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# Transport of branched tetraether lipids from the Tagus River basin to the coastal ocean of the Portuguese margin: consequences for the interpretation of the MBT'/CBT paleothermometer

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## Abstract

Branched glycerol dialkyl glycerol tetraethers (brGDGTs), which are transported from soil to marine sediment by rivers, have been used to reconstruct the mean annual air temperature (MAAT) and soil pH of the drainage basin using the methylation index of branched tetraethers (MBT, recently refined as MBT') and cyclization index of branched tetraethers (CBT) from coastal marine sediment records. In this study we are tracing the brGDGTs from source to sink in the Tagus River basin, the longest river system on the Iberian Peninsula, by determining their concentration and distribution in soils, river suspended particulate matter (SPM), riverbank sediments, marine SPM, and marine surface sediments. The concentrations of brGDGTs in river SPM were substantially higher and their distributions were different compared to those of the drainage basin soils. This indicates that brGDGTs are mainly produced in the river itself. In the marine environment, the brGDGT concentrations rapidly decreased with increasing distance from the Tagus estuary. At the same time, the brGDGT distributions in marine sediments also changed, indicating that marine in-situ production also takes place. These results show that there are various problems that complicate the use of the MBT'/CBT for paleoreconstructions using coastal marine sediments in the vicinity of a river. However, if the majority of brGDGTs are produced in the river, it might be possible to reconstruct the environmental (temperature and pH) conditions of the river water using appropriate aquatic calibrations, provided that marine core locations are chosen in such a way that the brGDGTs in their sediments are predominantly derived from riverine in-situ production.

## 1 Introduction

Branched glycerol dialkyl glycerol tetraethers (brGDGTs) are membrane-spanning lipids, most likely derived from heterotrophic (Pancost and Sinninghe Damsté, 2003; Oppermann et al., 2010; Weijers et al., 2010) bacteria that occur ubiquitously in peat

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(e.g. Weijers et al., 2006a) and soil (e.g. Weijers et al., 2007a). The major brGDGTs contain a variety of methyl groups (4–6) and may contain up to two cyclopentane moieties formed by internal cyclization (Sinninghe Damsté et al., 2000; Weijers et al., 2006a). Four of these methyl groups are present in mid-chain positions of the two C<sub>28</sub> linear chains of the tetraether structure (Fig. 1), whilst the others are present at the C-5 and C-5' positions. Recently, De Jonge et al. (2013) identified four new isomers of the previously described pentamethylated and hexamethylated brGDGTs in a Siberian peat. These isomers are characterized by the presence of methyl groups at the C-6 and C-6' instead of the C-5 and C-5' positions. Concerning the biological origin of the brGDGTs, it has been found so far that brGDGT Ia (see for structures Fig. 1) is produced by some species of Acidobacteria (Sinninghe Damsté et al., 2011). However, it remains unclear whether other bacteria are also able to produce brGDGTs.

The distribution of brGDGTs, as expressed by the degree of methylation (methylation index of branched tetraethers; MBT) and cyclization (cyclization index of branched tetraethers; CBT) of the brGDGTs, in soil correlates with mean annual air temperature (MAAT) and soil pH (Weijers et al., 2007a). The MBT/CBT proxy is one of the few quantitative temperature proxies that have been introduced for terrestrial environments. The MBT/CBT proxy has been used to reconstruct past MAAT changes in diverse settings: marine (e.g. Weijers et al., 2007b; Donders et al., 2009; Rueda et al., 2009; Bendle et al., 2010) and lacustrine (Niemann et al., 2005; Tyler et al., 2010; Zink et al., 2010; Fawcett et al., 2011; D'Anjou et al., 2013) sediments, peat (Ballantyne et al., 2010), and loess deposits (Peterse et al., 2011a; Zech et al., 2012; Jia et al., 2013).

To reconstruct terrestrial climate changes using the MBT/CBT proxy, sediment cores in front of river outflows have been used (e.g. Weijers et al., 2007b). Initially, it was thought that brGDGTs were only produced in soils, washed into rivers by soil erosion, and transported to the marine environment where they are deposited in sediments. Consequently, it was thought that the MBT/CBT records of marine sediment cores would represent an integrated signal of the whole river drainage basin. An initial study that applied the MBT/CBT proxy in Congo deep-sea fan sediments (Weijers et al.,

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2007b) showed its potential to reconstruct changes of MAAT of the Congo basin over the last glaciation. However, subsequent studies have shown that in-situ production in rivers (Yang et al., 2013; Zell et al., 2013a, b) and in the marine environment (Peterse et al., 2009; Zhu et al., 2011; Hu et al., 2012; Strong et al., 2012; Zell et al., 2014) may affect the original brGDGT signal of soil and, therefore, complicates the use of the MBT/CBT proxy. Depending on the river systems, it seems that the influence of in-situ production can differ. In addition, other potential factors may hamper the application of the MBT/CBT proxy in coastal sediments. For example, an increased input of brGDGTs from a certain area of the drainage basin could obscure the representativeness of the entire river basin (Bendle et al., 2010; Strong et al., 2012). Therefore, it is of utmost importance to further investigate how different environmental conditions affect the application of the MBT/CBT proxy. Recently, the MBT was adjusted to the MBT', by excluding brGDGT IIIb and IIIc, because they occur less frequently in soil (Peterse et al., 2012). Hereafter, we will therefore use the term of the MBT'/CBT instead of the MBT/CBT.

The relative amount of brGDGTs to the isoprenoid GDGT, crenarchaeol, which is produced predominantly in the marine environment by Thaumarchaeota may indicate a substantial input of soil organic matter to the ocean. This is expressed with the Branched and Isoprenoid Tetraether (BIT) index (Hopmans et al., 2004), which is a helpful tool to decide where the MBT'/CBT proxy can be applied or not. Initially, a value of the BIT index of 1 was thought to indicate an environmental sample only containing soil organic matter, while a value of 0 was thought to reflect only aquatic organic matter. However, crenarchaeol is also produced in soils which can lead to a value of the BIT index of <1.0 (Weijers et al., 2006b; Kim et al., 2010; Peterse et al., 2010; Yang et al., 2011). The BIT index is also influenced by the amount of crenarchaeol produced in the marine environment (e.g. Fietz et al., 2011; Smith et al., 2012; Wu et al., 2013) and by degradation processes (Huguet et al., 2008, 2009). This shows that also for the BIT index further investigation is needed to understand how it





collected during the PACEMAKER 64PE332 cruise with the R/V *Pelagia* between 14 and 29 March 2011. Marine SPM samples were collected at four stations along the Tagus transect from the Tagus estuary mouth towards the deep sea canyon and at 2–5 different water depths (Fig. 2b, Table 1). 64 to 240 L of seawater were filtered over ashed GF-F filters (Whatman GF-F, 0.7  $\mu\text{m}$  pore size, 142 mm diameter) with a McLane in-situ-pump system (WTS, McLane Labs, Falmouth, MA). For the OC and stable carbon isotope analysis, about 8 L of seawater were separately filtered on GF-F filters (0.7  $\mu\text{m}$  pore size, 47 mm diameter). Marine sediment cores were retrieved at 6 stations using a multicorer developed by Oktopus GmbH. In this study the surface sediments (top 0.5 cm of the multicores) were used. All samples were frozen immediately after sampling and freeze-dried before analysis.

### 3.2 Environmental parameters and bulk geochemical analysis

The pH of the Tagus River water was measured with a pH analyzer (Metrohm pH-meter 744 and combined pH-Electrode LL-Solitrode Pt1000, pH range 0–14,  $T$  range –130–200  $^{\circ}\text{C}$  stored in 3 molL<sup>-1</sup> KCl). The electrode was calibrated with CertiPUR buffer solutions (pH 7.00 and 9.00); quality control was assured using CertiPUR buffer solutions with pH 6.00 and 8.00 analyzed in parallel with each batch of samples. The measurements were performed in the laboratory within 1 h after collection. The pH of the soil and riverbank sediment samples was measured in a mixture with distilled water 1 : 3.5 ( $v : v$ ). This mixture was stirred vigorously and left to settle down for 20 min. For the pH measurements a pH analyzer (Wissenschaftlich-Technische Werkstätten pH 315i/SET and probe pH-Electrode SenTix 41, pH range 0–14,  $T$  range 0–80  $^{\circ}\text{C}$ , stored in 3 molL<sup>-1</sup> KCl) was calibrated with CertiPUR buffer solutions with pH 4.01, 7.00, and 10.00.

