



Use of lipid biomarkers for identification of regional sources and dechlorination characteristics of polychlorinated biphenyls in the East China Sea



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HIGHLIGHTS

- Lipid biomarkers are introduced to study the environmental behaviors of PCBs.
- Regional sources of PCBs in the East China Sea sediments are different.
- Dechlorination of PCBs in the East China Sea sediments occurs in the hypoxic zone.

ARTICLE INFO

Article history:

Received 23 February 2014

Received in revised form 28 April 2014

Accepted 15 May 2014

Available online xxxx

Editor: Adrian Covaci

Keywords:

Lipid biomarker

Polychlorinated biphenyls (PCBs)

Regional source

Dechlorination

East China Sea

ABSTRACT

Terrestrial organic matter (TOM) indicators could serve as proxies in studying the environmental behavior of organic pollutants because they are transported into the shelf seas along with the TOM. In this study, comparisons between polychlorinated biphenyls (PCBs) and TOM indicators of $\sum C_{27} + C_{29} + C_{31}$ *n*-alkanes, as well as branched and isoprenoid tetraether (BIT) index, were performed to examine the regional sources of PCBs in the East China Sea. The results indicated that sedimentary PCBs in the mud area southwest of the Cheju Island, coastal area north of the 29°N, and coastal area south of the 29°N were mainly from atmospheric deposition, riverine input of the Yangtze River, and local coastal sources via atmospheric deposition, respectively. The broad resemblance of the spatial patterns of non-definitive indicators of PCB dechlorination, hypoxia, and \sum ladderane lipids suggested that deep dechlorination mainly occurred at the coastal areas and center shelf southwest of Cheju Island.

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1. Introduction

Covering only 10% of the total seafloor, estuaries and shelf seas bury more than 90% of marine sedimentary organic matters (OMs) because of high terrestrial inputs and marine primary productivity (Hedges and Keil, 1995). High total organic carbon (TOC) content and sedimentation rate in the shelf seas could preserve organic pollutants (Arzayus

et al., 2001; Mai et al., 2002). Moreover, shelf seas have been considered as important reservoirs of anthropogenic organic contaminants. In the past few decades, numerous persistent organic pollutants (POPs) have been transported and buried in these regions, which are heavily affected by humans through surface runoffs and atmospheric deposition (Arzayus et al., 2001; Jönsson et al., 2003; Wafo et al., 2006).

Sedimentary OMs in estuaries and their surrounding regions mainly consist of marine organic matter (MOM) and terrestrial organic matter (TOM) (Hedges and Keil, 1995). Recently, some lipid compounds derived from plants, bacteria, or archaea, such as long-chain odd-carbon *n*-alkanes, long-chain even-carbon *n*-alkanols, and fatty acids, have been proposed as useful biomarkers for evaluating TOM contributions on sedimentary OM (Amo and Minagawa, 2003; Xing et al., 2011a, 2011b; Zhao et al., 2000). Brassicasterol, dinosterol, and C_{37} alkenones produced by marine algae are reliable MOM indicators. In addition, the content ratios of *n*-alkanes to algal biomarkers can be used to

Abbreviations: BIT, branched and isoprenoid tetraether; ECS, East China Sea; KC, Kuroshio Current; MOM, marine organic matter; OHE, Old Huanghe Estuary; SPM, suspended particulate matter; TOC, total organic carbon; TOM, terrestrial organic matter; TWC, Taiwan Warm Current; YR, Yangtze River; YRE, Yangtze River Estuary; YSCC, Yellow Sea Coastal Current; ZFCC, Zhejiang–Fujian Coastal Current.

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estimate the relative contribution of TOM in marine environments (Amo and Minagawa, 2003; Xing et al., 2011b).

