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ORIGINAL ARTICLE

Occurrence and distribution of hydroxylated isoprenoid glycerol dialkyl glycerol tetraethers (OH-GDGTs) in the Han River system, South Korea

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Abstract We investigated the occurrence and distribution of terrestrial-derived hydroxylated isoprenoid glycerol dialkyl glycerol tetraethers (OH-GDGTs) in the Han River system and their potential impact on the application of the ring index of OH-GDGTs (RI-OH) as a sea surface temperature (SST) proxy in the eastern Yellow Sea. Thereby, we analyzed various samples collected along the Han River and from its surrounding areas (South Korea, *n* = 34). The OH-GDGTs were found in all samples investigated. OH-GDGT-0 was the dominant OH-GDGT component in the estuary and marine samples while OH-GDGT-2 was generally dominant in the soils, the lake sediments and the river suspended particulate matter (SPM). Our results thus suggests a possible warm bias of the RI-OH-derived summer SSTs in the coastal zone to which a large amount of terrestrial organic matter is being supplied. Further studies are necessary to better assess the applicability of the RI-OH proxy in the eastern Yellow Sea.

Keywords Hydroxylated isoprenoid glycerol dialkyl glycerol tetraethers (OH-GDGTs) · Sea surface temperature (SST) · Han river · Yellow Sea

1 Introduction

The isoprenoid glycerol dialkyl glycerol tetraethers (isoGDGTs) are cell membrane lipids of Archaea (Schouten et al. 2013 and references therein). Based on the relative abundance of isoGDGTs, Schouten et al. (2002) introduced the TEX_{86} (TetraEther indeX of tetraethers consisting of 86 carbon atoms) as a sea surface temperature (SST) proxy. Applications of the TEX_{86} in various marine sediment core sites have shown its potential to reconstruct annual mean SSTs, especially where the use of other proxies was limited (Schouten et al. 2013 and references therein). However, it appears that the application of the TEX_{86} proxy in marginal seas is complicated due to the large inputs of terrestrial-derived isoGDGTs (e.g. Weijers et al. 2006). Recently, a new suite of isoGDGTs with one or two hydroxyl groups in one of the biphytanyl moieties (OH-GDGTs) have been reported to widely occur in marine sediments (e.g. Liu et al. 2012). Huguet et al. (2013) observed a significant correlation between the relative abundance of OH-GDGTs to the total isoGDGTs and SSTs in marine surface sediments at a global scale. Furthermore, Fietz et al. (2013) suggested that the relative number of cyclopentane rings in OH-GDGTs could be used as a SST proxy in the polar oceans. Likewise, Lü et al. (2015) proposed a new SST proxy, so-called the ring index of OH-GDGTs (RI-OH), more suitable for reconstructing warm, summer seasonal SSTs in the Chinese coastal seas as follows:

$$\mathrm{RI-OH} = \frac{[\mathrm{OH-GDGT-1}] + 2[\mathrm{OH-GDGT-2}]}{[\mathrm{OH-GDGT-1}] + [\mathrm{OH-GDGT-2}]} \tag{1}$$

$$\mathrm{RI-OH} = 0.057 \times \mathrm{SSTsummer} + 0.005; \quad R^2 = 0.87, n = 54, p < 0.01 \tag{2}$$

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The RI-OH proxy represents more warmer seasonal SSTs rather than annual mean SSTs in the Chinese coastal seas due to both high productivity of Thaumarchaeota (Hu et al. 2013) and to enhanced grazing and particle flux following phytoplankton blooms due to high river discharge (cf. Yamamoto et al. 2013) in summer and autumn.