For the OC and stable carbon isotope analysis, the riverine and marine SPM filters were decarbonated with HCl vapor as described by Lorrain et al. (2003). Soils, riverbank sediments, and marine surface sediments were decarbonated with 2 molL<sup>-1</sup> HCl (overnight at 50  $^{\circ}\text{C}$ ). All samples were analyzed with a Thermo Flash EA 1112

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Elemental Analyzer interfaced with a Thermo Finnigan Delta<sup>Plus</sup> mass spectrometer. OC is expressed as the weight percentage of dry sediment (wt. %). The analyses were determined in duplicate and the analytical error was on average better than 0.1 wt. % for the OC content. Isotope values were calibrated to a benzoic acid standard ( $\delta^{13}\text{C}_{\text{OC}} = -27.8\text{‰}$  with respect to Vienna Pee Dee Belemnite (VPDB) calibrated on NBS-22) and corrected for blank contribution. The analytical error was usually smaller than  $\pm 0.1\text{‰}$  for  $\delta^{13}\text{C}_{\text{OC}}$ .

### 3.3 Lipid extraction and analysis

The soils and riverbank sediments were extracted using an accelerated solvent extraction (ASE) technique due to the fact that the Bligh and Dyer (BD) method is very time consuming. For the ASE extraction, 2–10 g freeze dried soils and riverbank sediments were extracted 3 times using a mixture of dichloromethane (DCM):methanol (MeOH) (9:1,  $v:v$ ) at a temperature of 100 °C and a pressure of 1500 psi for 5 min with 60% flush and purge 60 s. The extract was collected in a vial and solvents were removed using Caliper Turbovab<sup>®</sup> LV. The total extracts were taken up in DCM, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and blown down under a stream of nitrogen. For GDGT quantification, 0.1  $\mu\text{g}$  of an internal standard ( $\text{C}_{46}$  GDGT; Huguet et al., 2006) was added to the total extracts. The total extracts were separated over an  $\text{Al}_2\text{O}_3$  column (activated for 2 h at 150 °C) into two fractions using hexane:DCM (1:1,  $v:v$ ), and DCM:MeOH (1:1,  $v:v$ ), respectively.

In order to analyze both CL and IPL-derived GDGTs, a second extraction method was used, i.e. a modified BD technique (Pitcher et al., 2009). 4 soils, 4 riverbank sediments, and all the river and marine SPM samples and marine surface sediments were extracted with this BD method. The Bligh and Dyer extracts (BDE) were separated into a CL fraction and an IPL fraction over a silica gel (activated overnight) column with *n*-hexane:ethyl acetate (1:1,  $v:v$ ) and MeOH as eluents, respectively (Pitcher et al., 2009). For the GDGT quantification, 0.01  $\mu\text{g}$  of  $\text{C}_{46}$  GDGT internal standard

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was added to each fraction. The CL fractions of the BDEs were separated into three fractions over an  $\text{Al}_2\text{O}_3$  column (activated for 2 h at  $150^\circ\text{C}$ ) using hexane : DCM (9 : 1,  $v : v$ ), hexane : DCM (1 : 1,  $v : v$ ), and DCM : MeOH (1 : 1,  $v : v$ ), respectively. Part of the IPL fraction was hydrolyzed to obtain IPL-derived CLs. The CL polar fractions, the hydrolyzed IPL fractions, and the non-hydrolyzed IPL fractions were analyzed for CL GDGTs. The non-hydrolyzed IPL fractions were also analyzed, because it was reported by Pitcher et al. (2009) that during the separation of CL and IPL fractions a small amount of the CL GDGTs were carried over into the IPL fraction. Therefore, it was necessary to implement a correction to more accurately calculate the amounts of CL and IPL-derived GDGTs as described by Weijers et al. (2011).

All samples were analyzed using a high performance liquid chromatography–atmospheric pressure positive ion chemical ionization–mass spectrometry (HPLC–APCI–MS) with an Agilent 1100 series LC–MSD SL. The GDGTs were separated on an Alltech Prevail Cyano column ( $150\text{mm} \times 2.1\text{mm}$ ;  $3\mu\text{m}$ ) using the method described by Schouten et al. (2007) and modified by Peterse et al. (2012). The compounds were eluted isocratically with 90 % A and 10 % B for 5 min at a flow rate of  $0.2\text{mLmin}^{-1}$ , and then with a linear gradient to 16 % B for 34 min, where A = hexane and B = hexane : isopropanol (9 : 1,  $v : v$ ). The injection volume was  $10\mu\text{L}$  per sample. Selective ion monitoring of the  $[\text{M} + \text{H}]^+$  of the different brGDGTs and crenarchaeol was used to detect and quantify them. Quantification was achieved by calculating the area of the corresponding peak in the chromatogram and comparing it with the peak area of the internal standard and correcting for the different response factors (Huguet et al., 2006). The analytical error was determined by duplicate measurements of 12 CL GDGTs and 7 IPL derived brGDGTs fractions. For the concentration of the sum of brGDGTs, the analytical error was 11 % for the CL GDGTs and 6 % for the IPL-derived GDGTs. Crenarchaeol concentrations had a standard deviation of 17 % for the CL GDGTs and 10 % for the IPL-derived GDGTs.



## 4 Results

### 4.1 Tagus soils

16 soil samples that were collected along the Tagus River (Fig. 2) were analyzed. The OC content ranged from 0.1 to 5.9 wt. %, the  $\delta^{13}\text{C}_{\text{OC}}$  was  $-26.7 \pm 1.6\%$  (average  $\pm$  standard deviation [ $1\sigma$ ]) (Table 1). Soil pH was on average  $7.4 \pm 1.0$  (Table 1). CL brGDGTs were found in all soils with an average concentration of  $3.2 \pm 3.4 \mu\text{g g}_{\text{OC}}^{-1}$  (Fig. 3a). Of the 4 soils for which IPL-derived brGDGTs were measured  $7 \pm 2\%$  of the total brGDGTs amount was IPL-derived (Fig. 3b). The distribution of CL brGDGTs strongly varied between the soils, but brGDGT IIa ( $53 \pm 10\%$ ) and Ia ( $24 \pm 15\%$ ) were in general the most abundant compound (Fig. 4a). The BIT index was  $0.62 \pm 0.28$  in the CL GDGTs and  $0.50 \pm 0.38$  in the IPL-derived GDGTs (Fig. 3e–f). The CL MBT' was  $0.30 \pm 0.13$  and the CL DC  $0.16 \pm 0.13$  (Fig. 3g). The MBT' of IPL-derived brGDGTs was  $0.41 \pm 0.11$  (Fig. 3h). Only in soil TRS19 the concentration of IPL-brGDGTs was sufficiently high to calculate the DC, which was 0.39 (Fig. 3g–j). CL crenarchaeol concentration in soils was on average  $1.1 \pm 0.8 \mu\text{g g}_{\text{OC}}^{-1}$  and a substantial amount ( $53 \pm 36\%$ ) of the total crenarchaeol amount was IPL-derived (Fig. 3c and d).

The CL brGDGT and CL crenarchaeol concentrations obtained by ASE extraction were on average 4.6 and  $1.5 \mu\text{g g}_{\text{OC}}^{-1}$ , respectively, higher than with the BD method. Furthermore, the BIT index was on average 0.08 lower, the MBT' 0.01 higher, and the DC 0.02 higher in ASE extracted samples compared to BD extracted samples. This shows that the CL fractions extracted by BD and the GDGTs extracted by ASE give similar results, which is why they were treated as comparable results in the discussion.

### 4.2 Tagus River SPM

The pH of the river water was relatively constant at  $7.4 \pm 0.1$  over the annual cycle and the amount of SPM in the river water ranged from 28 to  $165 \text{ mg L}^{-1}$  (Fig. 5b; Table 1). The OC content of SPM varied between 1.0 and 2.6 wt. % and the  $\delta^{13}\text{C}_{\text{OC}}$  was

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–29.1±0.8‰ (Table 1). The average CL brGDGT concentration was 43±16 µg g<sub>OC</sub><sup>-1</sup> and the percentage of IPL-derived brGDGTs was 12±8 (Fig. 3a and b). The CL brGDGT distribution in river SPM was more uniform compared to those of the soils and the riverbank sediments (Fig. 4b). The most abundant CL brGDGTs were brGDGT IIa (39±5%) and Ia (24±3%) but with more abundant brGDGT IIIa (10±10%) than in the soils. The crenarchaeol concentration was on average 13±6 µg g<sub>OC</sub><sup>-1</sup> and the percentage of IPL-derived crenarchaeol was 23±13 (Fig. 3c and d). This resulted in a BIT index of 0.71±0.08 in the CL fractions and of 0.56±0.13 in the IPL-derived fractions (Fig. 3e–f). The average CL MBT' and DC values were 0.35±0.04 and 0.28±0.02, respectively, while the average IPL-derived MBT' and DC values were 0.40±0.05 and 0.27±0.04, respectively (Fig. 3g–j). The brGDGT and crenarchaeol concentrations in the Tagus River SPM fluctuated over the year; the highest concentrations (in ng L<sup>-1</sup>) were seen in September and May (Fig. 6a). The brGDGT concentrations normalized on OC were highest in November and December, while crenarchaeol concentrations normalized on OC were highest in February–June (Fig. 6b). The highest percentage of IPL-derived brGDGTs was found in March and that for crenarchaeol in January and February (Fig. 6c). The CL BIT increased in November, while the CL MBT' and DC decreased in November (Fig. 7). IPL-derived BIT MBT' and DC all increased in March and April.

