean (OC), and distilled (C) water under quasi-aerobic conditions. Horizontal straight lines represent GDGT composition in river (black) and ocean water (grey) suspended particulate material (SPM).

BGD
11, 11569–11596, 2014