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

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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 μg/g organic carbon (OC) and crenarchaeol ranged from 0.6 to 19 μg/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 $\delta^{13}C$ 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.

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 ($\delta^{13}C$) 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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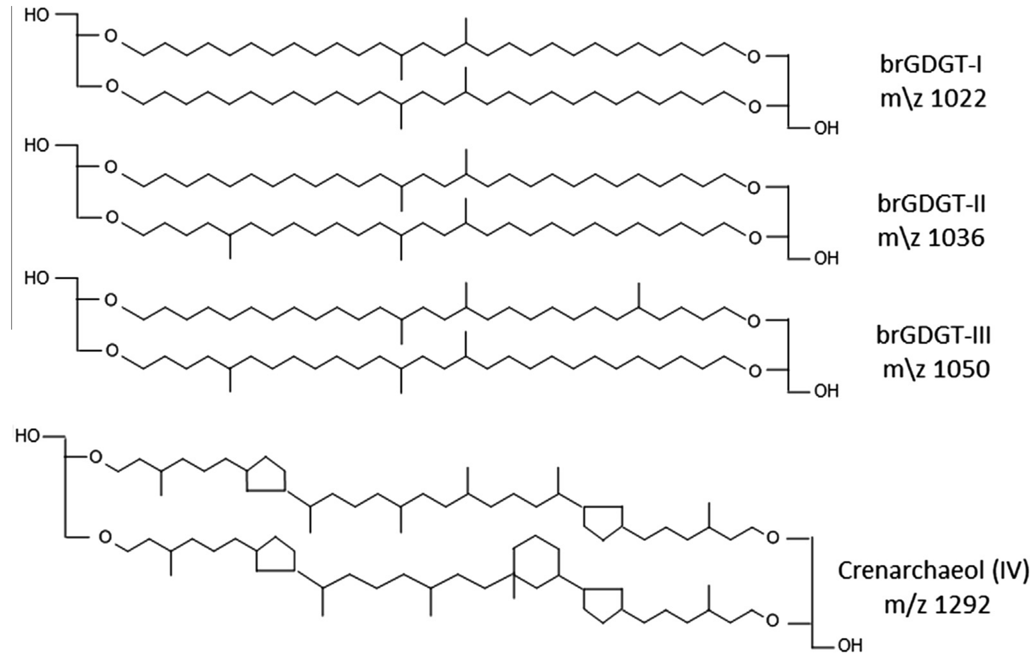

Fig. 1. Structure of brGDGTs (I–III) and crenarchaeol (IV).

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 $\leqslant$2000 m^3/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 km^2 and an average discharge of 65.8 m^3/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 m^2, 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.