### 4.3 Tagus riverbank sediments

Ten riverbank sediments were analyzed. The OC content ranged from 0.2 to 3.7 wt.%, the δ<sup>13</sup>C<sub>OC</sub> from –23.6 to –28.6‰, and the pH from 6.9 to 8.2 (Table 1). CL brGDGTs were present with an average concentration of 15.2±11.9 µg g<sub>OC</sub><sup>-1</sup> (Fig. 3a). For four riverbank sediments the IPL-derived brGDGTs were also measured: 7±3% of the total brGDGTs amount were IPL-derived (Fig. 3b). The average distribution of CL brGDGTs (Fig. 4c) revealed that brGDGT IIa (39±7%) and Ia (17±5%) were the most abundant compounds. CL crenarchaeol concentration in riverbank sediments was

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on average  $4.7 \pm 4.7 \mu\text{g}_{\text{OC}}^{-1}$  and  $54 \pm 26\%$  of the total crenarchaeol amount was IPL-derived (Fig. 3c and d). The BIT index was  $0.65 \pm 0.23$  in the CL GDGTs and  $0.30 \pm 0.05$  in the IPL-derived GDGTs (Fig. 3e and f). The CL MBT' was  $0.31 \pm 0.05$  and the CL DC  $0.37 \pm 0.11$ . The MBT' and DC of IPL-derived brGDGTs were on average  $0.45 \pm 0.10$  and  $0.22 \pm 0.12$ , respectively (Fig. 3g–j).

#### 4.4 Marine SPM

The amount of SPM in marine water varied between  $0.6$  and  $2.3 \text{ mg L}^{-1}$  with the higher values closest to the estuary mouth (Table 1). The OC content of the SPM ranged from  $1.6$  to  $10 \text{ wt. \%}$  and the  $\delta^{13}\text{C}_{\text{OC}}$  from  $-24.1$  to  $-26.9\text{‰}$  (Table 1). In general, the OC content of SPM was higher in surface than in bottom waters (Fig. 8a) and  $\delta^{13}\text{C}_{\text{OC}}$  was more enriched in surface waters compared to bottom waters (Fig. 8b). The CL brGDGT concentrations varied widely between  $0.06$  and  $31 \mu\text{g}_{\text{OC}}^{-1}$  with an average amount of  $4 \pm 9 \mu\text{g}_{\text{OC}}^{-1}$ . The percentage of IPL-derived brGDGTs of the total amount of brGDGTs was  $15 \pm 13$ . CL brGDGT concentrations decreased from the estuary mouth towards the deep sea canyon (Fig. 8c). The highest concentration was found in the surface water at the shallowest station A ( $31 \mu\text{g}_{\text{OC}}^{-1}$ ). The CL brGDGTs were not detectable in the surface water of the canyon station furthest away from the estuary mouth (station F). In all stations but the one closest to the estuary mouth higher brGDGT concentrations were found in the bottom than in surface waters (Fig. 8c). The most abundant CL brGDGTs were IIa ( $32 \pm 10\%$ ) and Ia ( $26 \pm 9\%$ ) (Fig. 4d). CL crenarchaeol concentrations varied between  $82$  and  $242 \mu\text{g}_{\text{OC}}^{-1}$  (Fig. 8d). The percentage of IPL-derived crenarchaeol was  $20 \pm 10$ . The BIT index ranged between  $< 0.01$  and  $0.18$  with an average CL BIT of  $0.03 \pm 0.06$  and IPL derived BIT  $0.02 \pm 0.03$ . The highest BIT values were measured closest to the estuary mouth (Fig. 9a and b).

Due to low CL and IPL-derived brGDGT concentrations, MBT' and DC could not be calculated for all SPM samples because not all of the necessary brGDGTs were detected. The MBT' and DC of CL brGDGTs were  $0.49 \pm 0.06$  and  $0.26 \pm 0.14$ ,

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respectively. For IPL-derived brGDGTs the MBT' and DC were  $0.54 \pm 0.14$  and  $0.13 \pm 0.13$ , respectively (Fig. 9c–f).

#### 4.5 Marine surface sediments

The marine surface sediments had the average OC content between 0.01 and 1.7 wt. % and the  $\delta^{13}\text{C}_{\text{OC}}$  values varied between  $-21.9$  and  $-24.4$ ‰ (Table 1; Figs. 8G–H). The CL brGDGT concentrations (Fig. 8i) were higher at stations closed to the estuary mouth (stations A–C) with values declining from 130 to  $16 \mu\text{g g}_{\text{OC}}^{-1}$ . The surface sediments from the off-shore stations D–F had lower concentrations (between 23 and  $7 \mu\text{g g}_{\text{OC}}^{-1}$ ). The percentage of IPL-derived brGDGTs was on average  $11 \pm 1$ . The most abundant brGDGTs were IIa ( $31 \pm 5$  %) and Ia ( $22 \pm 3$  %) (Fig. 4e). The crenarchaeol concentrations varied between 120 and  $600 \mu\text{g g}_{\text{OC}}^{-1}$  (Fig. 8j). The percentage of IPL-derived crenarchaeol was  $7 \pm 2$  (Fig. 8i). The BIT index varied between 0.16 and 0.02 in the CL fractions and 0.21 and 0.04 in the IPL-derived fractions, with a clear decreasing trend towards the deep sea canyon station (Fig. 9g). The average CL MBT' was  $0.43 \pm 0.02$  and the CL DC was  $0.35 \pm 0.06$ . The MBT' of the IPL-derived brGDGTs was on average  $0.58 \pm 0.03$  and the DC  $0.30 \pm 0.06$ . For both CL and IPL fractions, MBT' did not show a trend with increasing distance from the coast (Fig. 9h), whereas DC showed a trend toward higher values (Fig. 9i).

## 5 Discussion

### 5.1 Characteristics of the bulk organic matter

The organic matter content of soil in dry and warm climates is usually low (Jobbágy and Jackson, 2000), which is also observed in the Tagus basin (on average  $1.8 \pm 2.2$  wt. %, Table 1). In river SPM, the OC content was similar to that of soil and relatively constant around the year (on average  $1.9 \pm 0.5$  wt. %) (Fig. 5c, Table 1). The  $\delta^{13}\text{C}_{\text{OC}}$  values

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of soils, riverbank sediments, and river SPM showed an average value of  $-27.5 \pm 2\%$ , which is a typical  $C_3$  higher plant signal (e.g. Fry and Sherr, 1984). In contrast, in marine SPM and surface sediments, the  $\delta^{13}C_{OC}$  values (on average  $-25.1 \pm 2\%$  and  $-23.1 \pm 2\%$ , respectively) were higher in comparison to those of the Tagus basin samples and increased from inshore to offshore (Fig. 8a and h). This suggests that the proportion of marine-derived OC to the total OC pool increased from close to the Tagus estuary to the deep sea canyon site. In addition, a higher OC content of SPM was recorded in the upper water layers where marine primary production takes place.

In the marine sediment sampled close to the river estuary the OC content was lower than in the open ocean (Fig. 8g). Jouanneau et al. (1998), who studied the OC contents in marine sediments of this area in more detail, also showed that the OC content was low close to the river estuary. This is because the OC content was closely related to the sediment grain size and the average grain size of the surface sediments was larger close to the river estuary. Therefore, the OC content of surface sediments increased towards the mud belt at 100 m water depth. The OC content may also increase at greater water depth due to marine production. Our  $\delta^{13}C_{OC}$  data from the marine surface sediments indicate that the majority of the OC on the Portuguese shelf is of marine origin. Already in the estuary, only 50 to 65 % of OC content is estimated to be of terrestrial origin (Alt-Epping et al., 2007). The Tagus River acts mainly as a supplier of terrigenous lithogenic particles to the coastal ocean, while the majority of the terrestrial organic matter is retained inside the estuary (Jouanneau et al., 1998).