Previous reports have indicated that *n*-alkanes could enter oceans through fluvial and atmospheric inputs (Bird et al., 1995; Gagosian et al., 1981; Simoneit et al., 1977). Branched glycerol dialkyl glycerol tetraethers (GDGTs) in marine sediments are mainly from river inputs (Hopmans et al., 2004). Branched and isoprenoid tetraether (BIT) index, which is the relative abundance of branched GDGTs over crenarchaeol (Sinninghe Damsté et al., 2002), can reflect the fluvial TOM entering into marine environments through surface runoffs (Hopmans et al., 2004). Comparable distribution characteristics are expected to improve the identification of POP sources because TOM and POPs are from land (Zhao et al., 2013b).

In a recent study, ladderane lipids, which are unique membrane lipids of anammox bacteria and prevalent within oxygen minimum zone, have been found to be potential biomarkers for indicating anammox in marine sediments (Jaeschke et al., 2009a) and anaerobic water columns (Kuypers et al., 2003). The correlation between ladderane lipids and sediment/water depth of minimum oxygen zones suggests the limiting effects of oxygen on anammox (Jaeschke et al., 2007, 2009b). We proved in our previous study that ladderane lipids could be indicative of hypoxia (Zhao et al., 2013a). Therefore, the introduction of ladderane lipids is beneficial in the evaluation of the environment fates of POPs.

Polychlorinated biphenyls (PCBs) are one of the priority POPs because of their global distribution, food web bioaccumulation, and potential adverse effects on humans (Jones and de Voogt, 1999; Safe, 1993). PCB occurrence and distribution in Chinese marginal sea have been a concern in recent years. Congener compositions, geographical characteristic, TOC, and grain size have been used to investigate their distribution characteristics and sources (Duan et al., 2013; Gao et al., 2013; Yang et al., 2011, 2012). Studies have shown that PCBs are transferred into the East China Sea (ECS) mainly via surface runoff, industrial wastewater, and atmospheric deposition. However, reports on PCB sources are still preliminary and limited, especially in the sea shelf area, because they cannot specifically reflect the regional sources of PCBs. Furthermore, the fate of PCBs has not been elucidated because of lack of comparable data for environment factors.

In the present study, PCBs and biomarkers of $C_{27} + C_{29} + C_{31}$ *n*-alkanes, branched GDGTs, crenarchaeol, and ladderane fatty acids in the surface sediments of the ECS were studied. The regional sources and dechlorination behavior of PCBs in the ECS were investigated, and the utilization of lipid biomarkers in studying anthropogenic contaminants was further explored (Dachs et al., 1999; Salau et al., 1997).

2. Materials and methods

2.1. Sample collection

ECS is one of the largest shelf seas in the world and an important terrestrial matter sink in China. The Yangtze River (YR) is the dominant surface runoff and source of sediments of the ECS. It discharges into the ECS approximately 0.5×10^{15} g yr⁻¹ of terrestrial particulate matters annually (Wang et al., 2008), with approximately 12×10^{12} g yr⁻¹ of OM (Wu et al., 2003). In addition, the Qiantang River, Ou River, and Min River may have local or even regional importance, despite their considerably lower contributions (<4% of YR) on the terrestrial matters entering the ECS (Liu et al., 2007). The main tidal currents affecting the sediment dispersal in ECS are shown in Fig. 1. These currents include the Zhejiang–Fujian Coastal Current (ZFCC), Taiwan Warm Current (TWC), Yellow Sea Coastal Current (YSCC), and Kuroshio Current (KC). Most of Yangtze-derived sediments are transported southwards along the coast by the ZFCC and trapped in the inner shelf as blocked by the TWC and KC, forming an elongated Zhejiang–Fujian mud wedge from the Yangtze mouth into the Taiwan Strait (Liu et al., 2007). The YSCC has a key role in transporting sediments from the Old Huanghe Estuary (OHE) to the mud area southwest off the Cheju Island (Milliman et al., 1989).

