Environmental Pollution 212 (2016) 147–154

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

# Occurrence and levels of polybrominated diphenyl ethers in surface sediments from the Yellow River Estuary, China☆

Zijiao Yuan [a, b, c, d], Guijian Liu [a, b, c, *], Michael Hon Wah Lam [c, d], Houqi Liu [a], Chunnian Da [a]

[a] CAS Key Laboratory of Crust-Mantle Materials and the Environment, School of Earth and Space Sciences, University of Science and Technology of China, Hefei, Anhui 230026, China
[b] State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, The Chinese Academy of Sciences, Xi'an, Shaanxi 710075, China
[c] University of Science and Technology of China–City University of Hong Kong Joint Advanced Research Centre, Suzhou, Jiangsu 215123, China
[d] Department of Biology & Chemistry, City University of Hong Kong, Tat Chee Avenue, Hong Kong SAR, China

ARTICLE INFO

*Article history:*
Received 18 November 2015
Received in revised form
18 January 2016
Accepted 20 January 2016
Available online xxx

*Keywords:*
Yellow river
Polybrominated diphenyl ethers
Surface sediments
Congener profiles
Possible sources

ABSTRACT

A total of 21 surface sediments collected from the Yellow River Estuary, China were analyzed for 40 kinds of polybrominated diphenyl ethers (PBDEs) using gas chromatography-mass spectrometry (GC–MS). Their levels, spatial distribution, congener profiles and possible sources were investigated. Only ten congeners were detected in the sediments. The total concentrations of the lower brominated BDEs ($\sum PBDEs_{low}$, PBDEs excluding BDE 209) and BDE 209 ranged from 0.482 ng/g to 1.07 ng/g and 1.16 –5.40 ng/g, with an average value of 0.690 and 2.79 ng/g, respectively, which were both at the low end of the global contamination level. The congener profiles were dominated by BDE 209, with the average value accounting for 79.2% of the total PBDEs in the sediment samples. Among the nine lower brominated BDE congeners, BDE 47, 99 and 183 had high abundances. Although the commercial Penta/Octa-BDE products have been banned in most countries, the residual commercial Penta/Octa/Deca-BDE products and the debromination of highly brominated BDE compounds such as BDE 209 were still found to be the possible sources for the trace level of PBDEs in the present study area. In spite of the gradual removal of the commercial PBDEs in the world, the present research results further suggested that scientific attention should not be reduced on the issue of environmental contamination caused by these outdated chemical compounds.



## 1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of widely used brominated flame retardants (BFRs) in the world since 1960s and the production of PBDEs has increased quickly, leading to the cumulative production of over 2 million tons (Rayne et al., 2003; Shaw and Kannan, 2009; Wiseman et al., 2011). Pentabromodiphenyl ether (Penta-BDE), octabromodiphenyl ether (Octa-BDE) and decabromodiphenyl ether (Deca-BDE) were the three major commercial formulations of PBDEs (La Guardia et al., 2006). However, owing to their persistence, potential for endocrine disruption and bioaccumulation, and long-range transport ability, PBDEs were of great environmental concern in the past few years and the production of the Penta- and Octa-PBDE technical mixtures were banned in the European Union and North America in 2004, resulting in the gradual removal of PBDEs (Hale et al., 2006; Moon et al., 2007; Su et al., 2014). Nevertheless, the use of Deca-BDE is not subject to any regulatory restrictions in most countries and the Deca-BDE commercial mixture is still the dominant BFRs used in China (Mai et al., 2005; Ni et al., 2013; Zou et al., 2007). BDE 209 is the main component of Deca-BDE commercial mixture and it can degrade or metabolize into lower brominated congeners, which are more bioavailable, persist and toxic than BDE 209 (La Guardia et al., 2007; Lagalante et al., 2011; Söderström et al., 2004; Van den Steen et al., 2007). In recent years, despite the gradual removal of commercial PBDEs, they have been widely detected in air (Li et al., 2015), water (Yang et al., 2015), sediments (Nouira et al., 2013), soil (Parolini et al., 2013), plant (Wang et al., 2011), marine mammal

☆ This paper has been recommended for acceptance by Jay Gan.

