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Source, settling and degradation of branched glycerol dialkyl glycerol tetraethers in the marine water column

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Abstract

Branched glycerol dialkyl glycerol tetraethers (branched GDGTs) are commonly found in distal marine sediments. However, their presence in the water column, source and delivery process are not fully understood. In this study, we examined seasonal and depth variation in the flux of branched GDGTs in sinking particles and underlying sediment at 39°N, 147°E in the mid-latitude NW Pacific from November 1997 to August 1999.

Branched GDGTs showed synchronous variation in their sinking flux at different depths, and the variation was similar to that of lithogenic material of eolian dust origin. Their degrees of cyclization and methylation were nearly constant and bear some resemblance to those of alkaline soils. This suggests that westerly winds transport branched GDGTs to the study site via the atmosphere from continental Asia. The sinking flux of branched GDGTs was higher in 1999 than in 1998, presumably reflecting changes in the migration path of Asian dust in response to the El Niño-Southern Oscillation.

Synchronous variation in branched GDGT concentrations at different depths implies rapid vertical transport of branched GDGTs to deep water with a sinking velocity exceeding 260 m d^{-1}. The sinking flux of the branched GDGTs decreased with increasing depth, but the rate of decrease was much smaller than those of other compounds. The preservation efficiency of branched GDGTs was 3.5–6.4% of surface inputs at the water–sediment interface, which is much higher than those of isoprenoid GDGTs (1.0–1.3%) and other compounds. The branched and isoprenoid tetraether (BIT) index values were extremely low (i.e. <0.0015) in comparison with any other studies so far. The BIT values in the surface sediment were five times higher than those in sinking particles, which is attributed to the preferential preservation of branched GDGTs in oxic environments.

Keywords: Branched GDGT; Sediment trap; Eolian dust; Acidobacteria; North Pacific

1. INTRODUCTION

Branched glycerol dialkyl glycerol tetraethers (branched GDGTs; Structure are shown in Appendix I) are common in peats, soils, and river, lake, and marine sediments (Schouten et al., 2000; Sinninghe Damsté et al., 2000; Hopmans et al., 2004; De Jonge et al., 2013). They are thought to be derived from bacteria (Weijers et al., 2006; Sinninghe Damsté et al., 2011). Branched GDGTs in environmental samples consist of C_{66}, C_{67}, and C_{68} homologs with 0–2 cyclopentane moieties (Weijers et al., 2006). Assuming that branched GDGTs are derived solely from

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soil bacteria, Hopmans et al. (2004) proposed the branched and isoprenoid tetraether (BIT) index as an index of terrestrial soil contribution in marine sediments. Weijers et al. (2007) proposed a new paleotemperature index, methylation index and cyclization ratio of branched tetraethers (MBT/CBT), based on the empirical correlation between MBT/CBT values in soils and mean annual air temperatures.

Branched GDGTs are commonly found in coastal marine sediments (e.g., Hopmans et al., 2004; Schouten et al., 2012). Studies on riverine particles and coastal sediments have demonstrated that branched GDGTs are likely transported to the coastal ocean via rivers (e.g., Kim et al., 2007; De Jonge et al., 2015; Sinninghe Damsté, 2016). However, in situ production of branded GDGTs in coastal environments has also been postulated based on their distributions (e.g., Peterse et al., 2009; Zhu et al., 2011; Park et al., 2014; Zell et al., 2014; Sinninghe Damsté, 2016). Branched GDGTs are also commonly found in distal marine sediments (e.g., Yamamoto et al., 2008; Yamamoto and Polyak, 2009; Fietz et al., 2012; Weijers et al., 2014). There are two potential sources of branched GDGTs in open marine sediments, i.e., terrestrial and marine. Yamamoto et al. (2008) and Yamamoto and Polyak (2009) found branched GDGTs in central Arctic sediments, which was attributed to ice transportation of terrestrial organic matter. Fietz et al. (2013) found branched GDGTs in dust samples in the Atlantic Ocean, which was likely transported from Northwest Africa. Weijers et al. (2014), however, argued that the contribution of dust-associated branched GDGTs is smaller in tropical Atlantic offshore sediments than the contribution of in situ produced GDGTs in marine environments. Our knowledge of the abundance of branched GDGTs in the ocean water column and offshore marine sediments is still limited.

