



Signatures of tetraether lipids reveal anthropogenic overprinting of natural organic matter in sediments of the Thames Estuary, UK



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ARTICLE INFO

Article history:

Received 16 June 2015

Received in revised form 9 December 2015

Accepted 4 January 2016

Available online 8 January 2016

Keywords:

BrGDGTs

BIT index

Crenarchaeol

$\delta^{13}\text{C}$

Sewage

London

ABSTRACT

Intertidal foreshore sediments from a 110 km stretch of the Thames Estuary were analysed for glycerol dialkyl glycerol tetraethers (GDGTs) to track soil organic matter (OM) input and evaluate the impact of coastal urbanisation on their distribution. Concentration of branched (br)GDGTs ranged from < 1 to 15 $\mu\text{g/g}$ organic carbon (OC) and crenarchaeol ranged from 0.6 to 19 $\mu\text{g/g}$ OC. An overall decrease in brGDGTs was observed from the inner Thames (Brentford) to the outer Thames (Isle of Grain), suggesting a drop in soil OM input towards the sea. In contrast, crenarchaeol concentration was highest around east London rather than towards the open sea. Such elevated crenarchaeol concentration occurred in the section of the river most influenced by anthropogenic pollution, such as discharge points for London's major sewage treatment plants, docks and power plants. The non-systematic spatial distribution of crenarchaeol was also reflected in the branched isoprenoid tetraether (BIT) index. The highest BIT values occurred upstream and in close proximity to salt marshes (0.8–1), whereas the lowest values (0.3–0.5) were towards the sea. However, unusually low values (0.4) were observed in the river section that had high crenarchaeol concentration. In contrast, bulk $\delta^{13}\text{C}$ values were insensitive to London's anthropogenic influence. This suggests that the natural systematic decrease in BIT index in the estuary is overprinted by London's anthropogenic activity between Deptford Creek and Tilbury. We therefore advise caution when interpreting the BIT index for sediments in close proximity to megacities discharging industrial and municipal waste that can become incorporated into the near surface sedimentary record.

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1. Introduction

Estimation of the world's river transport to the oceans is ca. 0.8 Gt C/yr (Sabine et al., 2004), of which ca. 0.38 Gt is in the form of organic carbon (OC; Ludwig et al., 1996). Estuaries modulate these carbon fluxes via physical, biological and geochemical processes. Therefore, understanding the movement of OC within estuaries remains an important component of the global carbon budget. Due to the fact that many of the world's megacities are located in close proximity to river estuaries (e.g. Paris, New York, Shanghai, Mumbai), it is essential to evaluate this recent influence on coastal OC (Vane et al., 2011).

Most studies that track the origin and fate of OC in estuaries have been based predominantly on bulk organic parameters such as C/N and the stable isotopic composition ($\delta^{13}\text{C}$) of OC. However, interpretation of such data can be compromised by the wide range

of values imparted by different terrigenous sources of organic matter (OM) and preferential remineralisation of N relative to C (Kemp et al., 2010; Khan et al., 2013). Recent studies have suggested that some of the limitations of the bulk geochemical approach can be overcome using biomarkers specific to organisms (e.g. Kim et al., 2012; Zhu et al., 2013). One class of lipid biomarker commonly used is high molecular weight (MW) *n*-alkanes. They are major components of epicuticular wax from vascular plant leaves (Eglinton and Hamilton, 1963) and have a strong odd/even carbon number predominance. The major *n*-alkanes in higher plants are normally C_{27-33} and, due to their relatively high MW, are more stable than shorter chain homologues and other *n*-alkyl components. However, in urbanised estuaries the concentrations and distributions of *n*-alkanes from natural OM are prone to overprinting from *n*-alkanes from crude oil and/or refined fuel spills, as well as urban run-off (Stout and Wang, 2007).

A more recent biomarker class used to trace the terrigenous input to aquatic sediments is the branched glycerol dialkyl glycerol tetraethers (brGDGTs; Figs. 1 and 1S). They are found mainly in soil and peat, although some studies have demonstrated possible

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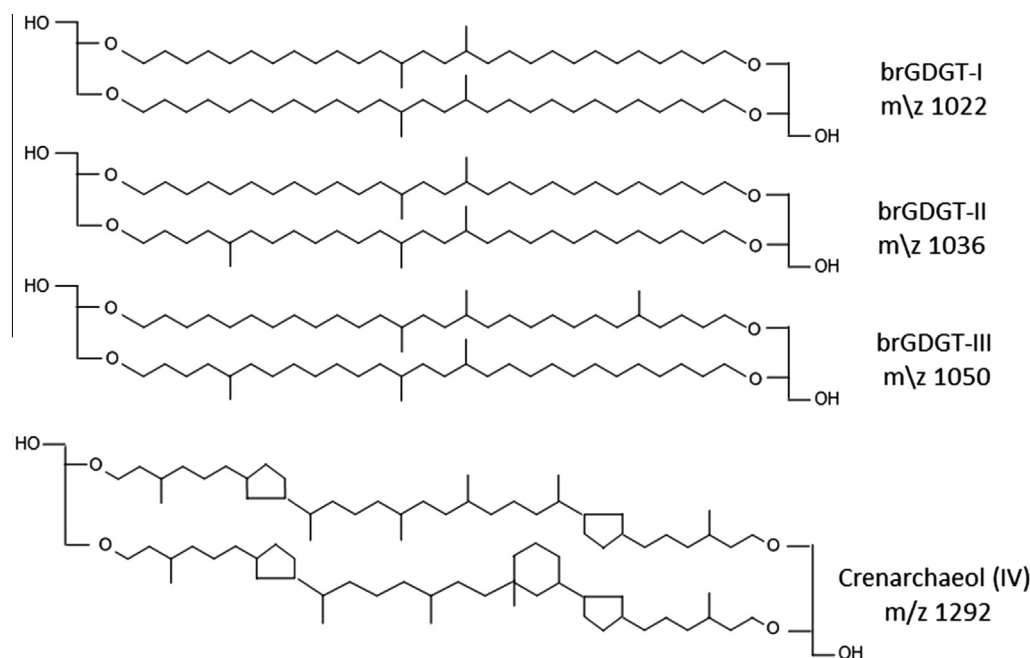


Fig. 1. Structure of brGDGTs (I–III) and crenarchaeol (IV).

production in marine, lacustrine and riverine environments (Peterse et al., 2009; Tierney and Russell, 2009; Liu et al., 2014; Zell et al., 2014a). They are thought to be produced by heterotrophic bacteria dwelling in anaerobic soil environments, with the Acidobacteria phylum as the only known producer (Sinninghe Damsté et al., 2011). The relative concentrations of brGDGTs have been used to trace soil OM input to the marine environment via the branched and isoprenoid tetraether (BIT) index (Hopmans et al., 2004), with the presumption that marine Thaumarchaeota are the primary source of crenarchaeol (Cren.), an isoprenoid tetraether biomarker (Fig. 1). More recently, the index has been applied to a variety of non-marine aquatic ecosystems, including lakes and rivers (Schouten et al., 2013 and references therein). The primary advantage of the index in comparison with the *n*-alkanes lies in the fact that it provides a general signal of soil OM and not for specific vegetation.