## 5.2 GDGTs in soils of the Tagus drainage basin.

BrGDGTs and crenarchaeol were found in all Tagus soils. The relative amount of brGDGTs to crenarchaeol, which is defined in the BIT index, was relatively low (BIT =  $0.7 \pm 0.2$ ) compared to soils in general (cf. Schouten et al., 2013 for an overview). It has been reported in several studies that the BIT decreases with increasing soil pH and is lower and more variable above a pH of 5.5 (Kim et al., 2010; Peterse et al., 2010; Yang et al., 2011). Indeed the pH of all but one of the soils studied was above 5.5. Recently,

reduced values of the BIT index in soils have also been attributed to a dry climate (Xie et al., 2012; Dirghangi et al., 2013; Menges et al., 2013). The reason for the low BIT could be that in dry soils, oxygen can penetrate further into the soil (Cleveland et al., 2010). Xie et al. (2012) suggested that oxic conditions might be unfavorable for the facultative anaerobic brGDGT producing bacteria, but may be beneficial for nitrifying (i.e. requiring oxygen) Thaumarchaeota, increasing crenarchaeol productions in soils.

The distribution of the brGDGTs varied strongly in the Tagus basin soils (Fig. 4), which led to highly variable MBT' and DC (or CBT) values (Fig. 10a). The variability in MBT' values is unexpected since in a global soil dataset (Peterse et al., 2012) they are related to MAAT and MAAT does not vary substantially (i.e. 10–17 °C, see Table 1) for the Tagus basin. However, it has been previously described that the MBT' shows a less strong relationship with MAAT in dry areas (mean annual precipitation (MAP) < 700–800 mm yr<sup>-1</sup>) than in other climate regions (Peterse et al., 2012; Xie, 2012; Dirghangi et al., 2013). The MAP at the sampling sites is indeed low at 450–910 mm yr<sup>-1</sup> (Table 1). A recent study of 23 Iberian soils (Menges et al., 2013) has revealed similar variable MBT' and DC (or CBT) values as we report here. In that study it is suggested that the MBT' is primarily related with the MAP and soil aridity. In our dataset the soils from > 900 m altitude showed a higher DC (i.e. > 0.3) compared to the rest of the soils, while those collected < 200 m altitude showed a relatively low DC (i.e. < 0.15) and a higher MBT' (i.e. > 0.4) (Fig. 10a). However, we did not observe a clear correlation of the DC and MBT' with altitude. The brGDGT composition in soils of the Tagus River watershed was thus quite variable. Soils are notoriously heterogeneous in composition (e.g. Williams et al., 2002) and the fact that the Tagus River basin is in an arid climate zone may further contribute to this poor correlation. Despite the variability of brGDGT distributions in Iberian soils, we will compare them with those in the river system to test if they are an important source for riverine brGDGTs.

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### 5.3 Sources of GDGTs in Tagus River SPM and riverbank sediments

Compared to soils, significantly higher concentrations (normalized to OC to account for differences in grain size) of both CL brGDGTs and CL crenarchaeol were found in river SPM (Fig. 3a and c). Higher crenarchaeol concentrations are expected since crenarchaeol is usually produced in higher amounts relative to brGDGTs in aquatic environments (Herfort et al., 2006; Kim et al., 2010). For riverine brGDGTs it is originally assumed that they originate from surrounding soils (Hopmans et al., 2004). Consequently, it would be expected that riverine brGDGTs have similar concentrations and distributions as the soils in the watershed of the river. The significantly higher CL brGDGT concentration in river SPM than in soils thus suggests that brGDGTs were also produced in-situ in the Tagus River. This could be revealed by a relatively high amount of brGDGTs with polar head groups (cf. Peterse et al., 2011b). The percentage of IPL-derived brGDGTs in river SPM was not significantly higher than in soils (Fig. 3b). However, if riverine brGDGTs would only derive from soil erosion, one would expect this number to drop since labile IPL brGDGTs would be preferentially broken down during transport.

A third line of evidence for in-situ production in the river comes from the distribution of brGDGTs (Fig. 4). If riverine brGDGTs are derived from two different sources, this can also often be detected in the brGDGT distribution. We compared the brGDGT distribution with the help of the MBT' and DC (Fig. 10a). In order to examine what MBT' and DC values a mixture of the brGDGTs from the drainage basin soils would theoretically have, we calculated a brGDGT concentration-weighted MBT' and DC. This is based on the assumption that soils that contain a higher concentration of brGDGTs will contribute more to the brGDGTs in the river. The weighted CL MBT' and CL DC values were 0.36 and 0.10, respectively (Fig. 10a). These values are substantially influenced by soil samples 7 and 8b (both from < 200 m altitude), because they have high brGDGT concentrations compared to all other soils. If low-altitude soils are not considered, the weighted average (MBT' = 0.18, DC = 0.11) falls in the cloud of the

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majority of the soils (Fig. 10a). Irrespective of which average is used, Fig. 10a shows that the average DC in river SPM is substantially higher (i.e. 0.28 vs. 0.10), which again supports that brGDGTs are produced in the river.

In a study of brGDGTs in SPM of the Amazon River (Brazil), it is shown that the brGDGT concentration and distribution can be influenced by hydrological changes, meaning that during times of increased precipitation higher amounts of brGDGTs are washed into the river from soils (Zell et al., 2013b). This influences the brGDGT distribution in rivers because it affects the amount of soil-derived relative to in-situ-produced brGDGTs in the river. In addition, the brGDGTs produced in the river might reflect environmental conditions in the river that change over the annual cycle. We evaluated temporal variations in the brGDGT composition of the SPM (sampled close to the river mouth) to shed further light on the potential origins of brGDGTs. The Iberian Peninsula is typically characterized by a period of higher precipitation from October to March and thus higher Tagus River discharge (Fig. 5a). However, during the SPM sampling period (2011–2012) the Iberian Peninsula experienced a relatively dry winter (Trigo et al., 2012). A profound increase in precipitation is evident for October and November, but December–March were unusually dry (Fig. 5a). This precipitation pattern does not show a clear relationship with the SPM concentration profile (Fig. 5b) and the concentration of brGDGTs (Fig. 6a and b), as would be expected if increased precipitation would result in increased soil erosion and subsequent input in the river system, although it should be noted that we did not measure the SPM and brGDGT fluxes. A further complication is that the Tagus River is strongly regulated with dams that are used to provide drinking water and water for agricultural purposes to Spain and Portugal and also to generate hydroelectricity. Therefore, the flow through the river is not only influenced by precipitation. In terms of compositional changes in SPM, it is noteworthy that at the peak of maximum precipitation in November 2011, the BIT index is at a maximum (0.84) and the DC of the brGDGT shows the lowest value (0.25). This could be interpreted as an increased contribution of soil-derived brGDGTs, although the value for the DC is still far away from the average for soils in the watershed (0.10–

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0.11; Fig. 10c). With respect to the temporal changes in the MBT', the lowest values are recorded for November–March (Figs. 10b) with the largest changes observed for the IPL-derived brGDGTs. MBT' (and MBT) are also related to temperature in aquatic systems (Tierney et al., 2010; Zink et al., 2010; Pearson et al., 2011; Sun et al., 2011).

Hence, MBT' could be used as evidence for in-situ production of brGDGTs in the river as MBT' would then follow the changes in temperature over the annual cycle, whereas in case of a dominant soil origin for the brGDGTs, this would not be expected because of their residence time in soils (Weijers et al., 2011). Our data show that seasonal hydrological changes may have an influence on the brGDGT distribution in the Tagus River, but these changes are not evident enough to make an estimate of the contributions of the two sources for brGDGTs in this river system.

Compared to the SPM, which was only sampled close to the river mouth, riverbank sediments were sampled at several stations along the river. In most of the riverbank sediment the DC was higher than in river SPM. However, the MBT' and DC of the riverbank sediment close to the river mouth (samples 6 and 8a) were similar to those of the river SPM, which was also collected close to the river mouth. This shows that the DC of brGDGTs most likely varies along the river. Numerous dams in the Tagus River hold back the sediment from the upstream parts and, thereby, they might decrease the influence of brGDGTs from the upstream drainage basin on the downstream river.