The aforementioned studies were based on the distributions of nine individual branched GDGTs quantified by high-performance liquid chromatography with a cyanoalkysilane column. Recently, De Jonge et al. (2013) showed that the C_{67} and C_{68} branched GDGTs have 5- and 6-methyl isomers that can be quantified separately using a silica gel column. Very recent studies indicated that the 6-methyl isomers tend to be more abundant than the 5-methyl isomers in alkaline soils (De Jonge et al., 2014a) and suspended particles in rivers (De Jonge et al., 2014b, 2015). These new findings suggest that the isomeric ratio can be used to identify the source of branched GDGTs.

This study examined the seasonal and depth variation of the branched GDGT fluxes and molecular composition of sinking particles using a time-series sediment trap experiment at a mooring station (39°N, 147°E; Fig. 1) in the mid-latitude NW Pacific to understand the seasonality, source, sinking processes and degradation of branched GDGTs in the water column and their influence on the BIT and MBT/CBT indices. The underlying sediments were also analyzed to evaluate the preservation of branched GDGTs at the water–sediment interface and the effects of branched GDGT degradation on the BIT and MBT/CBT indices.

2. STATION WCT-2 AND PREVIOUS RESULTS

The study site, station WCT-2, is located in the western North Pacific offshore of Japan (Fig. 1). It is situated in the main path of the northern westerlies in an area where dust from the deserts of inland China and Mongolia is deposited (Tanaka and Chiba, 2005).

Seasonal cycles were observed in the composition and flux of biogenic matter during the 21 months from November 1997 to August 1999 at station WCT-2 (Mohiuddin et al., 2002; Yamamoto et al., 2007). Diatom frustules were a major component of the sinking particles. Organic carbon, calcium carbonate, and biogenic opal fluxes began to increase in February/early March and reached a maximum from early May to early July; then, they decreased abruptly in late July, and remained essentially nearly constant after August. The biogenic fluxes in the middle and deep traps exceeded those in the shallow trap from April to June 1999, which was attributed to the lateral influx of particles in deeper traps (Mohiuddin et al., 2002). In contrast to biogenic matter, lithogenic material showed a significant difference in sinking flux between 1998 and 1999; the flux was lower in 1998 than in 1999.

Alkenones and isoprenoid GDGTs were examined at station WCT-2 (Yamamoto et al., 2007, 2012). The sinking flux of alkenones increased abruptly in mid-March/April and showed multiple maxima in the spring to fall. Conversely, the sinking flux of isoprenoid GDGTs showed maxima from May 1998 to February 1999. The peaks of the isoprenoid GDGT sinking flux corresponded to the peaks of the sinking fluxes of organic carbon, biogenic opal and lithogenic material.

3. SAMPLES AND METHODS

3.1. Samples

Moored time-series sediment traps were deployed at three different depths at the WCT-2' site (39°00′N, 147°00′E) in the western North Pacific from 19 November 1997 to 10 August 1999 (Table 1). The traps were set and recovered during the Western Pacific Environmental Assessment Study-CO_2 Ocean Sequestration for Mitigation of Climate Change (WEST-COSMIC) cruises in 1997, 1998, and 1999 aboard the R/V Hakurei-maru No. 2 (Mohiuddin et al., 2002). Sample cups at shallow and deep depths were replaced every 13 days from 19 November 1997 to 6 August 1998 (NH97 sampling interval) and every 18 days from 26 August 1998 to 10 August 1999 (NH98 sampling interval). The sample cups at middle depths were replaced every 22 days from 19 November 1997 to 10 August 1998 (NH97 sampling interval) and every 30 days from 27 August 1998 to 10 August 1999 (NH98 sampling interval). The cups were filled with 1% $HgCl_2$ seawater (pH = ~7). Recovered particles were separated into a coarse fraction (>1 mm diameter) and a fine fraction (<1 mm) by sieving. The coarse fraction was made up of scoriae and swimmers. The fine fraction was collected on a membrane filter (0.6 μm pore diameter), dried at 60 °C