The index has been applied to several rivers around Europe, Asia and America (Kim et al., 2006, 2007, 2012, 2014; Sun et al., 2011; Zhu et al., 2011, 2013; Strong et al., 2012; Zell et al., 2013a,b, 2014a,b). Most of these studies focussed on large scale rivers, e.g. the Amazon and Yellow rivers (Kim et al., 2012; Zhu et al., 2011) with only a few focussing on smaller rivers with annual discharge ≤ 2000 m³/s (e.g. Kim et al., 2007; Zell et al., 2014a). Results from rivers from the Gulf of Lions, France showed that the BIT index is a suitable tracer for soil OM and reported historical palaeoflood events at periods when continental material was delivered more directly to the study site (Kim et al., 2006, 2007, 2014). However, some studies have reported a mixed source of production between soil and river for brGDGTs and crenarchaeol (Kim et al., 2014; Zell et al., 2013a,b, 2014a), which can complicate interpretation of the proxy when applied in rivers.

This study aimed to improve understanding of the behaviour of OC in the tidal River Thames by measuring the spatial distribution of sedimentary brGDGTs, crenarchaeol and the BIT index. The principal hypothesis for testing was whether or not the index can faithfully record soil carbon input in an urbanised river estuary. Secondary aims were to establish the extent to which anthropogenic disturbance masks the natural distribution and compare the utility of the BIT index with bulk geochemical proxies.

2. Study area

The River Thames is the largest river that is entirely in England, with a total length of 354 km, a catchment area of 12,935 km² and an average discharge of 65.8 m³/s (Marsh and Hannaford, 2008). It has a spring tidal range of between 5.2–6.6 m and extends 110 km from Teddington Lock through London and out to the southern North Sea. The Thames basin contains many major urban centres accommodating around a fifth of the UK population (ca. 12 million) of which > 10 million live in Metropolitan London (Merrett, 2007). London is intersected by 33 tributaries and about 60 municipal and commercial discharge points. Numerous industries, ports, sewage treatment plants and power stations discharge into the tidal Thames in order to maintain sanitation, prevent flooding and facilitate other activities such as power generation. Consequently, the estuary has recently undergone extensive river management to minimise coastal flooding caused by surge tides and avoid the flooding of London upstream of the Thames Barrier at Woolwich Reach. Nevertheless, the estuary receives significant amounts of particulate OM from multiple sources i.e. allochthonous input containing natural and anthropogenic particulates, autochthonous riverine input and marine input from the southern North Sea (Abril et al., 2002; Bristow et al., 2013).

3. Material and methods

3.1. Sample collection

Sampling of Thames sediments was carried out in November 2010 and October 2011 (Tables 1, 1S and Fig. 2). Sites were accessed via a jet boat attached to the Port of London Authority Vessel (PLA) Driftwood II, using predetermined GPS co-ordinates to accurately locate each position to ± 3 m. At each location, surface sediments (0–5 cm) were collected from four corners of a square of ca. 2 m², using a stainless steel trowel. The four corner samples and one central sample were combined and transported to shore in a polyethylene zip lock bag. The sediments were stored in a cool box at 4 °C, transported to the laboratory and immediately frozen at ca. –20 °C.

and the < 2 mm fractions ground to a fine powder (Beriro et al., 2014).

3.2. Total OC (TOC), stable carbon isotope ($\delta^{13}\text{C}$) composition and total nitrogen (N)

TOC and $\delta^{13}\text{C}$ were measured using identical methods to those of Khan et al. (2013). Briefly, samples were treated with 1 M HCl, left overnight, washed with deionised water, and oven dried at 60 °C. Analysis was performed with a Europa Scientific Elemental Analyser. The reference material used for $\delta^{13}\text{C}$ analysis was IA-R001 [$\delta^{13}\text{C}$ CV-PDB (Peedee Belemnite), -26.43‰]. For quality control purposes check samples of IA-R001, IA-R005 ($\delta^{13}\text{C}$ CV-PDB, -26.03‰) and IA-R006 ($\delta^{13}\text{C}$ CV-PDB -11.64‰) were also analysed during the batch analysis of the samples. IA-R001, IA-R005 and IA-R006 were calibrated against, and traceable to, IAEA-CH-6 ($\delta^{13}\text{C}$ CV-PDB, -10.43‰), an inter-laboratory comparison standard distributed by the International Atomic Energy Agency (IAEA), Vienna. Replicate analysis of samples indicated an average standard deviation of 0.08‰. Total N of the original samples was analysed using the above elemental analyser. The reference material used during N analysis was IA-R001 (N 1.88%).

3.3. *n*-Alkane and GDGT analysis

Freeze-dried sediment was extracted using an automated solvent extractor (Dionex 200) operated at 100 °C and 7.6×10^6 Pa with dichloromethane (DCM):MeOH (9:1, v:v) to provide a total lipid extract (TLE). Internal standards (tetracosane-D50, squalane, hexatriacontane-D74) were added before extraction, while another (C_{46} GDGT) was added to the TLE, which was separated into an apolar and a polar fraction in a glass pipette packed with Al_2O_3 (5×0.5 cm), using 4 ml *n*-hexane/DCM (9:1, v:v) and MeOH/DCM (1:1, v:v). Recovery of the internal standards was > 85%. The *n*-alkanes were analysed using gas chromatography (GC) with a Hewlett Packard 6890 equipped with flame ionization detection (FID) and an Agilent DB-1 ms UI column (60 m \times 0.25 mm id., 0.1 μm film thickness). Oven temperature programme was: 60 °C (1 min) to 320 °C (held 15 min) at 10 °C/min: 1 μl was injected at 280 °C in splitless mode for 0.7 min, split 1:30 thereafter. He carrier gas was at 1 ml/min.

The polar fraction was filtered through a polytetrafluoroethylene filter (PTFE, 0.45 μm) and analysed using a high performance liquid chromatography-mass spectrometry (LC-MS) with a Thermo TSQ Quantiva MS instrument coupled to an Ultimate 3000 series HPLC instrument following a slightly modified method from Schouten et al. (2007). A Prevail Cyano column (2.1 \times 150 mm, 3 μm ; Alltech, Deerfield, IL, USA), maintained at 30 °C, was used. Tetraethers were eluted isocratically with 99% hexane and 1% isopropanol (IPA) for 5 min, followed by a linear gradient to 1.8% IPA in 45 min. Flow rate was 0.2 ml/min. Detection was achieved using atmospheric pressure positive ion chemical ionization MS (APCI-MS) in single ion monitoring (SIM) mode. Conditions for APCI-MS were: sheath gas 20, auxiliary gas 2, ion transfer tube 325 °C, vaporizer 400 °C, positive ion discharge 2. GDGT distributions were determined by integrating the summed peak areas in the respective $[\text{M}+\text{H}]^+$ chromatograms and converted to concentration by comparison to the internal standard peak. The BIT index was calculated according to Hopmans et al. (2004):

$$\text{BIT} = \frac{[\text{I}] + [\text{II}] + [\text{III}]}{[\text{I}] + [\text{II}] + [\text{III}] + [\text{IV}]}$$

where [I], [II] and [III] are the concentration of branched (br) GDGTs and [IV] the concentration of the isoprenoid GDGT, crenarchaeol (Figs. 1 and 1S).