### 5.4 Sources of GDGTs in marine SPM and surface sediments

It should be considered that the results from the marine SPM only give a “snap shot” at the moment of sampling (i.e. March 2011, chosen to reflect the end of the season with highest amount of rainfall) and should, thus, be interpreted cautiously. The crenarchaeol concentrations were higher in marine SPM and surface sediments than in river SPM, which shows that marine Thaumarchaeota were the predominant source of crenarchaeol in the marine environment. In SPM IPL-derived crenarchaeol was higher than in sediments (Fig. 8f and l), suggesting that crenarchaeol production takes place predominantly in the water column. In the marine sediment the crenarchaeol

concentration showed no clear trend from land to ocean (Fig. 8j). At the time of sampling the input of brGDGTs from the river into the marine system was evident. Higher CL brGDGT concentrations were detected at the stations (A–C) close to the river estuary but these concentrations were already lower than those in river SPM (Fig. 8c). Higher CL brGDGT concentrations were also found in the bottom water SPM as compared to shallow water SPM (Fig. 8c). This may indicate that the brGDGT in river SPM are (partially) transported by a bottom nepheloid layer. This terrestrial input to the bottom nepheloid layer is also clearly indicated by the lower  $\delta^{13}\text{C}_{\text{OC}}$  values in the bottom SPM (Fig. 8b). IPL-derived brGDGTs in marine SPM show a completely different pattern (Fig. 8e) and do not seem to be transported from the Tagus River into the ocean.

A further clue towards potential sources of brGDGTs in the marine system can be obtained by comparing their distributions. Figure 4 shows that marine SPM is on average less dominated by brGDGT IIa than river SPM. Furthermore, the MBT' and DC values of brGDGTs in marine SPM varied more than those of Tagus River SPM (Fig. 10a). The spatial distribution of CL MBT' (Fig. 9c) and DC values (Fig. 9e) showed lower MBT' and higher DC values in the deeper water layers than in surface waters. This trend was also apparent in the MBT' and DC values of IPL brGDGTs (Figs. 9B and 9D), although less data could be obtained. The input of brGDGTs in river SPM is still clear from these plots since MBT' and DC values of the coastal stations (A–C) are comparable to those in river SPM. Further away from the river estuary, brGDGTs in marine SPM do not only show a substantially lower concentration but the changing DC and MBT' values also reveal a different distribution (Fig. 9c–f). This can only be explained by a rapid dilution of the river SPM with in-situ production of brGDGTs in the marine water column (albeit at much lower levels than in the river). This is consistent with expected alterations in brGDGTs since the higher pH of sea water and lower temperatures in deeper waters would give rise to the observed spatial patterns (i.e. higher DC and lower MBT' values).

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The brGDGT composition of marine surface sediments, in contrast to that of marine SPM, may provide a signature that is averaged over seasons and years. However, it may be affected by in-situ production in the sediment (cf. Peterse et al., 2009). As was seen for marine SPM (Fig. 8c), the CL brGDGT concentrations normalized per  $g_{OC}$  in the marine sediments was highest at the station (A) closest to the estuary with a markedly declining trend with further distance from the river estuary (Fig. 8i). Surprisingly, the CL brGDGT concentration at station A was even higher than that in the Tagus River SPM (Fig. 8g). This might be caused by faster degradation of other riverine organic matter, while CL brGDGTs were more stable and consequently slightly increased in concentration (normalized on OC) (cf. Huguet et al., 2008). Overall, the concentration trend is in line with rapid dilution of brGDGTs delivered from the river to the ocean.

A next step is to consider the brGDGT distribution of the marine sediments. The MBT' of CL brGDGTs was slightly higher than that of the Tagus River SPM (Fig. 10a) and showed no spatial variation (Fig. 9h). The DC in the coastal station A was similar to that of river SPM (Fig. 10a), but it showed a clear increase from the coast to the ocean (Fig. 9i), consistent with the trend in marine SPM (Fig. 9e). IPL-derived brGDGT had a constant MBT' but it was higher than that of CL GDGTs. The DC of IPL-derived brGDGTs in marine sediment showed a similar increase with increasing distance offshore as for CL brGDGTs, although the trend was more scattered (Fig. 9i). Overall, these observed distributional changes are in line with an increasingly important contribution of marine in-situ production of brGDGTs with increasing distance from the river estuary.

If the MBT' and DC would in general change in the same way from river to ocean it would help to make predictions on how the MBT'/CBT proxy in marine sediments should be interpreted. Similar studies have been carried out in other locations. An increase of the DC from soil to the marine environment has been described so far in all studied locations (Yangtze River (Zhu et al., 2011), Pearl River (Zhang et al., 2012), a Norwegian fjord (Peterse et al., 2009) and the Amazon River, Zell et al., 2014).





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to the Tagus River basin. Secondly, due to the much higher concentrations of brGDGTs in the Tagus River SPM compared to the soils and their different brGDGT distributions, it is likely that the brGDGTs in the Tagus River are predominantly produced in the river. This means that the brGDGTs in the river do not represent the brGDGT distribution of the soils, which makes it impossible to reconstruct river basin soil conditions using brGDGTs transported by the Tagus River. Thirdly, from the river estuary to the open marine environment brGDGT distributions (and consequently MBT' and CBT values) changed again, due to the increasing influence of in-situ produced marine brGDGTs. This shows that at least for the Tagus River system, but probably more generally, brGDGTs in marine sediments cannot directly be used to reconstruct soil pH and MAAT of the river basin.

Since the majority of the brGDGTs in the Tagus River are likely produced in the river, it might be possible to reconstruct the environmental conditions in the river instead of those of the river basin soils. It is well known that brGDGT soil calibrations differ from those reported for aquatic environments (Tierney et al., 2010; Zink et al., 2010; Pearson et al., 2011; Sun et al., 2011). However, calibrations for river water have not yet been reported. Therefore, for the reconstruction of the river pH and temperature the application of a lake calibration is currently used (cf. De Jonge et al., 2014). A number of calibrations have been reported for the MBT'/CBT, but so far no lake calibrations for the MBT'/CBT exist to the best of our knowledge. Furthermore, river water temperatures were not measured when river SPM was collected and we were not successful to obtain Tagus River temperature data from the existing database neither. Therefore, we are for the moment unable to test if climate reconstructions using Tagus River-derived brGDGTs should, in principle, be possible.

In order to prevent strong influence of marine in-situ produced brGDGTs, it is recommendable to use cores that were taken close to the river mouth. How far away from the river the brGDGTs from the river are still dominant over the ones produced in the marine environment can be influenced by several factors, for example the degradation processes in the estuary, sedimentation rates and the ocean currents. The

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BIT index might be a good indicator for high river influence. In general the higher the BIT the more likely it is that there is more river input and thus a more similar MBT' and DC that is most similar to that of the river SPM. From our data we can see that at a BIT < 0.05, especially the DC was quite different. Therefore, we recommend certainly not to apply the MBT'/CBT in sediment records with a BIT < 0.05. Further studies are needed to understand what influences the MBT' and DC in brGDGTs that are produced in the marine environment. In general this study shows that there are many factors that can complicate the use of the MBT'/CBT to reconstruct river basin temperature and soil pH from marine sediment cores. Therefore, it is absolutely necessary to investigate the basin soils, river SPM and marine surface sediments before interpreting the MBT'/CBT records from a marine sediment core. This severely complicates paleostudies going back further in time.

## 6 Conclusion

Our study shows that in the case of the Tagus River system there are several problems concerning the use of the MBT'/CBT to reconstruct river basin MAAT and soil pH. Firstly, soil brGDGTs in dry environment do not accurately predict the MAAT and soil pH, secondly, brGDGTs in the river SPM are mainly produced in-situ, and thirdly MBT' and DC values in marine sediments are further influenced by brGDGTs produced in the marine environment. Since the majority of brGDGTs seem to be produced in the aquatic environment, it is probably possible to use a lake (or river) calibration to reconstruct the environmental conditions of the river itself. This indicates that in order to decide whether the MBT'/CBT can be used to reconstruct the terrestrial paleoenvironmental changes from marine sediment cores, it is essential to test the MBT'/CBT of drainage basin soils and river SPM. If it is decided that the MBT'/CBT can be used for environmental reconstructions, the core should be taken as close to the river as possible to minimize the influence of brGDGTs produced in the marine environment.

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**Table 1.** Environmental and bulk geochemical data of soils and riverbank sediments collected in the Tagus River basin.

