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Sedimentary records of hydroxylated and methoxylated polybrominated diphenyl ethers in the southern Yellow Sea

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ABSTRACT

Although hydroxylated (OH-) and methoxylated (MeO-) polybrominated diphenyl ethers (PBDEs) have caused much concern in recent years, few reports had discussed on their input history. In this study, we measured the contents of nine MeO-BDEs, ten OH-BDEs, and total organic carbon (TOC) of two sediment cores from the southern Yellow Sea. 6-MeO-BDE-47, 2'-MeO-BDE-68, 6-OH-BDE-47, and 2'-OH-BDE-68 were the predominant congeners in HH12, while only 2'-OH-BDE-68 and 6-OH-BDE-47 were frequently detected in core HH11. The records showed that OH-/MeO-BDEs in both cores had increased rapidly since the 1950s. Their existence was detected at the bottom layers (~1800 s) prior to the production of PBDEs (1960s), thus OH-/MeO-BDEs originate from natural origins rather than artificial PBDEs. Comparisons between TOC and OH-/MeO-BDEs indicated that TOC is a potential factor affecting the accumulation of OH-/MeO-BDEs in marine environments. Similar trends and significant correlations between OH-BDEs and MeO-BDEs suggest their common origins or interconversion.

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Polybrominated diphenyl ethers (PBDEs) have been extensively used as brominated flame retardants (BFRs) in many industrial and consumer products in the previous decades. Owing to their ubiquitous environmental occurrence and potential adverse effects on ecosystems and people (Law et al., 2006), pentabromodiphenyl and octabromodiphenyl ethers were listed as persistent organic pollutants in the Stockholm convention (UNEP, 2009). Hydroxylated PBDEs (OH-BDEs) and methoxylated PBDEs (MeO-BDEs), which are structural analogs of PBDEs, have become an increasing concern in recent years. The toxicological effects of OH-/MeO-BDEs

had been identified and characterized in a number of studies over the past decade because of their potential adverse effects on organisms. Several in vitro studies had indicated that OH-BDEs exhibit higher neurotoxic and endocrine disrupting potency than PBDEs (Dingemans et al., 2008; Meerts et al., 2001) and greater dioxin-like activity than MeO-BDEs (Su et al., 2012). Relative to OH-BDEs, some MeO-BDEs were found to have a stronger effect on mRNA abundance of steroidogenic enzymes in the H295R cell line (He et al., 2008).

OH-/MeO-BDEs have been widely detected in marine organisms, such as sponges (Bowden et al., 2000; Carté and Faulkner, 1981; Fu et al., 1995; Handayani et al., 1997), algae (Asplund et al., 2001; Kuniyoshi et al., 1985; Malmvärn et al., 2005, 2008), fishes (Valters et al., 2005; Zhang et al., 2010), and marine animals (Kelly et al., 2008; Weijs et al., 2009). Among the detected OH-/

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MeO-BDEs, 6-OH-BDE-47, 2'-OH-BDE-68, 6-MeO-BDE-47, and 2'-MeO-BDE-68 are the most common and dominant congeners in the marine biota. These congeners with OH-/MeO- functional groups substituted in the *ortho* position of the diphenyl ether backbone are natural compounds, as determined by ^{14}C isotope techniques (Guitart et al., 2011; Teuten et al., 2005). Large amounts of bioactive polyhalogenated diphenyl ether (PHDE) compounds are known to have been isolated from sponges. Among these bioactive compounds, OH-BDEs are considered to be synthesized as their chemical defenses against potential predators and bacterial invasion despite their possible production by the symbiont cyanobacteria (Faulkner et al., 1994). Therefore, marine sponges are considered as one of the important producers of these *ortho*-substituted OH-/MeO-BDEs. Relatively high levels of these natural compounds have been observed in numerous marine species because of their bio-accumulation via the food web.

However, only a limited number of studies on these *ortho*-substituted OH-/MeO-BDEs in marine abiotic environments are available (Vetter et al., 2009; Zhang et al., 2012). Bio-accumulation in marine organisms generally comprises sedimentary OH-/MeO-BDEs because sediments serve as sinks and reservoirs for various organic pollutants. A recent study (Zhang et al., 2010) indicated that OH-BDEs in Chinese sturgeon (*Acipenser sinensis*) came from a natural accumulation in the marine environment. From a toxicological standpoint, sedimentary OH-/MeO-BDEs are potential threats because they re-suspend and bio-accumulate via the food web. In addition, global climate changes in the past decades have altered marine ecosystems (Hays et al., 2005; Hoegh-Guldberg and Bruno, 2010; Walther et al., 2002), including production variations of these natural compounds.

In this study, the contents of 10 OH-BDEs and 9 MeO-BDEs were measured in two sedimentary cores collected from the southern Yellow Sea (SYS). The objectives of this study are to investigate the vertical distributions of OH-/MeO-BDEs in the SYS, reconstruct their historical records, reveal the factors affecting their accumulation, and provide new information on their ecological risks in marine environments.