Instrumental reproducibility for the BIT index was determined from triplicate measurements of all samples, with an average standard deviation of ± 0.02 . The average standard deviation for each compound was < 0.04.

4. Results and discussion

4.1. Bulk geochemistry

4.1.1. TOC

The TOC content of the surface sediments varied from < 1% to 6% and decreased towards the sea (Fig. 3). This is explained by dilution of organic rich river sediment with organic poor marine sand from the southern North Sea (Bristow et al., 2013). The systematic decrease from land to sea was disrupted by lower TOC values (< 2%) at sites in central London and higher values at a few sites located towards the sea. The low values at sites 3, 8 and 10 (Figs. 2 and 3) may be explained by dilution of man-made sediment. Sites 3 and 8 are at Hammersmith and Waterloo bridges and were composed of a sand of uniform particle size, suggesting the processed sand had been deposited in the river during maintenance work at the bridges (Table 1S). Similarly, the anomalously low TOC content at site 10 was explained by the deposition of man-made material attributable in part to its location at the outflow of the Millwall docks (Table 1S). On the other hand, the increased values at sites 20, 24, 26 (Figs. 2 and 3) were explained by the close proximity of these sites to salt marshes, which export high amounts of OC (sites Swanscombe, 20, Cliffe, 24 and Halstow, 26; Khan et al., 2015), whereas those at sites 30 and 33 are most likely to have high OC values due to their location within a small tributary (Yantlet Creek, Table 1S).

4.1.2. $\delta^{13}\text{C}$ values

Sedimentary stable carbon isotope composition ($\delta^{13}\text{C}$) has been widely used to determine the provenance of OM in rivers (Kim et al., 2007; Khan et al., 2013). The primary rationale is that OC from C_3 terrigenous plants has $\delta^{13}\text{C}$ values of -28‰ to -25‰ , distinct from marine algae which yield values of -22‰ to -19‰ . Soil OC values are normally comparable with those of the source plant material but also depend on the extent of microbial respiration and decomposition. The values are stored in river sediments and salt marshes and can facilitate estimation of the source of OM (Kemp et al., 2010). The Thames surface sediments (Figs. 2 and 3) values ranged from -27‰ at more inland sites (5 and 20) to -22‰ for samples located from downstream (30 and 36). In general, the results suggest a stronger influence of terrigenous OM until Cliffe (site 24) and a smooth increase in marine OM from this point to the open sea (Figs. 2 and 3). However, other influences on the $\delta^{13}\text{C}$ signature must be considered. Indeed, it has been suggested that the isotopic composition of surface sediments in rivers can be influenced by agricultural products, human sewage and industrial input (Yu et al., 2010). Here, inspection of the $\delta^{13}\text{C}$ values (Fig. 3) at sites close to London's major sewage treatment plant (STP) discharge points, namely, Bow Creek [site 12, Abbey Mills combined sewer overflow (CSO)], Gallions Reach and Barking (sites 14 and 15, Beckton STP) and Dagenham (site 1, Crossness and Riverside STP) revealed no major changes, suggesting that the additive effect of sewage and/or industrial effluent was too low to overcome the mainly terrigenous natural $\delta^{13}\text{C}$ signature. In fact, the distribution of the $\delta^{13}\text{C}$ values correlates reasonably well with the distance from Teddington Lock (R^2 0.6), as shown in Fig. 3.

4.2. Organic proxies

4.2.1. *n*-Alkanes

The apolar fraction was dominated by an unresolved complex mixture (UCM). The high MW *n*-alkane peaks above the UCM did

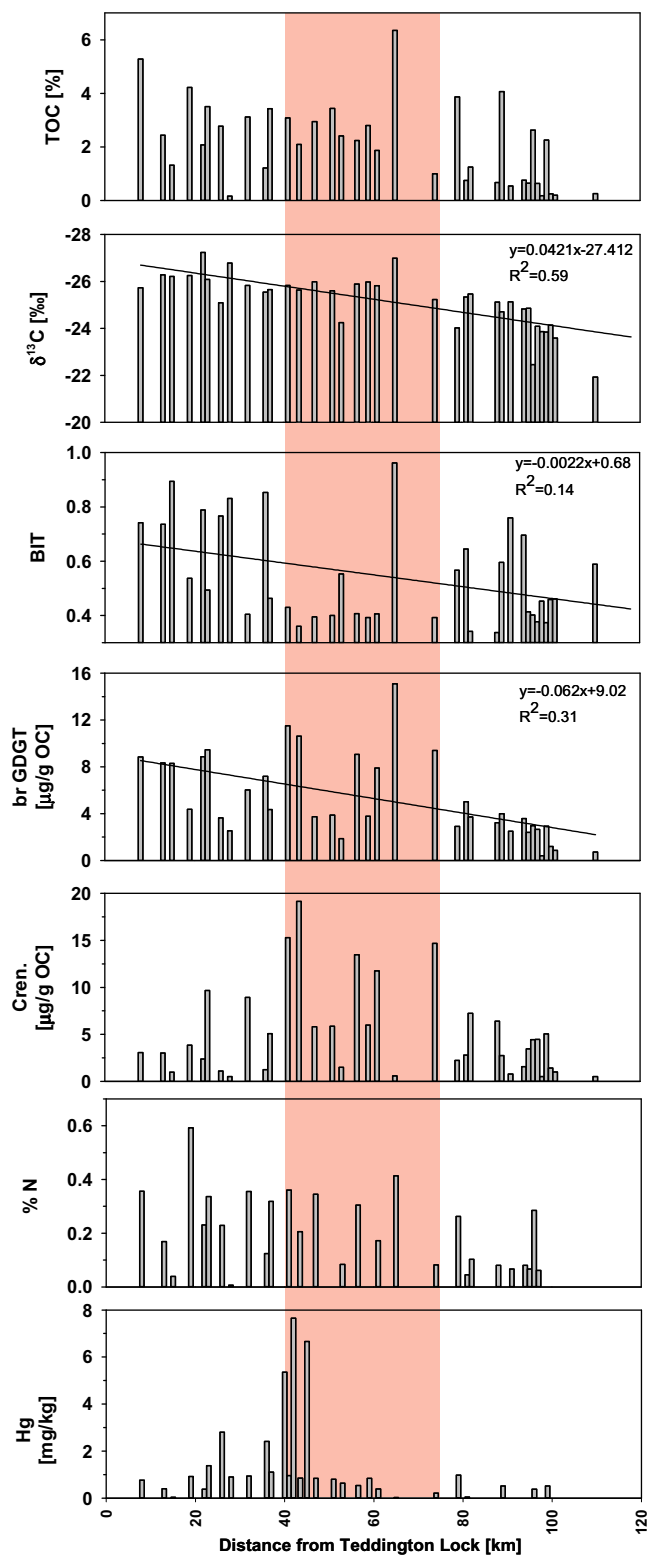


Fig. 3. Bulk parameters (TOC, N, $\delta^{13}\text{C}$ and Hg) together with BIT index values and GDGT concentration from surface sediments of the Thames Estuary. Red shade highlights the area of the Thames Estuary with higher concentration of crenarchaeol (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article).