Sample name	Sampling date (dd/mm/yyyy)	Long.	Lat.	Altitude (m)	Measured pH	$\delta^{13}\text{C}_{\text{OC}}$ (‰ VPDB)	OC (wt. %)	MAAT* (°C)	MAP* (mm)
Tagus soils									
TRS-3	03/06/2012	-5.72	39.77	249	6.7	-29.0	0.7	17	664
TRS-4	03/06/2012	-6.51	39.68	278	6.7	-28.7	0.7	16	619
TRS-5	03/06/2012	-6.48	39.63	344	7.2	-28.4	2.2	16	579
TRS-7	06/06/2012	-8.73	39.07	29	5.5	-27.5	5.0	17	697
TRS-8b	06/06/2012	-8.04	39.47	28	6.7	-27.8	3.0	17	913
TRS-9	06/06/2012	-8.00	39.46	102	5.7	-27.2	0.5	16	903
TRS-10	06/06/2012	-4.65	39.94	380	7.8	-28.5	1.5	16	504
TRS-12	07/06/2012	-3.57	40.04	496	7.4	-25.1	0.2	14	508
TRS-13	07/06/2012	-2.96	40.27	581	7.8	-27.0	6.9	14	475
TRS-14b	07/06/2012	-2.97	40.26	580	8.3	-25.3	0.8	14	465
TRS-15	07/06/2012	-2.91	40.42	678	8.4	-25.7	0.9	13	517
TRS-16	07/06/2012	-2.84	40.51	768	7.8	-24.8	0.1	14	491
TRS-18	07/06/2012	-2.59	40.70	729	8.6	-23.4	0.1	13	595
TRS-19	07/06/2012	-2.28	40.67	1217	8.5	-25.7	0.1	10	710
TRS-20	07/06/2012	-2.20	40.78	1100	8.4	-26.1	0.1	11	671
TRS-21	07/06/2012	-2.16	40.79	931	7.6	-26.8	5.8	13	557
Tagus riverbank sediments									
TRS-1a	03/06/2012	-5.68	39.84	268	6.9	-26.9	0.9	16	758
TRS-1b	03/06/2012	-5.68	39.84	268	8.2	-27.6	1.5	16	758
TRS-2a	03/06/2012	-5.74	39.76	242	7.8	-23.6	3.3	16	858
TRS-2b	03/06/2012	-5.74	39.76	242	7.7	-25.1	0.5	17	656
TRS-6	06/06/2012	-8.98	38.95	0	7.9	-26.3	1.7	17	677
TRS-8a	06/06/2012	-8.04	39.47	23	7.1	-26.5	0.2	17	913
TRS-11	07/06/2012	-4.02	39.86	493	7.7	-27.0	1.3	15	386
TRS-14a	07/06/2012	-2.97	40.26	580	7.4	-27.1	3.0	14	465
TRS-17	07/06/2012	-2.59	40.70	717	7.8	-29.6	3.7	13	545
TRS-22	07/06/2012	-2.16	40.80	901	8.0	-29.8	0.6	12	946

\* Data from Ninyerola et al. (2005)

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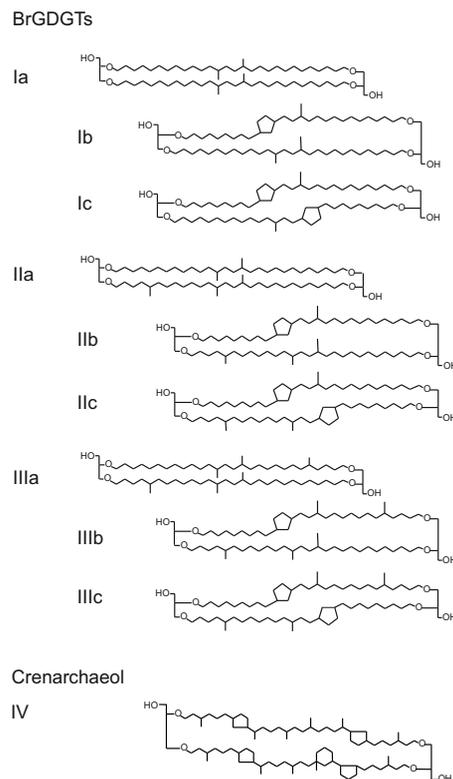
**Table 2.** Environmental and bulk geochemical data of Tagus River SPM, marine SPM and marine sediment.

Sample name	Station	Sampling date (dd/mm/yyyy)	Long.	Lat.	Water depth (m)	Measured pH	$\delta^{13}\text{C}_{\text{OC}}$ (‰ VPDB)	OC (wt. %)	SPM (mg L <sup>-1</sup> )
Tagus River SPM									
TR 2#1 Sup	TR	12/07/2011	-8.99	38.95	0	8.1	-29.2	2.6	74
TR 3#1 Sup	TR	16/09/2011	-8.99	38.95	0	7.9	-28.4	1.8	165
TR 4#1 Sup	TR	18/10/2011	-8.99	38.95	0	7.4	-30.9	2.5	62
TR 5#1 Sup	TR	22/11/2011	-8.99	38.95	0	7.6	-28.9	1.3	63
TR 6#1 Sup	TR	16/12/2011	-8.99	38.95	0	8.0	-29.4	2.4	35
TR 7#1 Sup	TR	16/01/2012	-8.99	38.95	0	7.9	-29.8	2.4	28
TR 8#1 Sup	TR	17/02/2012	-8.99	38.95	0	8.0	-29.4	1.0	45
TR 9#1 Sup	TR	16/03/2012	-8.99	38.95	0	8.1	-29.0	2.2	20
TR 10#1 Sup	TR	12/04/2012	-8.99	38.95	0	8.1	-28.5	1.9	112
TR 11#1 Sup	TR	24/05/2012	-8.99	38.95	0	7.9	-28.5	1.7	121
TR 12#1 Sup	TR	24/06/2012	-8.99	38.95	0	8.0	-27.8	1.3	34
Marine SPM									
64PE332-27-1-1m	A	24/03/2011	-9.36	38.61	1	-	-24.6	3.6	2.3
64PE332-27-1-19m	A	24/03/2011	-9.36	38.61	19	-	-25.0	2.9	2.3
64PE332-28-3-1m	C	24/03/2011	-9.37	38.56	1	-	-24.2	9.8	0.6
64PE332-28-3-20m	C	24/03/2011	-9.37	38.56	20	-	-23.8	6.8	0.9
64PE332-28-3-50m	C	24/03/2011	-9.37	38.56	50	-	-23.9	5.3	0.6
64PE332-28-3-93m	C	24/03/2011	-9.37	38.56	93	-	-24.6	3.2	1.0
64PE332-32-1-1m	E	25/03/2011	-9.43	38.39	1	-	-25.8	9.6	0.5
64PE332-32-1-50m	E	25/03/2011	-9.43	38.39	50	-	-24.6	10.0	0.4
64PE332-32-1-200m	E	25/03/2011	-9.43	38.39	200	-	-26.0	2.5	0.8
64PE332-32-1-500m	E	25/03/2011	-9.43	38.39	500	-	-26.2	3.4	0.4
64PE332-32-1-1051m	E	25/03/2011	-9.43	38.39	1051	-	-26.9	3.0	0.7
64PE332-36-4-1m	F	27/03/2011	-9.48	38.23	1	-	-24.1	9.2	0.4
64PE332-36-4-50m	F	27/03/2011	-9.48	38.23	50	-	-25.1	6.9	0.4
64PE332-36-4-200m	F	27/03/2011	-9.48	38.23	200	-	-25.1	6.9	0.8
64PE332-36-4-1000m	F	27/03/2011	-9.48	38.23	1000	-	-26.1	1.6	1.0
64PE332-36-4-2431m	F	27/03/2011	-9.48	38.23	2431	-	-26.3	2.5	0.6
Marine surface sediments									
64PE332-27-3	A	24/03/2011	-9.36	38.61	20	-	-24.4	0.2	-
64PE332-29-2	B	25/03/2011	-9.35	38.58	48	-	-23.3	0.1	-
64PE332-28-1	C	24/03/2011	-9.37	38.56	94	-	-24.9	1.7	-
64PE332-31-2	D	25/03/2011	-9.42	38.42	478	-	-21.9	1.4	-
64PE332-33-1	E	26/03/2011	-9.43	38.39	1052	-	-22.2	1.3	-
64PE332-36-3	F	27/03/2011	-9.48	38.23	2432	-	-22.2	0.9	-

"-" = no data

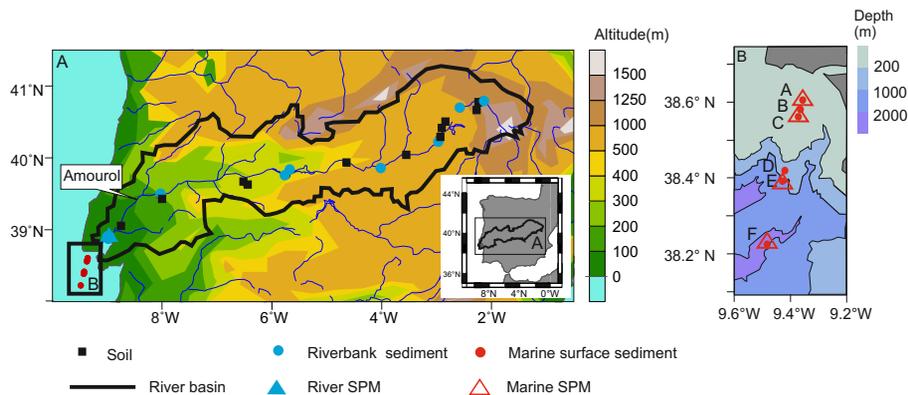
**Tagus brGDGT  
transport:  
consequences for the  
MBT'/CBT**