The Yellow Sea (West Sea of Korea) is a semi-enclosed, northwestern Pacific marginal sea into which two of the largest rivers in the world, the Huanghe (Yellow River) and the Changjiang (Yangtze River), and several smaller Korean rivers (e.g. Han River), are flowing, supplying high amounts of terrigenous sediments (e.g. Alexander et al. 1991). Hence, similar to the TEX_{86} proxy, the RI-OH proxy may be subject to the influence of terrestrial-derived OH-GDGTs in the Yellow Sea. The previous study conducted in the Yangtze Estuary (Lü et al. 2015) showed that the large inputs of terrigenous organic matter to the Yangtze Estuary appear to have no significant impact on the RI-OH proxy. However, so far there is, to the best of our knowledge, no study conducted in the river basin itself which examines the occurrence of terrestrial-derived OH-GDGTs and their potential to affect marine signals in marginal seas.

In this study, we describe the occurrences and sources of OH-GDGTs in the Han River basin and the adjacent marginal sea, i.e. the eastern Yellow Sea (Fig. 1). Thereby, we examined the impact of the terrestrial-derived OH-GDGTs on the RI-OH as a SST proxy in the eastern Yellow Sea to which a large amount of terrigenous organic matter is being supplied.

2 Materials and methods

We collected various samples along the Han River and from its surrounding areas (Fig. 1): mountain/farm soils (n = 9), river/estuary suspended particulate matter (SPM, n = 6), surface sediments from Lake Soyang (n = 8), riverbank sediments (n = 3), coastal marine sediments (n = 3), and offshore sediments (n = 5). For the GDGT quantification, 0.1–0.5 μg C_{46} GDGT internal standard was added into the samples prior extraction. All the samples were extracted with an Accelerated Solvent Extractor (ASE) using a mixture of DCM:MeOH (9:1, v:v). The total lipid extracts were separated into three fractions, with hexane:DCM (9:1, v:v), hexane:DCM (1:1, v:v) and DCM:MeOH, (1:1, v:v). The GDGTs were analyzed using a high performance liquid chromatography–atmospheric pressure positive ion chemical ionization–mass spectrometry (HPLC-APCI-MS) with an Agilent 6130 series LC/MSD SL. Based on the selective ion monitoring of the $[M + H]^+$ of the different GDGTs, quantification was achieved by calculating the area of its corresponding peak in the chromatogram and comparing it with the peak area of the internal standard and correcting for the different response factors (cf. Huguet et al. 2006). OH-GDGTs were quantified as in-source fragmentation products of OH-GDGTs (m/z 1300, 1298, 1296) as described by Fietz et al. (2013).

3 Results and discussion

The OH-GDGTs were found in all samples investigated. But they were below the detection limit in three downstream SPM samples. The 2OH-GDGT was a minor component mostly below the detection limit. The concentrations of isoGDGTs, OH-GDGTs, and brGDGTs are in the range of 9–1600, 0.1–50, and 6–6500 ng/g dry weight (dw), respectively. The relative abundances of OH-GDGTs accounted for only 0.1%–4% of total GDGTs, while isoGDGTs and brGDGTs contributed 7%–83% and 12%–93% respectively. The relative abundances of OH-GDGTs to total GDGTs were higher in estuary and marine samples