not always show an odd predominance, with the carbon preference index (CPI_{27-31}) ranging from 0.6 to 10. The non-systematic variation in CPI_{27-31} values and high UCM, probably indicated multiple

n-alkane sources so we did not assess the *n*-alkanes further (Stout and Wang, 2007).

4.2.2. GDGT concentration

BrGDGTs and isoprenoid GDGTs were present at all 36 sites. BrGDGT concentration ranged from 15 $\mu\text{g/g}$ OC at Swanscombe (20) to < 1 $\mu\text{g/g}$ OC towards the estuary mouth (Fig. 3). In general, concentration was variable, with high values maintained until Tilbury (21), whereupon it decreased. This spatial distribution may be explained by a decrease in input of soil OM relative to marine influence going downstream. Crenarchaeol concentration varied from a maximum of 19 $\mu\text{g/g}$ OC at Bow Creek (River Lea) and Silvertown (sites 12 and 13) and minimum values of 0.6 $\mu\text{g/g}$ OC towards Teddington and towards the outer estuary (Fig. 3). Interestingly, the highest crenarchaeol concentration was in the middle of the estuary and not towards the North Sea, where we would expect a higher concentration of marine Thaumarchaeota, the source organism of this GDGT. The highest concentration of crenarchaeol was at Albert Bridge (6) in central London, Silvertown (13) and Erith (17) and at sites close to urban tributaries at Butlers Wharf and Bow Creek (9 and 12), as well as major STPs (19 and 21). Site 12 (Bow Creek) is also expected to be influenced by the outflow from the large Abbey Mills CSO in the course of the River Lea (Figs. 2 and 1S).

The GDGT concentration values are comparable with those in sediments and suspended particulate matter from other rivers in Europe (Kim et al., 2006, 2007, 2014; Zell et al., 2014a). For example, the sediments here had crenarchaeol and brGDGT values in the same range as the ones from the Tagus River (Zell et al., 2014a). However, results from the Tagus River bank sediments and catchment soils suggested in situ production of brGDGTs based on differences between their brGDGT concentration and distribution (Zell et al., 2014a). For the Thames, in situ production cannot be totally discarded but the decreasing trend in brGDGT concentration along the estuary and the high concentration in samples near marshes suggest that the majority of brGDGTs are contributed from soil around the catchment. Also, no major changes in the distribution of the brGDGTs were recorded, suggesting that they may always come from soil entering the river. Nevertheless, as in situ production of brGDGTs in river sediments has been reported (Zell et al., 2013b, 2014a), future studies of catchment soils are needed for a better understanding of the sources of the brGDGTs in the River Thames. In situ production in the Yenisei River was also identified via the application of an improved method that enables separation of the 5-methyl and 6-methyl brGDGT isomers (De Jonge et al., 2015). It will be therefore useful to test this new method in future analyses of sediments from the Thames.

4.2.3. Anthropogenic influence on the tetraether lipid signature of Thames sediments

The spatial distribution of the BIT index values along the tidal Thames is summarised in Fig. 3. The maximal BIT value of ca. 1 at Swanscombe probably reflects the high concentration of brGDGTs produced in salt marsh sediments (Wang et al., 2013). In contrast, the lowest value of 0.3 was at sites in the mouth of the estuary and outflows of large tributaries (sites 23 and 25; Fig. 2 and Table 1S). Here, the BIT index is defined by an increase in crenarchaeol concentration. Although the BIT index exhibits the expected trend, with higher values upstream and lower values towards the mouth of the estuary, the low values found in the mid-estuary in the area between Deptford Creek and Tilbury (sites 11–20) are marked by relatively high brGDGT concentration but a relatively larger increase in crenarchaeol concentration. One possible explanation for the increase in crenarchaeol is the high nutrient input (including N) associated with industrial discharge and/or sewage effluent expected in this area (Vane et al., 2015). It has been suggested that crenarchaeol is a biomarker for

ammonia-oxidising Thaumarchaeota (Schouten et al., 2013 and references therein), which would explain the increase in crenarchaeol at sites with high N content. The N data (Fig. 3) do not suggest an increase in nutrient concentration around East London. However, it has been reported that, in the Thames, N concentration is not a good indicator of sewage input and that the majority of N input is from diffuse sources, e.g. groundwater and agricultural (Bristow et al., 2013; Bowes et al., 2014). Although N does not seem to stimulate the production of crenarchaeol in the river around East London, this does not exclude the possibility of crenarchaeol coming directly from STP effluent, as reported from the Perpignan STP effluent in France (Kim et al., 2007). In addition, studies have reported the presence of ammonia-oxidising Archaea in waste water treatment plants (e.g. Park et al., 2006; Zhang et al., 2009). This notion of anthropogenic disturbance is supported by the location of two of London's major STPs (Beckton and Crossness; Fig. 2) that treat wastewater from a population of ca. 5.5 million (Defra, 2007) in the East London Area. London's sewage system is currently based upon three main STPs (Mogden, Beckton and Crossness) as well as pumped discharge points and 57 CSOs. The latter are situated throughout the central London reaches and at times of heavy rainfall combine and discharge surface run-off and sewage into the Thames. However, although many of the CSO outflows are located in the section preceding the STPs, the CSO outflow does not seem to have an impact on the crenarchaeol concentration (with the exception of sites 12 and 13 that may be affected by the large Abbey Mills CSO), possibly because the volume of effluent is lower than the main STP, infrequent and/or diluted. We recognise that the presence of numerous industries, ports and jetties in the East London area, as well as major STPs (Vane et al., 2014), makes it difficult to assign a definitive source of introduced GDGTs. Indeed, the Hg spatial distribution in the Thames surface sediments (Vane et al., 2015), used as indicative of an anthropogenic signature from industries like e.g. power production, metal processing and landfill waste (including waste incineration and sewage treatment), showed maximum values in the same area of East London compared with the highest crenarchaeol concentration (sites 12 and 13, Figs. 2 and 3). This suggests that the crenarchaeol distribution is also, but not only, influenced by similar

industries that are the main source of Hg pollution in the Thames. However, at this point, based on the ecology of the source organism of crenarchaeol and the physical location of the main points of sewage discharge in the Thames, it is reasonable to speculate that the changes in BIT index and GDGT spatial distribution here are possibly recording the effect of STPs in the River Thames, although it is still not possible to identify if it is by stimulating their production in the river or by additional input.