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**Fig. 1.** Chemical structure of brGDGTs (Ia–IIIa) and crenarchaeol (IV).[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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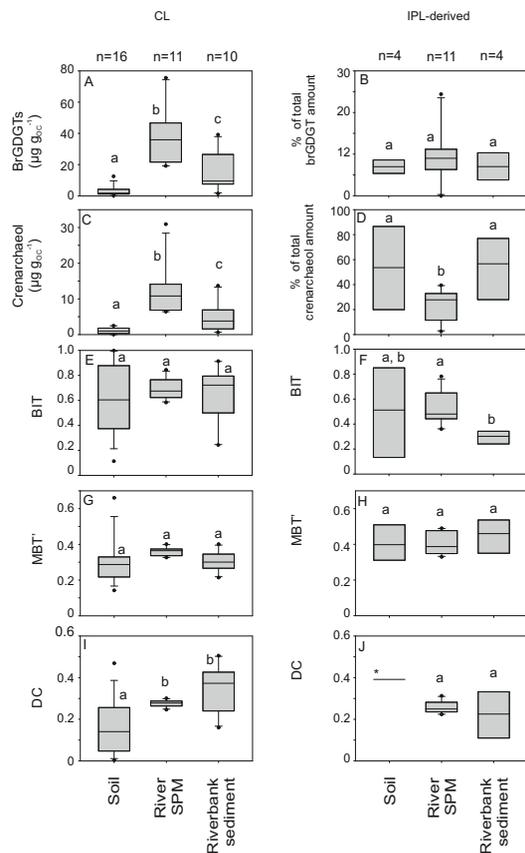


**Fig. 2.** (A) Overview of the study area with the sampling sites of soils, riverbank sediments, and river SPM and (B) detailed sampling locations of marine SPM and surface sediments.

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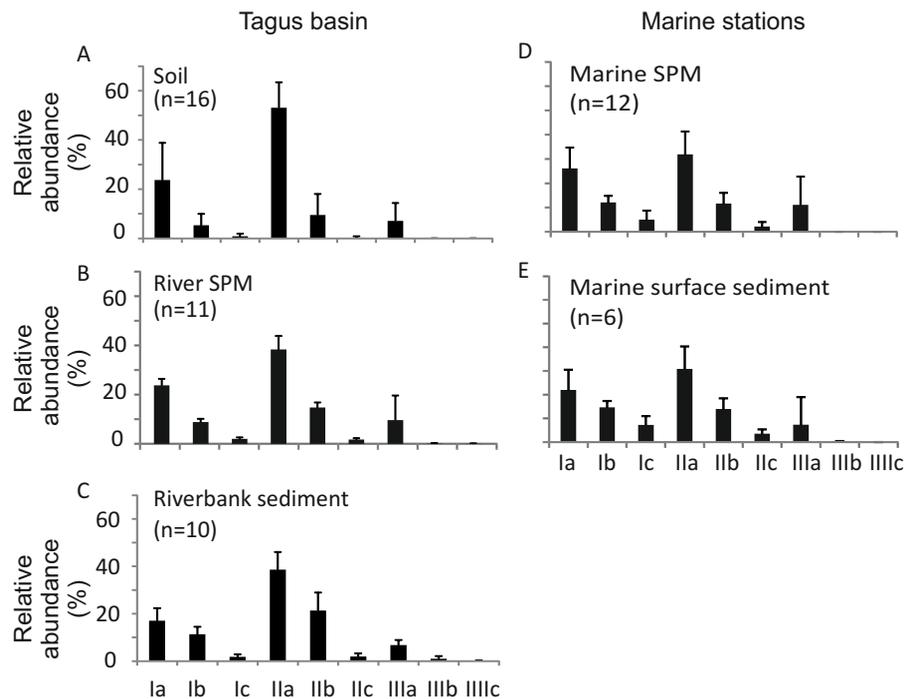
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**Fig. 3.** Boxplots of (A–D) the CL brGDGT and CL crenarchaeol concentrations and the percentage of IPL-derived brGDGTs and crenarchaeol and (E–J) BIT, MBT', and DC of CL and IPL-derived GDGTs in soils, river SPM, and riverbank sediments, \* indicates that the data was available only for one sample.

## Tagus brGDGT transport: consequences for the MBT'/CBT

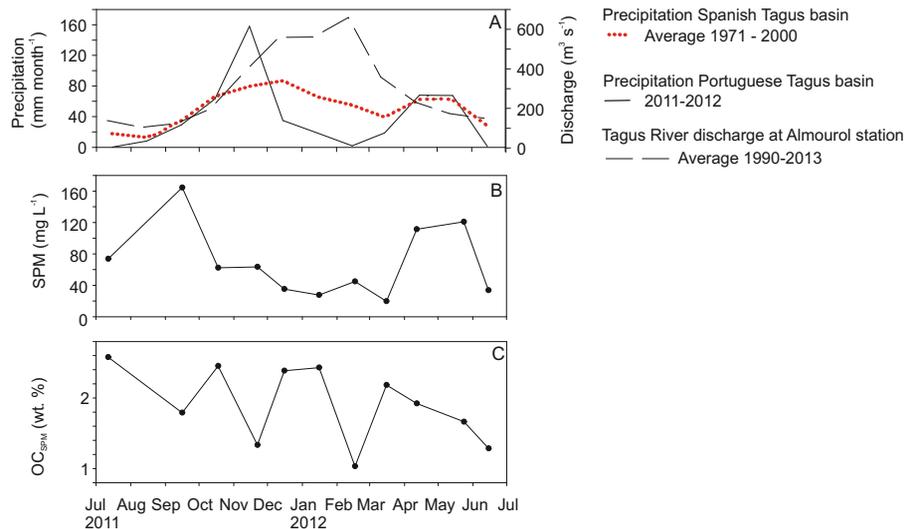
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**Fig. 4.** Average CL brGDGT distribution of **(A)** Tagus soils, **(B)** Tagus River SPM, **(C)** riverbank sediments, **(D)** marine SPM, and **(E)** marine surface sediments.

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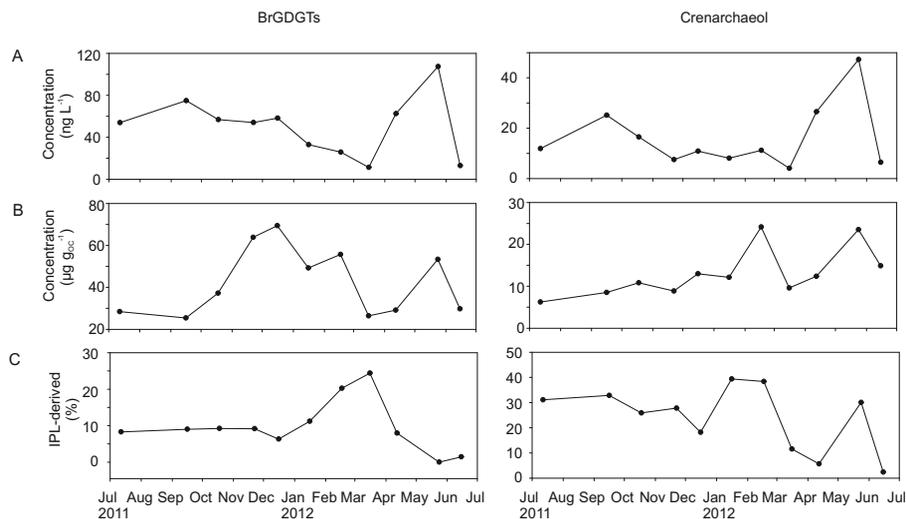
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**Fig. 5.** (A) Mean monthly precipitation in the Portuguese and Spanish parts of the Tagus River basin and Tagus River discharge at Almourol station (data source: Sistema Nacional de Informação de Recursos Hídricos), (B) SPM concentration at the Tagus River station, and (C) amount of OC in the SPM (wt. %) of the Tagus River.

