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Polybrominated diphenyl ethers in marine sediments of Sanggou Bay in east China

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) were measured in the surface sediments collected in August 2015 in Sanggou Bay, China. The total concentrations of 13 PBDEs, including BDE-17, -28, -47, -66, -71, -85, -99, -100, -138, -153, -154, -183 and -190, and concentrations of BDE-209 were 0.223–1.259 ng/g and 0.865–9.275 ng/g, respectively. The PBDE levels increased from the outer bay to the inner bay. BDE-209 was the predominant congener, followed by BDE-47, BDE-71, and BDE-99. Significant positive correlations were observed for tri-BDEs with organic carbon ($r = 0.598$, $p < 0.05$) and with clay content ($r = 0.592$, $p < 0.05$). Principal component analysis revealed that PBDEs in Sanggou Bay were mainly derived from the usage, dismantling and degradation of commercial products (penta-, octa-, and deca-BDEs), which were then transported through continental runoff and atmospheric deposition. The ecological risks were mainly attributed to deca-BDE congeners with moderate risk level.

Since the 1970s, polybrominated diphenyl ethers (PBDEs), a class of brominated flame retardants (BFRs), have been widely used in plastics, textiles, electronic circuitry, and other materials to reduce fire hazards (Li et al., 2006). The three main commercial PBDE products are differentiated in terms of their average bromine contents; these products are the penta-BDEs (predominantly BDE-47 and BDE-99), octa-BDEs (predominantly BDE-183), and deca-BDEs (predominantly BDE-209) (Alaee et al., 2003). China is a large manufacturer and consumer of flame retardants, with a total annual production volume of 200,000 t (Chen et al., 2013). Many BFR factories are located in the eastern region of China, such as in Shandong and Jiangsu, and these factories mainly produce deca-BDE technical mixtures and tetrabromobisphenol-A (Jin et al., 2008). Furthermore, a portion of the BFRs in China are imported from other countries, especially because three of the largest BFR manufacturers in the world market their BFR products in China (Mai et al., 2005). The domestic demand for PBDEs in China has increased at a rate of 8% per year since 2000, and deca-BDEs account for the major proportion of this demand (Mai et al., 2005). According to a preliminary inventory, the historical amount of deca-BDE technical mixtures in China reached up to 358,180 t by the end of 2011 (Deng et al., 2016).

Given the absence of chemical bonding, PBDEs can be easily released into the surrounding environment during production, usage, and dismantling (Rahman et al., 2001). PBDEs can also be transported to coastal areas via atmospheric deposition, land runoff, and direct industrial and domestic wastewater discharges (Wang et al., 2016). PBDEs are strongly adsorbed in sediments because of their lipophilicity, and the sediments are sinks of PBDEs in aquatic environments. Because of their persistence, potential bioaccumulation, and possible adverse effects on wildlife and humans, PBDEs have become an environmental concern all over the world. Consequently, the usage of penta- and octa-products was restricted under the Stockholm Convention in 2009 (Yu et al., 2011). China has joined the Stockholm Convention, and penta- and octa-products will be phased out no later than the end of the year 2030 (Chen et al., 2012). Moreover, the Europe Union restricted the usage of deca-BDEs in 2008, and the United States also restricted the production, import, and sale of deca-BDEs at the end of 2013, because of their potential harm to the environment and humans via debromination to form lower toxic PBDE congeners (Yu et al., 2011). However, deca-BDEs are still produced and used in many countries, including China.

Sanggou Bay is located in the east region of the Shandong Peninsula and is a semi-enclosed bay in the Yellow Sea. It is one of the most intensive aquaculture areas in northeast China. With the rapid development of aquaculture and agriculture in recent years, the quantities of industrial and domestic wastewater discharges entering Sanggou Bay have increased. The existing studies on Sanggou Bay have mainly focused on eutrophication and heavy metal pollution (Sun et al., 2007; Yan et al., 2008). However, the studies on persistent organic pollutants (POPs) in Sanggou Bay and the occurrence of PBDEs are insufficient. The present study is aimed at investigating the concentrations and composition of PBDEs, as well as their spatial distribution, in Sanggou Bay to explore the PBDE sources and to assess the risk of PBDEs in Sanggou Bay.