A higher correlation between BIT index and crenarchaeol (R^2 0.35 in linear correlation, R^2 0.47 in log correlation; Fig. 4B) was found in comparison with BIT index and brGDGTs (R^2 0.08 in linear correlation; Fig. 4A). Although the BIT index is driven by crenarchaeol, the use of brGDGT concentration may be better suited to trace soil OC at the Thames Estuary. In fact, while the distributions of $\delta^{13}\text{C}$ and BIT values in the River Thames were distinct (R^2 0.12; Fig. 4C), brGDGT concentration correlated better with $\delta^{13}\text{C}$ (R^2 0.43; $p < 0.0001$; Fig. 4D), despite the fact that the latter seems to be rather invariant with respect to the middle-estuary anthropogenic disturbance. This is in agreement with studies which found that the BIT index can be dominated by crenarchaeol and that the use of brGDGT concentration may instead be a better indicator of soil input to marine and lacustrine settings (Fietz et al., 2011; Smith et al., 2012).

4.3. Downcore analysis

Three short sediment cores (ca. 50 cm) from the inner Thames at Chelsea (5), inner-mid Thames at Gallions Reach (14) and outer Thames at Grain Spit (31) were analysed to evaluate how consistent GDGT concentration and the terrigenous proxies (BIT index and $\delta^{13}\text{C}$) were with depth. The $\delta^{13}\text{C}$ values clearly traced the terrigenous input variation in surface sediments along the tidal Thames but did not record a strong variation down-profile. The core at Chelsea (5) showed values ranging from -27.2‰ to -28.4‰ , suggesting a stronger input of terrigenous OM, the middle core had slightly more enriched values ranging from -25.5‰ to -26‰ and the downstream site values ranged from -24‰ to -24.5‰ , confirming lower input from terrigenous OM relative to marine sources. This range of values is consistent with those

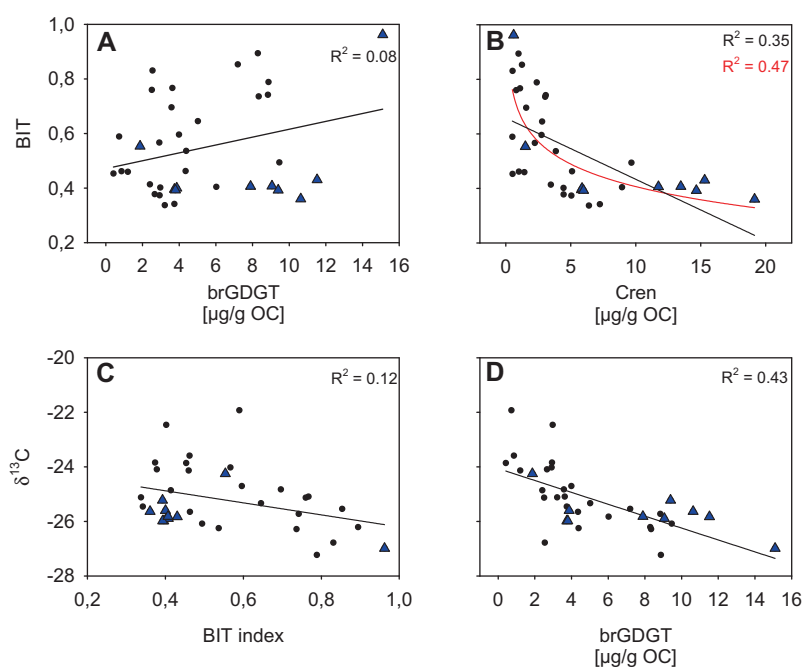


Fig. 4. Cross plot between BIT index, $\delta^{13}\text{C}$ and GDGT concentrations (brGDGTs and crenarchaeol). Triangles show position of samples 12–21.

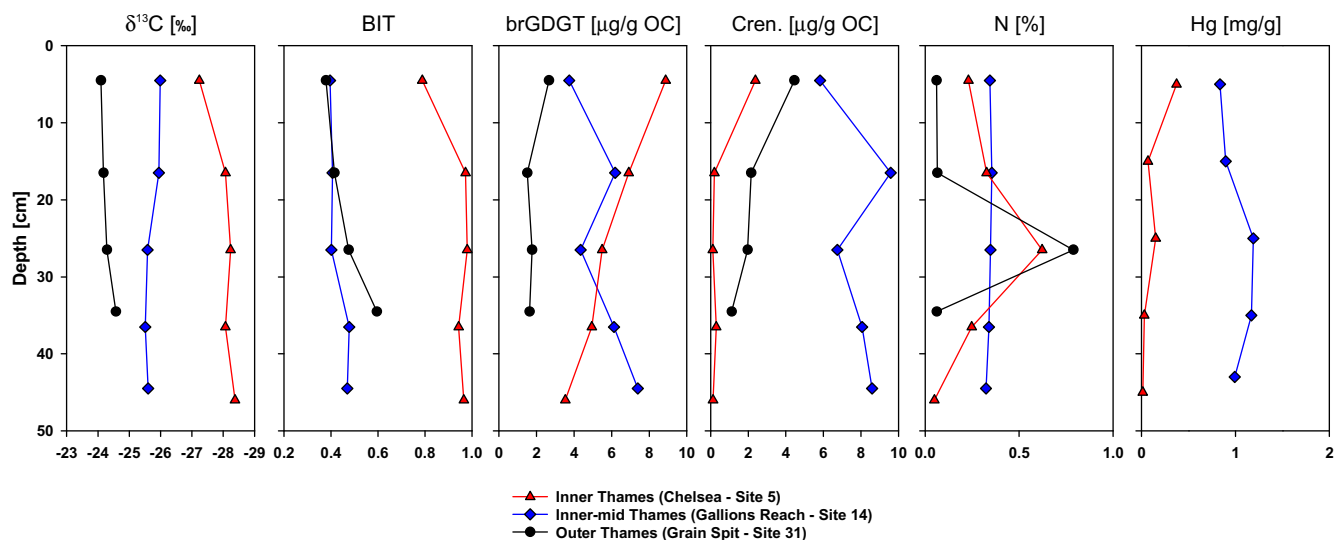


Fig. 5. Downcore variation of terrestrial proxies ($\delta^{13}\text{C}$ and BIT index), GDGT concentration, N and Hg in three cores. Numbers in parentheses show location of the cores in Fig. 2.

reported for suspended particulate matter in the Thames $\delta^{13}\text{C}$ (-30‰ to -21.5‰) and supports the established view that the Thames OC isotopic signature remains terrigenous-riverine dominated well into the outer estuary due in part to the export of salt marsh vegetation (Bristow et al., 2013; Khan et al., 2015).