* Corresponding author. CAS Key Laboratory of Crust-Mantle Materials and the Environment, School of Earth and Space Sciences, University of Science and Technology of China, Hefei, Anhui 230026, China.
*E-mail address:* lgj@ustc.edu.cn (G. Liu).

http://dx.doi.org/10.1016/j.envpol.2016.01.058
0269-7491/

(Zhu et al., 2014a), birds (Erratico et al., 2015), and human tissues (Bramwell et al., 2014; Fromme et al., 2015; Król et al., 2014). Therefore, it is of great significance to continuously study the current contamination level of PBDEs in various environmental media, thus obtaining the action effect of PBDE restrictions and developing effective counter measures to reduce their adverse effects on the environment.

The Yellow River, with a main stream 5464 km long and drainage area of 795 thousand km$^2$, is the second largest river in China and one of the largest rivers in the world (Xu et al., 2007). It flows across nine Provinces in North China and ultimately run into the Bohai Sea through the present Yellow River Estuary in the city of Dongying in Shandong Province. Hydrophobic organic contaminants such as PBDEs are prone to be trapped in estuarine sediment through riverine inputs and atmospheric deposition (Zhao et al., 2011). Considering the rapid economic development in the adjacent Laizhou Bay area in the south of the estuary, where the largest BFR-manufacturing center in China located (Pan et al., 2011; Zhu et al., 2014b), the contamination caused by flame retardants such as PBDEs was expected to be serious in the Yellow River Estuary. The objectives of the present research work were to investigate the contamination level, spatial distribution, congener profile and possible potential sources of PBDEs in surface sediments collected from the Yellow River Estuary, further helping environmental researchers understand the global tendency of PBDE pollution under the situation of global restriction to this kind of contaminants, thus developing effective counter measures to control their adverse effects. To the best of our knowledge, this is the first study concentrating specifically on PBDEs in the Yellow River Estuary, China, which is a typical estuary area in the world.

## 2. Materials and methods

### 2.1. Study area and sample collection

A total of 21 surface sediments were collected using a stainless steel grab from the Yellow River Estuary in August, 2013 (Fig. 1). The investigated area covers approximately 100 km of shoreline from the estuary mouth and holds the sampling locations both in and out of the Yellow River Delta Natural Reserve (YRDNR). The Yellow River Delta has been reported as a typical petrochemical area (Xie et al., 2012): Shengli Oilfield, the second largest oilfield in China, is located here and many branch oilfields of Shengli are spread over the study area due to the abundant oil and gas resources in this region. In addition, Laizhou Bay area, which holds the famous chemical industrial base Weifang Binhai Economic Development Zone and the largest BFR-manufacturing center in China, is located in the south of the estuary area (Pan et al., 2011; Zhu et al., 2014b). The detailed sampling sites in this study were similar to our previously published paper (Yuan et al., 2015). After collection, all the samples were individually wrapped in clean aluminum foil, which were pre-combusted under 450 °C to remove organic influence, and were transported to the laboratory immediately. Sediment samples were kept in a freezer at −20 °C until further analysis.

