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A preliminary assessment of polychlorinated biphenyls and polybrominated diphenyl ethers in deep-sea sediments from the Indian Ocean

Zhineng Cheng^{a,d}, Tian Lin^{b,*}, Weihai Xu^c, Yue Xu^b, Jun Li^a, Chunling Luo^a, Gan Zhang^a

^a State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China ^b State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, 550002 Guiyang, China

^c South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China

^d University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Ten surface sediments were collected from the open Indian Ocean at depths below 4000 m in 2011, for the analysis of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs). The concentrations of Σ_{32} PCBs, Σ_7 PBDEs, and BDE-209 were 120–514, 49–152, and 7–133 pg/g, respectively. These concentrations are close to the lowest values recorded in the global marine environment. The PCBs had a relatively uniform composition, and were dominated by low chlorinated congeners. The concentrations of di-, tri-, and tetra-PCBs were strongly correlated with the total organic carbon (TOC), suggesting the dissolved PCBs were derived from the atmosphere via diffusive air–water exchange, and absorbed by phytoplankton. A high proportion of BDE209 was only detected in the sediment of the low fan of the Ganga River. There were weak correlations between low brominated BDEs and TOC, implying the degradation of BDE209 is a possible source of lower-brominated BDEs in deep-sea sediments.

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The deep-sea (>1000 m) is considered to be a pristine environment due to its remoteness from sources of anthropogenic pollution. Recently, there have been growing concerns about the impact of anthropogenic contaminants on deep-sea ecosystems (Solé et al., 2001; Koenig et al., 2013). There is increasing evidence that man-made substances; e.g. polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and organochlorine contaminants, including dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs), are being transported into the global deep-sea environment (Iwata et al., 1993; Lohmann et al., 2009). The deep-sea might act as a sink for highly persistent compounds that enter the marine environment (Lipiatou et al., 1997; Jonsson et al., 2003; Lohmann et al., 2006; Sobek and Gustafsson, 2014). However, deep-sea environments are remote and are among the least well-known natural systems in the world.

The Bay of Bengal (BOB) is the largest bay in the world, and is located in the northeastern part of the Indian Ocean. Roughly triangular in shape, it is bordered by India and Sri Lanka to the west, Bangladesh to the north, and Burma and the Andaman and Nicobar Islands to the east. PCB production in most of these countries was

* Corresponding author. E-mail address: lintian@vip.gyig.ac.cn (T. Lin).

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banned in the 1970s and 1980s, but the shipbreaking industry in India and Bangladesh continues to release PCBs into the Indian Ocean. More than half of the world's shipbreaking occurs in this region, with up to 0.25-0.8 metric tons of PCBs generated per scrapped merchant ship in India and Bangladesh. This has already led to PCB pollution issues in the surrounding area (Wurl et al., 2006; Chakraborty et al., 2013). PBDEs are another group of contaminants associated with anthropogenic activities (Kwan et al., 2013). The combined population of the tropical Asian countries surrounding the BOB has accounted for roughly 25% of the world's population since the 2000s, and thus it can be assumed that significant amounts of PBDE laden goods have been produced and consumed in the region. The wide usage of PBDEs in many consumer products will ensure the proliferation of PBDEs in the environment for many years to come (Kwan et al., 2013). Due to their persistence and potential for long-range atmospheric transport, PCBs and PBDEs are already ubiquitous in the equatorial air over the open Indian Ocean (Wurl et al., 2006). However, to the best of our knowledge, there has been no previous study that has reported the levels of PCBs and PBDEs in the sediments outside the BOB. Therefore, we determined the concentrations of 32 PCB congeners and 8 PBDE congeners and their composition in sediments collected from the open Indian Ocean, at a depth of 4000 m below

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the water surface. In addition, we compared the composition of PCBs and PBDEs, and suggested possible reasons for the differences identified.

From 12 April to 4 May 2011, 10 surface sediment samples (undisturbed top centimeter) were collected in the equatorial Indian Ocean area using a stainless steel grab bucket sampler. Sampling was conducted from the "Shiyan I" research vessel of the South China Sea Institute of Oceanology. The coordinates of the sampling sites were recorded by a global positioning system (0– $6^{\circ}E$, 80–98.5°N, Fig. 1, Table S1). The deep-sea sediment samples were wrapped with pre-combusted aluminum foil (450 °C, 4 h), placed into polytetrafluoroethylene (PTFE) zip lock bags, transported to the laboratory on board the ship soon after sampling, and stored in a freezer at -20 °C until analysis.

Analytical standards were obtained from Cambridge Isotope Laboratories (Andover, MA, USA). Thirty-two PCB congeners (seven indicator PCBs: PCB 28, 52, 101, 118, 138, 153, and 180; eight dioxin-like PCBs: PCB 77, 105, 114, 118, 126, 156, 169, and 189; and other PCBs: PCB 8, 37, 44, 49, 60, 66, 70, 74, 82, 87, 99, 128,

158, 166, 170, 179, 183, and 187) and eight PBDEs (BDE-28, -47, -99, -100, -153, -154, -183, and -209) were determined (Table S2). Both ¹³C-PCB 141 and BDE77 were added as internal standards, and PCB 30, 198, and 209 were used as surrogates. The laboratory treatment and analytical procedure for eluting PCBs and PBDEs in sediment samples is described in detail elsewhere (Wang et al., 2011a; Wang et al., 2011b; Wang et al., 2012; Huang et al., 2014).

Three procedural blanks were included in the sequential analysis of our samples to check for potential laboratory contamination and the repeatability of the analysis. There were no target compounds detected in any blank samples. Method detection limits (MDLs) were defined as the mean blank value plus three times the standard deviation of seven replicate spiked samples. When the compounds were not detected in the blanks, a standard of threefold the instrumental detection limit (IDL) was used as the MDL. The MDLs for the sediment samples were 0.183–0.264 pg/g for PCBs, 0.3–1.45 pg/g for seven PBDEs (BDE 28, 47, 99, 100, 153, 154, and 183), and 0.24–0.90 pg/g for BDE-209. The surrogate





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