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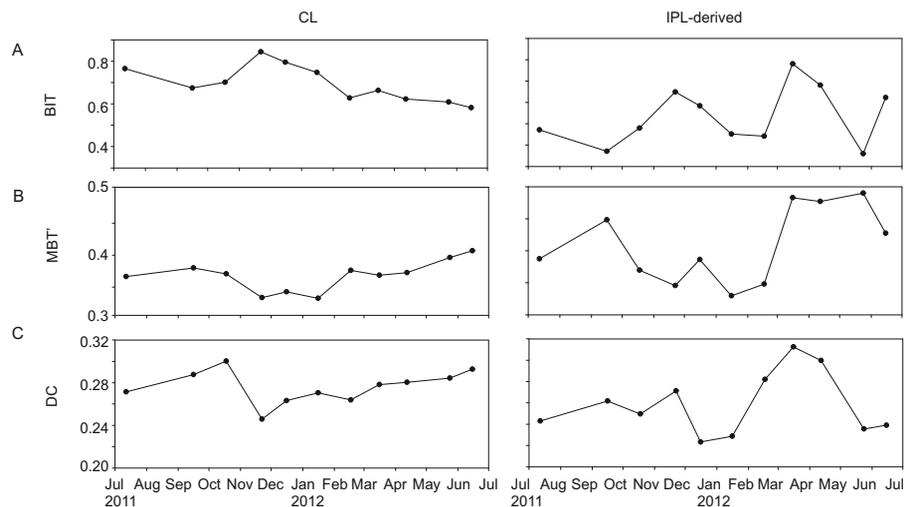
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**Fig. 6.** Variations in CL brGDGT and CL crenarchaeol concentrations and the percentage of IPL-derived brGDGTs and crenarchaeol in Tagus SPM over one year (2011–2012).

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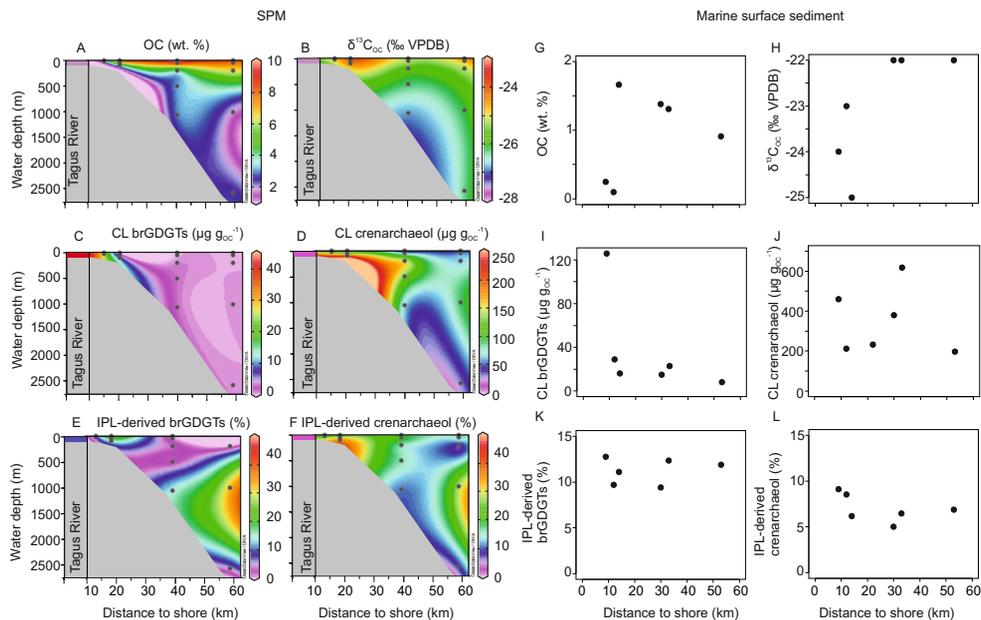


**Fig. 7.** Variations in CL and IPL-derived BIT, MBT' and DC in Tagus SPM over one year (2011–2012).

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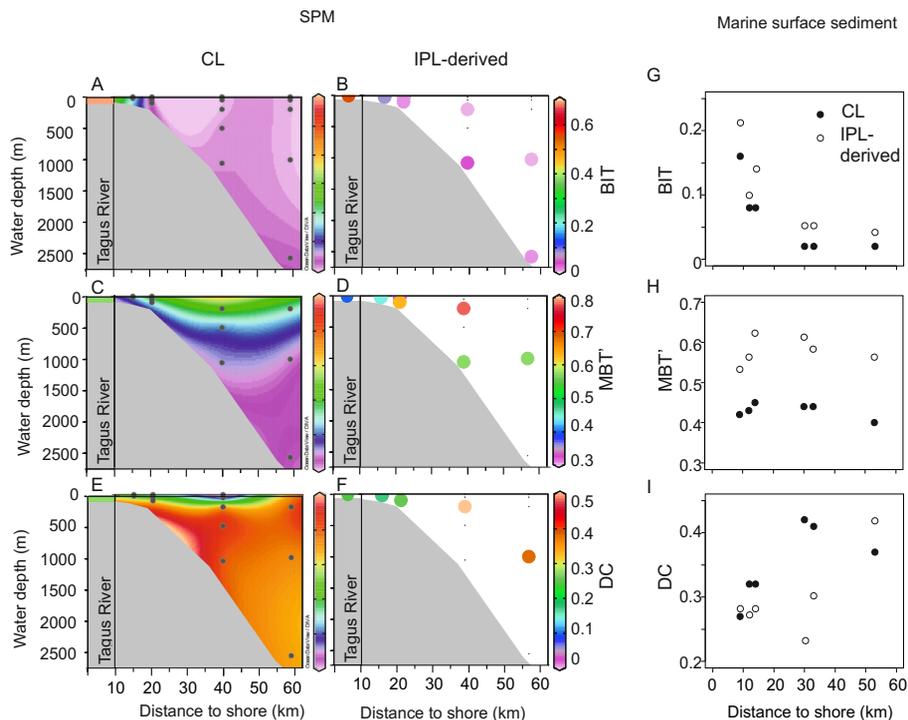


**Fig. 8.** OC content,  $\delta^{13}\text{C}_{\text{OC}}$ , CL brGDGT and CL crenarchaeol concentrations, and the percentage of IPL-derived brGDGTs and crenarchaeol (A–F) for marine SPM and (G–L) for marine surface sediments. The average values of the Tagus River SPM were also shown.

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## Tagus brGDGT transport: consequences for the MBT'/CBT

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**Fig. 9.** BIT, MBT' and DC of CL and IPL-derived GDGTs (A–F) for marine SPM and (G–I) for marine surface sediments. The average values of the Tagus River SPM were also shown.

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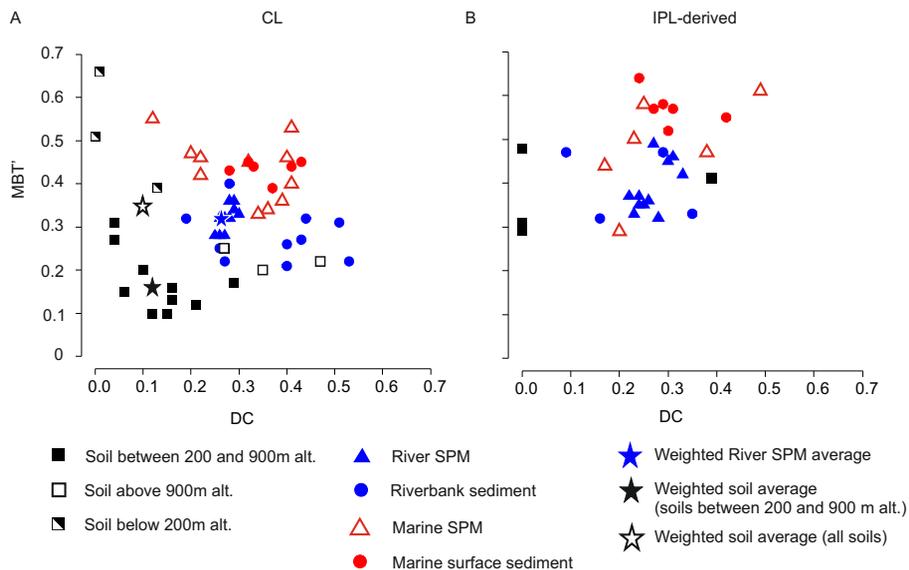
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## Tagus brGDGT transport: consequences for the MBT'/CBT

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**Fig. 10.** Scatter plots of MBT' vs. DC for **(A)** CL and **(B)** IPL-derived brGDGTs in all sample types. The weighted average values of the Tagus basin samples were also shown.

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