The down core BIT values at the three sites showed some minor variation. The inner Thames core at Chelsea (5) had the highest values, ranging between 0.8 in the surface and >0.95 deeper in the core. The inner-mid Thames at Gallions Reach (14) showed values ranging from 0.4 in the shallowest depths (0–25 cm) to 0.5 in the deeper parts (25–45 cm), and the values in the outer Thames at Grain Spit (31) were similar to the Gallions Reach core (14), ranging from 0.4 in the shallowest depths (0–25 cm) to 0.6 in the deeper part of the core (25–35 cm) (Fig. 5). This similarity between the inner-mid core (14) and the outer core (31) supports the result from the surface sediments, suggesting that the core from Gallions Reach (14) in east London had unusually low BIT values throughout the profile. Considering the GDGT concentration profiles, the core at Chelsea (5) showed the highest concentration of brGDGTs, decreasing from 9 to $3.5 \mu\text{g/g OC}$ down profile. The crenarchaeol concentration was the lowest of the three cores, decreasing down profile from 2 to $<0.2 \mu\text{g/g OC}$. The inner-mid core at Gallions Reach (14) had a brGDGT concentration increasing from 3.7 in the surface to $6.2 \mu\text{g/g OC}$ at 16.5 cm. A decrease in brGDGT concentration to $4.4 \mu\text{g/g OC}$ was observed at 26.5 cm, followed by an increase to $7.4 \mu\text{g/g OC}$ at the bottom of the core. Similar profile variations were observed for crenarchaeol concentration, with values between 5.8 and $9.6 \mu\text{g/g OC}$. It is notable that this core showed the highest crenarchaeol concentration compared with the inner and the outer core. The outer Thames core (31) showed the lowest concentration of brGDGTs, decreasing from $2.7 \mu\text{g/g OC}$ in the surface to $1.5 \mu\text{g/g OC}$ downcore. Crenarchaeol showed a similar profile, decreasing from 4.5 to $1.1 \mu\text{g/g OC}$ downcore.

The above evaluation of GDGT concentration suggests that the BIT profiles reflect the highest input of soil OM in the inner Thames core at Chelsea (5) and the lowest input of soil OM in the outer Thames core at Grain Spit (31). However, in the inner-mid Thames core from Gallions Reach (14), the low BIT values are due to high crenarchaeol concentration. This suggests that, as for the surface sediments, the BIT index is defined by the elevated crenarchaeol concentration due to anthropogenic influence rather than by a change in soil OM input. Another difference is the general

downcore increase in GDGT concentration at Gallions Reach (14) vs. the decreasing trend in the other cores (Fig. 5). This could reflect a higher historical anthropogenic influence at this site, where the lower near surface values may reflect improved river management practices and/or diminished industrial activity in east London. Indeed, a minor decrease in the Hg profile (Vane et al., 2015) at the top of this core (Fig. 5) was also recorded, suggesting a possible decrease in, or better environmental management of, industrial/municipal waste at this site. However, as in the surface sediments, the N profile (Fig. 5) did not match changes in GDGT concentration, suggesting that N is not the main driver of these changes. More research is needed to understand the exact reason why crenarchaeol increases in highly urbanised areas. Nevertheless, the results from the Thames Estuary suggest that comparison of crenarchaeol concentration with brGDGT concentration and the BIT index allow recognition of anthropogenic influence in downcore studies of highly urbanised areas.

5. Conclusions

This study reports the distribution of brGDGTs and crenarchaeol in sediments in an urban estuary, the tidal River Thames. Our results suggest that increased crenarchaeol concentration in urban estuaries reflects anthropogenic perturbation. Conversely, bulk stable carbon isotopes are insensitive to the elevated anthropogenic activity in and around London and suggest a predominance of terrigenous OM. Taken together, the results suggest that domestic and industrial urban discharge may have a major impact on archaeal lipids in estuarine sediments, which curtail application of the BIT index but could be potentially used for investigating historical changes in urbanisation. Future work should focus on the identification of the exact source of brGDGTs and crenarchaeol to better understand the link with increased crenarchaeol concentration in highly urbanised regions.

Acknowledgements

Collection of the sediment cores would not have been possible without the assistance of staff at the Port of London Authority (PLA). Particular thanks are due to PLA coxswain S. Wells and D. Marsh, as well as D. Simmonds and the crew of the vessel

Driftwood III. The study also benefitted from advice provided by PLA staff, including J. Pinder, A. Mortley and J. Buckby. The authors also thank L. Åkesson and all staff at the Environment Agency (Abbey Wood Office) for providing logistical support. The research was funded by the Climate and Landscape Change Directorate, British Geological Survey (BGS), United Kingdom. This paper is published with the permission of the Executive Director, BGS. Finally, we would like to thank T. Meador and an anonymous reviewer for providing comments and suggestions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.orggeochem.2016.01.003>.