Thirteen surface sediments (0–5 cm) were collected from Sanggou Bay (37.04–37.15°N, 122.45–122.64°E) in August 2015 using a box

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core sampler (Fig. 1). After collection, the samples were immediately transported to the laboratory and stored at −20 °C for further analysis. The sediment grain size was analyzed using the Rise-2028 laser particle size instrument and was classified according to the granularity classification standard (State Oceanic Administration, 2007). Total organic carbon (TOC) was determined with the potassium dichromate oxidation and ferrous sulfate titrimetric method (Schwartz, 1995).

The sediment samples were freeze-dried, ground, homogenized by sieving through a stainless steel (0.2 mm). 10 g of sediment samples was spiked with a known amount of surrogate standard and Soxhlet extracted with a mixture of acetone and hexane (v:v, 1:1, 150 mL) for 24 h. The extracts were purified through multi-layer silica columns. The extraction, cleanup, and analysis of PBDEs using a 6890 gas chromatograph coupled to a 5975C mass spectrometer (MS) (Agilent Technologies, Wilmington, DW, USA) were conducted according to the methods described by Ju et al. (2016). A standard mixture of PBDEs selected for quantitative analysis was purchased from AccuStandards (New Haven, CT, USA). The mixture contained 14 PBDE congeners (IUPAC Nos. 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, and 209). The ^{13}C-labeled polychlorinated biphenyl congener (^{13}C-PCB141) was used as the surrogate standard.

A procedural and solvent blank, surrogate standard for each sample, and sample duplicate were analyzed for quality control and assurance. The mean recovery of surrogate standard in all the sediment samples was 85% ± 10% for ^{13}C-PCB141. PBDE data were reported without surrogate recovery correction. A spiked procedural blank with a standard solution was analyzed every four samples, and the recoveries of 14 PBDE congeners were 80%–112%. All the targeted PBDEs in the solvent blank samples were below the detection limits. Quantitative analysis was performed by using a six-point calibration curve method. The limit of detection was determined as mean field blanks plus three times the standard deviation of the field blanks, ranging from 0.006 ng/g to 0.02 ng/g for all PBDE congeners, except for BDE-209, and 0.11 ng/g for BDE-209.

Principal component analysis (PCA) was used to identify the sources of pollutants in the environment. Concentrations of 14 PBDEs were normalized and analyzed by PCA. The normalization of data was carried out using the software SPSS 16.0, with the principle that the concentration data subtracted by the average concentration is divided by the standard deviation. The principal components (PCs) with eigenvalues >1 were extracted.

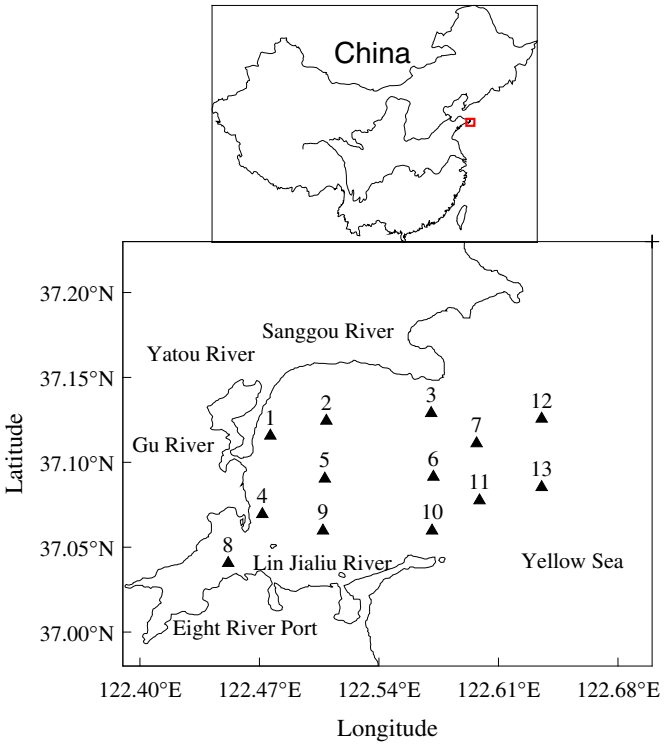

Fig. 1. Locations of sampling sites in Sanggou Bay.