In the past decades, intensified anthropogenic activities and population growth in the YR drainage basin and coastal areas have significantly affected the eco-environment of the ECS. Significant amounts of land-derived organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs) (Hung et al., 2011), organochlorine pesticides (OCPs) (Lin et al., 2012), polybrominated diphenyl ethers (PBDEs) (Chen et al., 2006), and short-chain chlorinated paraffins (C_{10} – C_{13} , SCCPs) (Zhao et al., 2013b), have been released into the ECS in various ways. In this study, 43 surface sediment samples (0 cm to 3 cm) were collected along nine inshore–offshore transects of the ECS (DH1 to DH8, HE) during the cruise in June 2011 (Fig. 1), using a multiple corer deployed from the R/V of Beidou of the Yellow Sea Fisheries Research Institute. All samples were then freeze-dried, homogenized, and stored at -20 °C until analysis.

2.2. Extraction and clean-up

Approximately 5.0 g sediment sample was spiked with ¹³C-labeled PCB surrogate standards (EPA 68A-LCS, Wellington Laboratories, Canada) and extracted using an accelerated solvent extraction (ASE300, Dionex, USA) with a solvent mixture of dichloromethane/*n*-hexane (1:1, v/v). Then, activated copper powder was added to remove sulfur. After distilling in a rotary evaporation, the extract was cleaned using a multilayer silica column filled with 1 g silica, 4 g basic silica (1.2%, w/w), 1 g silica, 8 g acidic silica (30%, w/w), 2 g silica, and 4 g anhydrous sodium sulfate from bottom to top, and prewashed with 80 mL *n*-hexane. The extract solution was then eluted with 100 mL *n*-hexane and was subsequently concentrated to a final volume of 20 μ L. Prior to instrumental analysis, ¹³C-labeled PCBs (EPA 68A-IS) were added as internal standards to determine the recoveries of the labeled surrogate standards.

For *n*-alkanes analysis, approximately 2.0 g of sediment sample, which was spiked with an internal standard mixture containing C_{19} *n*-alkanol and C_{24} deuterium-substituted *n*-alkane, was extracted for 15 min with dichloromethane/methanol (3:1, v/v) using ultrasonication. This extraction procedure was repeated four times. The combined extracts were first hydrolyzed with 6% KOH in methanol, extracted with *n*-hexane, and then cleaned using a silica gel column. The non-polar lipid fraction, eluted from the column with 8 mL *n*-hexane, was dried under a gentle nitrogen stream for instrumental analysis.

For the branched GDGTs and crenarchaeol, approximately 5.0 g sediment sample, which was spiked with C_{46} GDGT internal standard, was extracted with 10 mL methanol in an ultrasonic bath for 15 min. Then, the extract was transferred into clean vials after centrifugation at 3000 rpm for 3 min. The extraction procedure was repeated twice. Afterward, the sample was sequentially extracted with methanol/dichloromethane (1:1, v/v) and dichloromethane using ultrasonication. Each extraction was also repeated twice. The combined extracts were concentrated under a gentle nitrogen stream and processed through a small anhydrous sodium sulfate column to remove excess water. The solution was concentrated and further cleaned using an alumina column. Dichloromethane/*n*-hexane (8 mL, 1:9, v/v) was added to elute the non-polar lipid fraction. The polar fraction, eluted with 12 mL methanol/dichloromethane (1:1, v/v), was concentrated and subsequently filtered for instrumental analysis.

For ladderane lipids, 10.0 g sediments were extracted four times using ultrasonication with 15 mL dichloromethane/methanol (2:1, v/v). The combined extracts were treated with activated copper powder overnight to remove sulfur. The supernatant was then saponified with 1 mol/L KOH in methanol overnight. After saponification, *n*-hexane was used to extract the neutral components from the basic solution (pH > 13) for four times. The remaining solution was acidified to pH = 3 and subsequently extracted with *n*-hexane for four times to obtain acidic components. Both neutral and acidic components were dried over a small anhydrous sodium sulfate column. Acidic ladderane components were converted to their corresponding methyl esters (FAMES) using a BF₃/methanol (20%) solution. All obtained ladderane

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