Associate Editor—**B. van Dongen**

References

- Abril, G., Nogueira, M., Etcheber, H., Cabecadas, G., Lemaire, E., Brogueira, M.J., 2002. Behaviour of organic carbon in nine contrasting European estuaries. *Estuarine Coastal and Shelf Science* 54, 241–262. <http://dx.doi.org/10.1006/jecs.2001.0844>.
- Beriro, D.J., Vane, C.H., Cave, M.R., Nathanail, C.P., 2014. Effects of drying and comminution type on the quantification of Polycyclic Aromatic Hydrocarbons (PAH) in a homogenised gasworks soil and the implications for human health risk assessment. *Chemosphere* 111, 396–404. <http://dx.doi.org/10.1016/j.chemosphere.2014.03.077>.
- Bowes, M.J., Jarvie, H.P., Naden, P.S., Old, G.H., Scarlett, P.M., Roberts, C., Armstrong, L.K., Harman, S.A., Wickham, H.D., Collins, A.L., 2014. Identifying priorities for nutrient mitigation using river concentration–flow relationships: the Thames basin, UK. *Journal of Hydrology* 517, 1–12. <http://dx.doi.org/10.1016/j.jhydrol.2014.03.063>.
- Bristow, L.A., Jickells, T.D., Weston, K., Marca-Bell, A., Parker, R., Andrews, J.E., 2013. Tracing estuarine organic matter sources into the southern North Sea using C and N isotopic signatures. *Biogeochemistry* 113, 9–22. <http://dx.doi.org/10.1007/s10533-012-9758-4>.
- Defra, 2007. *Regulatory Impact Assessment – Sewage Collection and Treatment for London, UK*.
- De Jonge, C., Stadnitskaia, A., Hopmans, E.C., Cherkashov, G., Fedotov, A., Streletskaia, I.D., Vasiliev, A.A., Sinninghe Damsté, J.S., 2015. Drastic changes in the distribution of branched tetraether lipids in suspended matter and sediments from the Yenisei River and Kara Sea (Siberia): implications for the use of brGDGT-based proxies in coastal marine sediments. *Geochimica et Cosmochimica Acta* 165, 200–225.
- Eglinton, G., Hamilton, R.J., 1963. The distribution of *n*-alkanes. In: Swain, T. (Ed.), *Chemical Plant Taxonomy*. Academic Press, pp. 197–217.
- Fietz, S., Martínez-García, A., Hugué, C., Rueda, G., Rosell-Melé, A., 2011. Constraints in the application of the Branched and Isoprenoid Tetraether index as a terrestrial input proxy. *Journal of Geophysical Research* 116, C10032. <http://dx.doi.org/10.1029/2011JG007062>.
- Hopmans, E.C., Weijers, J.W.H., Schefuss, E., Herfort, L., Sinninghe Damsté, J.S., Schouten, S., 2004. A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid tetraether lipids. *Earth and Planetary Science Letters* 224, 107–116. <http://dx.doi.org/10.1016/j.epsl.2004.05.012>.
- Kemp, A.C., Vane, C.H., Horton, B.P., Culver, S.J., 2010. Stable carbon isotopes as potential sea-level indicators in salt marshes, North Carolina, USA. *Holocene* 20, 623–636. <http://dx.doi.org/10.1177/0959683609354302>.
- Khan, N.S., Horton, B.P., McKee, K.L., Jerolmack, D., Falcini, F., Enache, M.D., Vane, C.H., 2013. Tracking sedimentation from the historic A.D. 2011 Mississippi River flood in the deltaic wetlands of Louisiana, USA. *Geology* 41, 391–394. <http://dx.doi.org/10.1130/G33805.1>.
- Khan, S.N., Vane, C.H., Horton, B.P., Hillier, C., Riding, J.B., Kendrick, C., 2015. The use of bulk stable carbon isotope geochemistry in the reconstruction of Holocene relative sea levels and paleoenvironments, Thames UK. *Journal of Quaternary Science*. <http://dx.doi.org/10.1002/jqs.2784> (in press).
- Kim, J.H., Buscaill, R., Fanget, A.S., Eyrolle-Boyer, F., Bassetti, M.A., Dorhout, D., Baas, M., Berne, S., Sinninghe Damsté, J.S., 2014. Impact of river channel shifts on tetraether lipids in the Rhone prodelta (NW Mediterranean): implication for the BIT index as an indicator of palaeoflood events. *Organic Geochemistry* 75, 99–108. <http://dx.doi.org/10.1016/j.orggeochem.2014.06.011>.
- Kim, J.H., Ludwig, W., Schouten, S., Kerherve, P., Herfort, L., Bonnin, J., Sinninghe Damsté, J.S., 2007. Impact of flood events on the transport of terrestrial organic matter to the ocean: a study of the Tet River (SW France) using the BIT index. *Organic Geochemistry* 38, 1593–1606. <http://dx.doi.org/10.1016/j.orggeochem.2007.06.010>.
- Kim, J.H., Schouten, S., Buscaill, R., Ludwig, W., Bonnin, J., Sinninghe Damsté, J.S., Bourrin, F., 2006. Origin and distribution of terrestrial organic matter in the NW Mediterranean (Gulf of Lions): exploring the newly developed BIT index. *Geochemistry, Geophysics, Geosystems* 7 (Q11017), 11011–11020. <http://dx.doi.org/10.1029/2006gc001306>.
- Kim, J.H., Zell, C., Moreira-Turcq, P., Perez, M.A.P., Abril, G., Mortillaro, J.M., Weijers, J.W.H., Meziane, T., Sinninghe Damsté, J.S., 2012. Tracing soil organic carbon in the lower Amazon River and its tributaries using GDGT distributions and bulk organic matter properties. *Geochimica et Cosmochimica Acta* 90, 163–180. <http://dx.doi.org/10.1016/j.gca.2012.05.014>.
- Liu, X.-L., Zhu, C., Wakeham, S.G., Hinrichs, K.-U., 2014. In situ production of branched glycerol dialkyl glycerol tetraethers in anoxic marine water columns. *Marine Chemistry* 166, 1–8. <http://dx.doi.org/10.1016/j.marchem.2014.08.008>.
- Ludwig, W., Probst, J.L., Kempe, S., 1996. Predicting the oceanic input of organic carbon by continental erosion. *Global Biogeochemical Cycles* 10, 23–41. <http://dx.doi.org/10.1029/95gb02925>.
- Marsh, T.J., Hannaford, J., 2008. *The 2007 Summer Floods in England and Wales – A Hydrological Appraisal*. Centre for Ecology and Hydrology, UK.
- Merrett, S., 2007. The Thames catchment: a river basin at the tipping point. *Water Policy* 9, 393–404. <http://dx.doi.org/10.2166/Wp.2007.016>.
- Park, H.D., Wells, G.F., Bae, H., Criddle, C.S., Francis, C.A., 2006. Occurrence of ammonia-oxidizing archaea in wastewater treatment plant bioreactors. *Applied and Environmental Microbiology* 72, 5643–5647. <http://dx.doi.org/10.1128/Aem.00402-06>.
- Peterse, F., Kim, J.H., Schouten, S., Kristensen, D.K., Koc, N., Sinninghe Damsté, J.S., 2009. Constraints on the application of the MBT/CBT palaeothermometer at high latitude environments (Svalbard, Norway). *Organic Geochemistry* 40, 692–699. <http://dx.doi.org/10.1016/j.orggeochem.2009.03.004>.
- Sabine, C.L., Heimann, M., Artaxo, P., Bakker, D., Chen, C.-T.A., Field, C.B., Gruber, N., Le Quéré, C., Prinn, R.G., Richey, J.E., Lankao, P.R., Sathaye, J., Valentini, R., 2004. Current status and past trends of the global carbon cycle. In: Field, C.B., Raupach, M.R. (Eds.), *The Global Carbon Cycle: Integrating Humans, Climate, and the Natural World*. Scope 62. Island Press, Washington, DC, pp. 17–44.
- Schouten, S., Hopmans, E., Sinninghe, C., Damsté, J.S., 2013. The organic geochemistry of glycerol dialkyl glycerol tetraether lipids: a review. *Organic Geochemistry* 54, 19–61. <http://dx.doi.org/10.1016/j.orggeochem.2012.09.006>.
- Schouten, S., Hugué, C., Hopmans, E.C., Kienhuis, M.V.M., Sinninghe Damsté, J.S., 2007. Analytical methodology for TEX₈₆ paleothermometry by high-performance liquid chromatography/atmospheric pressure chemical ionization-mass spectrometry. *Analytical Chemistry* 79, 2940–2944. <http://dx.doi.org/10.1021/AC062339v>.
- Sinninghe Damsté, J.S., Rijpstra, W.I.C., Hopmans, E.C., Weijers, J.W.H., Foesel, B.U., Overmann, J., Dedysh, S.N., 2011. 13,16-Dimethyl octacosanedioic acid (isodiabolic acid), a common membrane-spanning lipid of Acidobacteria subdivisions 1 and 3. *Applied and Environmental Microbiology* 77, 4147–4154. <http://dx.doi.org/10.1128/Aem.00466-11>.
- Smith, R.W., Bianchi, T.S., Li, X., 2012. A re-evaluation of the use of branched GDGTs as terrestrial biomarkers: implications for the BIT index. *Geochimica et Cosmochimica Acta* 80, 14–29.
- Stout, S.A., Wang, Z., 2007. *Oil Spill Environmental Forensics: Finger-printing and Source Identification*. Elsevier, Amsterdam.
- Strong, D.J., Flecker, R., Valdes, P.J., Wilkinson, I.P., Rees, J.G., Zong, Y.Q., Lloyd, J.M., Garrett, E., Pancost, R.D., 2012. Organic matter distribution in the modern sediments of the Pearl River Estuary. *Organic Geochemistry* 49, 68–82. <http://dx.doi.org/10.1016/j.orggeochem.2012.04.011>.
- Sun, D.Y., Tan, W.B., Pei, Y.D., Zhou, L.P., Wang, H., Yang, H., Xu, Y.P., 2011. Late Quaternary environmental change of Yellow River Basin: an organic geochemical record in Bohai Sea (North China). *Organic Geochemistry* 42, 575–585. <http://dx.doi.org/10.1016/j.orggeochem.2011.04.011>.
- Tierney, J.E., Russell, J.M., 2009. Distributions of branched GDGTs in a tropical lake system: implications for lacustrine application of the MBT/CBT paleoproxy. *Organic Geochemistry* 40, 1032–1036.
- Vane, C.H., Beriro, D., Turner, G., 2015. Rise and fall of mercury (Hg) pollution in sediment cores of the Thames Estuary, London, UK. *Earth and Environmental Science Transactions of Royal Society of Edinburgh* 105, 285–296. <http://dx.doi.org/10.1017/S1755691015000158>.
- Vane, C.H., Chenery, S.R., Harrison, I., Kim, A.W., Moss-Hayes, V., Jones, D.G., 2011. Chemical signatures of the anthropocene in the Clyde estuary, UK: sediment-hosted Pb, Pb-207/206, total petroleum hydrocarbon, polyaromatic hydrocarbon and polychlorinated biphenyl pollution records. *Philosophical Transactions of the Royal Society A Mathematical Physical and Engineering Sciences* 369, 1085–1111. <http://dx.doi.org/10.1098/rsta.2010.0298>.
- Vane, C.H., Harrison, I., Kim, A.W., 2007. Assessment of polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in surface sediments of the Inner Clyde Estuary, UK. *Marine Pollution Bulletin* 54, 1301–1306. <http://dx.doi.org/10.1016/j.marpolbul.2007.04.005>.
- Vane, C.H., Kim, A.W., Beriro, D.J., Cave, M.R., Knights, K., Moss-Hayes, V., Nathanail, P.C., 2014. Polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) in urban soils of Greater London, UK. *Applied Geochemistry* 51, 303–314. <http://dx.doi.org/10.1016/j.apgeochem.2014.09.013>.
- Wang, H.Y., Liu, W.G., Zhang, C.L.L., Liu, Z.H., He, Y.X., 2013. Branched and isoprenoid tetraether (BIT) index traces water content along two marsh-soil transects surrounding Lake Qinghai: implications for paleo-humidity variation. *Organic Geochemistry* 59, 75–81. <http://dx.doi.org/10.1016/j.orggeochem.2013.03.011>.
- Yu, F.L., Zong, Y.Q., Lloyd, J.M., Huang, G.Q., Leng, M.J., Kendrick, C., Lamb, A.L., Yim, W.W.S., 2010. Bulk organic delta C-13 and C/N as indicators for sediment sources in the Pearl River delta and estuary, southern China. *Estuarine Coastal and Shelf Science* 87, 618–630. <http://dx.doi.org/10.1016/j.ecss.2010.02.018>.