### 2.2. Reagents and materials

PBDE standard solutions BDE-AAP-A-15X, which contains 39 PBDE congeners including 2-BDE (BDE 1), 3-BDE (BDE 2), 4-BDE (BDE 3), 2,6-di-BDE (BDE 10), 2,4-di-BDE (BDE 7), 3,3′-di-BDE (BDE 11), 2,4′-di-BDE (BDE 8), 3,4′-di-BDE (BDE 13), 3,4-di-BDE (BDE 12), 4,4′-di-BDE (BDE 15), 2,4,6-tri-BDE (BDE 30), 2,4′,6-tri-BDE (BDE 32), 2,2′,4-tri-BDE (BDE 17), 2,3′,4-tri-BDE (BDE 25), 2,4,4′-tri-BDE (BDE 28), 2′3,4-tri-BDE (BDE 33), 33′4-tri-BDE (BDE 35), 3,4,4′-tri-BDE (BDE 37), 2,4,4′6-tetra-BDE (BDE 75), 22′45′-tetra-BDE (BDE 49), 2,3′,4′,6-tetra-BDE (BDE 71), 2,2′4,4′-tetra-BDE (BDE 47), 2,3′,4,4′-tetra-BDE (BDE 66), 3,3′4,4′-tetra-BDE (BDE 77), 2,2′4,4′,6-penta-BDE (BDE 100), 2,3′4,4′6-penta-BDE (BDE119), 2,2′4,4′,5-penta-BDE (BDE99), 2,3′4,4′5-penta-BDE (BDE 118), 2,3,4,5,6-penta-BDE (BDE 116), 2,2′,3,4,4′-penta-BDE (BDE 85), 3,3′4,4′5-penta-BDE (BDE126), 2,2′,4,4′,6,6′-hexa-BDE (BDE155), 2,2′4,4′5,6′-hexa-BDE (BDE 154), 2,2′4,4′5,5′-hexa-BDE (BDE 153), 2,2′3,4,4′5′-hexa-BDE (BDE 138), 2,3,4,4′,5,6-hexa-BDE (BDE 166), 2,2′,3,4,4′,5′6-hepta-BDE (BDE 183), 2,2′3, 4,4′,5,6-hepta-BDE (BDE 181), 2,3,3′,4,4′,5,6-hepta-BDE (BDE 190), and individual standard of 2,2′,3,3′,4,4′,5,5′,6,6′-deca-BDE (BDE 209), were purchased from AccuStandard, Inc. (New Haven, CT, USA). PBDE surrogate standards MBDE −MXA (containing $^{13}C_{12}$-BDE 47, $^{13}C_{12}$-BDE 99 and $^{13}C_{12}$-BDE 153) were purchased from Wellington Laboratories (Guelph, Ontario, Canada). Silica gel (230–400 Mesh) was purchased from Riedel de Haen (Seelze, Lower Saxony, Germany). The internal standard m-terphenyl (99%) was purchased from J&K Chemical, China. Activated neutral alumina (75–300 Mesh) was purchased from International Laboratory, USA. Anhydrous sodium sulfate and copper were purchased from Sinopharm Chemical Reagent Co.(Shanghai, China). Before use, silica gel and anhydrous sodium sulfate were activated for more than 6 h at 500 °C. Acidified silica gel was prepared by adding 27 mL concentrated sulfuric acid dropwise to 50 g activated silica gel with stirring (Covaci et al., 2002). Activated copper powder was prepared by mixing copper

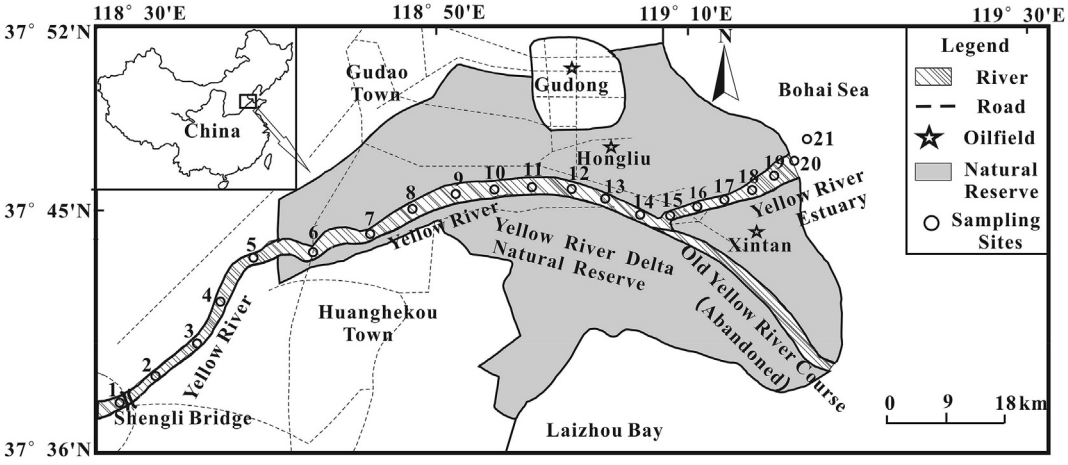


**Fig. 1.** Sampling locations in the Yellow River Estuary, China (Yuan et al., 2015).