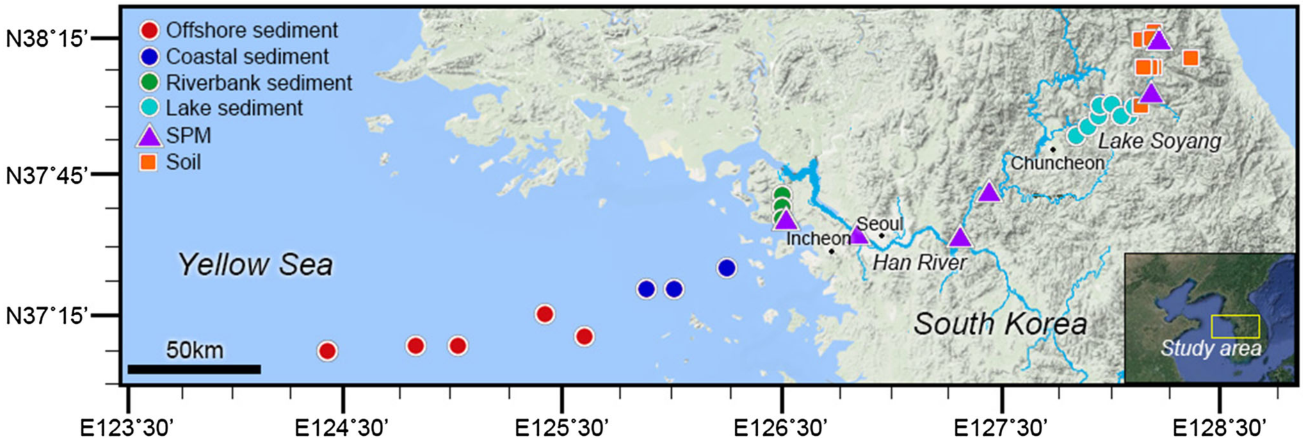

Fig. 1 A map showing the sampling sites investigated in this study

than in the river basin samples. The relative abundance of individual OH-GDGTs also varied among the samples. OH-GDGT-0 was the dominant OH-GDGT component in the estuary and marine environments, where its relative abundance accounted for 56 ± 10% of total OH-GDGTs. In contrast, OH-GDGT-2 was dominant in the soils and the lake sediments. The BIT values ranged from 0.1 to 1, with low values <0.3 in the marine sediments, suggesting that the marine sediments contain relatively small portion of terrestrial-derived GDGTs as shown by Yoon et al. (2016). The RI-OH values varied between 1.2 and 1.8, with the reconstructed summer SSTs of 21–32 °C.

The Principal Component Analysis (PCA) results of the fractional abundances of isoGDGTs and OH-GDGTs except for 2OH-GDGT-0 showed that the PC1 (53.5%) was closely related to OH-GDGT-0, OH-GDGT-1, and crenarchaeol with a negative loading and a positive loading of OH-GDGT-2 and all other isoGDGTs compounds except for GDGT-0. The PC2 (31.2%) predominantly reflected the presence of GDGT-0 with a negative loading. The subsequent Hierarchical Clustering on Principal Components (HCPC) results showed that all the marine sediments, the riverbank sediments collected near the river mouth, and the estuary SPM belonged to Cluster 1, while Cluster 2 represented the farm soils, the upstream river SPM collected before the rainy season, and the lake surface sediments collected in the lower part of Lake Soyang. Cluster 3 was associated with the upstream river SPM collected after the rainy season, the forest soils and some farm soils.

Our results revealed a distinctive distribution pattern of OH-GDGTs between the river basin (i.e. soils, lake sediments, and river SPM) and marine samples. The river basin samples with higher OH-GDGT-2 resulted in higher RI-OH values and accordingly higher RI-OH-derived summer SSTs than those of the marine samples. It is worthwhile to note that the RI-OH-derived summer SSTs were higher in the coastal sediments (25 ± 0.5 °C) than in the offshore sediments (22 ± 0.7 °C). This implies that terrestrial-derived OH-GDGTs might have influenced the RI-OH values in the coastal zone, biasing towards warmer summer SSTs.

4 Conclusions

The OH-GDGTs were found in all terrestrial and marine samples investigated. The estuary and marine samples showed different distribution patterns of OH-GDGTs in comparison to those of the river basin samples. Our results showed that terrestrial-derived OH-GDGTs with higher proportion of OH-GDGT-2 to the total OH-GDGTs pool may result in warmer RI-OH–derived summer SSTs in the coastal zone into which a large amount of terrestrial-derived organic matter is being supplied via rivers and/or coastal erosion. Accordingly, our study showed the occurrence and distribution of terrestrial-derived OH-GDGTs in the Han River system along the transport pathway of the terrestrial organic matter and the potential complications for the application of the RI-OH proxy in marginal seas. More studies should be conducted to constrain to what extent the terrestrial-derived OH-GDGTs may influence RI-OH-derived SSTs in the eastern Yellow Sea.

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