- Zell, C., Kim, J.H., Abril, G., Sobrinho, R.L., Dorhout, D., Moreira-Turcq, P., Damsté, J.S. S., 2013a. 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. *Frontiers in Microbiology* 4. <http://dx.doi.org/10.3389/Fmicb.2013.00228>.
- Zell, C., Kim, J.H., Balsinha, M., Dorhout, D., Fernandes, C., Baas, M., Sinninghe Damsté, J.S., 2014a. 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. *Biogeosciences* 11, 5637–5655. <http://dx.doi.org/10.5194/bg-11-5637-2014>.
- Zell, C., Kim, J.H., Hollander, D., Lorenzoni, L., Baker, P., Silva, C.G., Nittrouer, C., Sinninghe Damsté, J.S., 2014b. Sources and distributions of branched and isoprenoid tetraether lipids on the Amazon shelf and fan: implications for the use of GDGT-based proxies in marine sediments. *Geochimica et Cosmochimica Acta* 139, 293–312. <http://dx.doi.org/10.1016/j.gca.2014.04.038>.
- Zell, C., Kim, J.H., Moreira-Turcq, P., Abril, G., Hopmans, E.C., Bonnet, M.P., Sobrinho, R.L., Sinninghe Damsté, J.S., 2013b. Disentangling the origins of branched tetraether lipids and crenarchaeol in the lower Amazon River: implications for GDGT-based proxies. *Limnology and Oceanography* 58, 343–353. <http://dx.doi.org/10.4319/lo.2013.58.1.0343>.
- Zhang, T., Jin, T., Yan, Q., Shao, M., Wells, G., Criddle, C., Fang, H.H.P., 2009. Occurrence of ammonia-oxidizing Archaea in activated sludges of a laboratory scale reactor and two wastewater treatment plants. *Journal of Applied Microbiology* 107, 970–977. <http://dx.doi.org/10.1111/j.1365-2672.2009.04283.x>.
- Zhu, C., Wagner, T., Talbot, H.M., Weijers, J.W.H., Pan, J.M., Pancost, R.D., 2013. Mechanistic controls on diverse fates of terrestrial organic components in the East China Sea. *Geochimica et Cosmochimica Acta* 117, 129–143. <http://dx.doi.org/10.1016/j.gca.2013.04.015>.
- Zhu, C., Weijers, J.W.H., Wagner, T., Pan, J.M., Chen, J.F., Pancost, R.D., 2011. Sources and distributions of tetraether lipids in surface sediments across a large river-dominated continental margin. *Organic Geochemistry* 42, 376–386. <http://dx.doi.org/10.1016/j.orggeochem.2011.02.002>.