The Yellow Sea is a relatively shallow and semi-enclosed shelf sea surrounded by the Chinese mainland, the Korean Peninsula,

the Bohai Sea, and the East China Sea. The Yellow Sea is separated into SYS and northern Yellow Sea by the Shandong Peninsula. The SYS covers an area of 309,000 m^2 and has a mean depth of 46 m (Zhang et al., 2007). The Yellow River and the Yangtze River provide substantial sediment inputs for the SYS, although these two rivers do not flow directly into the SYS (Cai et al., 2003). The fact that ample terrigenous materials, including organic pollutants carried by these river-derived sediments, enter into the SYS, it has become an environmental hotspot in the past few decades (Duan et al., 2013; Zeng et al., 2013; Zhang et al., 2007, 2009). Two sedimentary cores, namely, HH12 (46 cm) and HH11 (36 cm), were collected from the central region of the SYS in June 2012 using R/V of DongFangHong2 of the Ocean University of China (OUC) during the Bohai Sea-Yellow Sea sharing cruise supported by the National Natural Science Foundation of China (NSFC) (Fig. 1). The sedimentary cores were divided into 2 cm sections, which were subsequently freeze-dried, homogenized, and stored at $-20\text{ }^\circ\text{C}$ until analysis.

Sample extraction, cleanup, and instrumental conditions for OH-/MeO-BDEs were based on the methods established by Sun et al. (2012) with some modifications. The samples were extracted in an ultrasonic bath, cleaned using acid silica gel and a silica gel column, and then concentrated or solvent-exchanged prior to GC/MS or LC/MS analysis. Previous studies had reported the sedimentation rates of two cores, namely, KC-6 (0.17 cm/year) and KC-48 (0.10 cm/year), corresponding to core HH11 and HH12, respectively, which were collected from the same region (Zhao et al., 1991). In this study, we referred to their sedimentation rates to reconstruct the chronology of core HH11 and HH12.

Seven-point standard calibration curves for the quantification of OH-/MeO-BDEs were prepared using 9 MeO-BDE and 10 OH-BDE standards within the concentration range of 2–200 ng/mL and surrogate standards with concentration of 50 ng/mL. The recovery tests for OH-BDEs and MeO-BDEs in matrix spike experiment ranged from 71% to 93% and 74% to 108%, respectively. The method detection limits (MDLs) for MeO-BDEs and OH-BDEs ranged from 11.7 pg/g dw to 21.1 pg/g dw and 1.3 pg/g dw to 6.1 pg/g dw, respectively. All glassware were rinsed with dichlorometh-

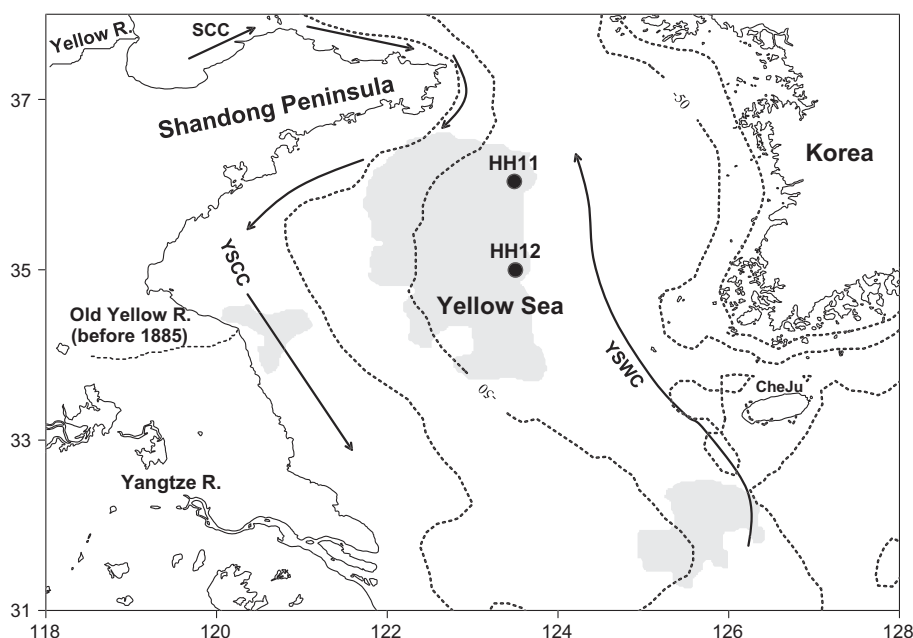


Fig. 1. Map of the study area and sampling sites for sedimentary core. Mud areas are marked in light gray. Major currents are indicated by the curve with arrow: SCC (Shandong Coastal Current), YSCC (Yellow Sea Coastal Current), and YSWC (Yellow Sea Warm Current).

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