The ecological risks of PBDEs were assessed according to the Federal Sediment Quality Guidelines (FSeQGs) (Environment Canada, 2013). The FSeQG standard concentrations normalized to 1% TOC for tri-, tera-, penta-, hexa and deca-BDE homologs are 44, 39, 0.4, 440 and 19 ng/g dry weight, respectively (Environment Canada, 2013). The risk quotient (RQ) was used to evaluate the contamination of PBDEs as follow (Wang et al., 2015b):

$$RQ = Ci/Csi$$

where Ci is the measured concentration of tri-, tera-, penta-, hexa or deca-BDE homologs in the surface sediments from Sanggou Bay, which is normalized to 1% TOC. Csi is the standard concentration based on FSeQGs. Three risk levels are classified as follows: $0.01 \le RQ \le 0.1$ indicates low risk, $0.1 \le RQ \le 1$ indicates moderate risk, and $RQ \ge 1$ indicates high risk (Liu et al., 2015).

Correlation was analyzed using Pearson correlation, and statistical analyses were carried out at a significance level of $\alpha = 0.05$. PCA and correlation analysis were performed using the software SPSS 16.0.

The total concentrations of 13 PBDEs ($\sum_{13}$PBDEs), including BDE-17, -28, -47, -66, -71, -85, -99, -100, -138, -153, -154, -183 and -190, ranged from 0.223 ng/g to 1.259 ng/g, with a mean value of 0.523 ng/g (Table 1). The BDE-209 concentrations ranged from 0.865 ng/g to 9.275 ng/g, with a mean value of 3.666 ng/g. The mean value of the total concentrations of 14 PBDEs ($\sum_{14}$PBDE) was 4.189 ng/g.

The levels of $\sum_{13}$PBDEs in this study are slightly higher than those in the Yangtze River Estuary (nd–0.55 ng/g) (Chen et al., 2006), similar to those in the Korean coastal area (0.23–1.0 ng/g) (Moon. et al., 2007), and slightly lower than those in the Bo Sea of China (0.07–5.24 ng/g) (Wang et al., 2009) and Qingdao coastal area (0.1–5.5 ng/g) (Yang et al., 2003). By contrast, the levels of $\sum_{13}$PBDEs in this study are obviously lower than those in the Pearl River Estuary (1.1–49.3 ng/g) (Chen et al., 2013) and Hong Kong coastal areas (1.7–53.6 ng/g) (Liu et al., 2005). For BDE-209, its concentrations are similar to those in the Bo Sea of China (0.46–6.44 ng/g) (Wang et al., 2015a), slightly higher than those in the southern Yellow Sea (0.07–1.97 ng/g) (Wang et al., 2016), and obviously lower than those in the Pearl River Estuary (26.3–3580 ng/g) (Chen et al., 2013) and Korean coastal area (0.22–493 ng/g) (Moon. et al., 2007). Therefore, the levels of PBDE contamination in Sanggou Bay are moderate in comparison with those in the other regions of the world.

The highest concentration of $\sum_{14}$PBDEs in the sediments was found at Station 4 (10.534 ng/g) located in the Gu River Estuary (Fig. 2). The low $\sum_{14}$PBDE concentrations were found at Stations 11–13 (<3.0 ng/g) located in the mouth of the bay. The concentrations of $\sum_{14}$PBDEs gradually decreased from the inshore to the offshore area, thus indicating the obvious influences of terrestrial input.

The main entrance to Sanggou Bay is the Gu River, which is located in the northwest bay and transports large quantities of household and industrial waste water into the bay. The input of pollutants, such as nitrogen, phosphorus and polychlorinated biphenyls, from the Gu River reportedly accounts for about 99% of the pollutants in Sanggou Bay (Wu, 2005). Moreover, the traffic and shipping activities in the large multifunction harbor located in the northwest area of Sanggou Bay serve as another source of PBDEs. Sanggou Bay is a semi-enclosed bay with a normal semidiurnal tide. The water flow rate in the bay increases at the mouth of the bay because of water exchange (Sun et al., 1998). In the 1980s, large-scale raft culture, which included kelp (*Laminaria japonica*), scallops (*Chlamys farreri*), and long oysters (*Crassostrea gigas*), began in Sanggou Bay (Xia et al., 2014), and this practice further

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