DISTRIBUTION AND LEVELS OF POLYBROMINATED DIPHENYL ETHERS IN THE SURFACE SEDIMENT AT THE MIDDLE AND LOWER REACHES OF YANGTZE RIVER DELTA REGION

Zhang T, Dong L, Zhang LF, Shi SX, Zhou L, Zhang XL, Huang YR

National Research Center for Environmental Analysis and Measurement, State Environmental Protection Key Laboratory for Dioxin Pollution Control, No. 1 Yuhuinanlu, Chaoyang District, Beijing 100029, China

Introduction

The Yangtze River Delta (YRD) is an important zone in China because of its relative higher GDP output, rapidly growing economic and more population than other regions, In 2008 its GDP output ranks 1 and accounts for 20 percent China grass national product[1]. It also has a history of Polybrominated diphenyl ethers (PBDEs) production and use from 80s' and flourished around the year of 2000[2], when PBDEs are widely used in the textile, electronic and furniture products and there are many related raw material and processing manufactories in YRD. Atmospheric PBDEs can be caught and dropped to the ground in the ways of dry and wet deposition, while PBDEs in soil, which originate from unintentional waste disposal or illegal e-waste dismantling activities, may be washed by the streams of small rivers and brooks passing by YRD. Both of them and the discharge from plants finally are collected to two main water-ways, i.e. Yangtze River and Beijing-Hangzhou Grand Canal, and then flow to the Yellow Sea. So YRD is a main source of PBDE pollution for Yellow Sea as well. In this study, 25 surface sediment samples were collected in a YRD region, i.e. three cities of Nantong, Wuxi and Suzhou, in order to investigate the PBDEs residue level in the sediment, and make comparison in China and around the world[2-5].

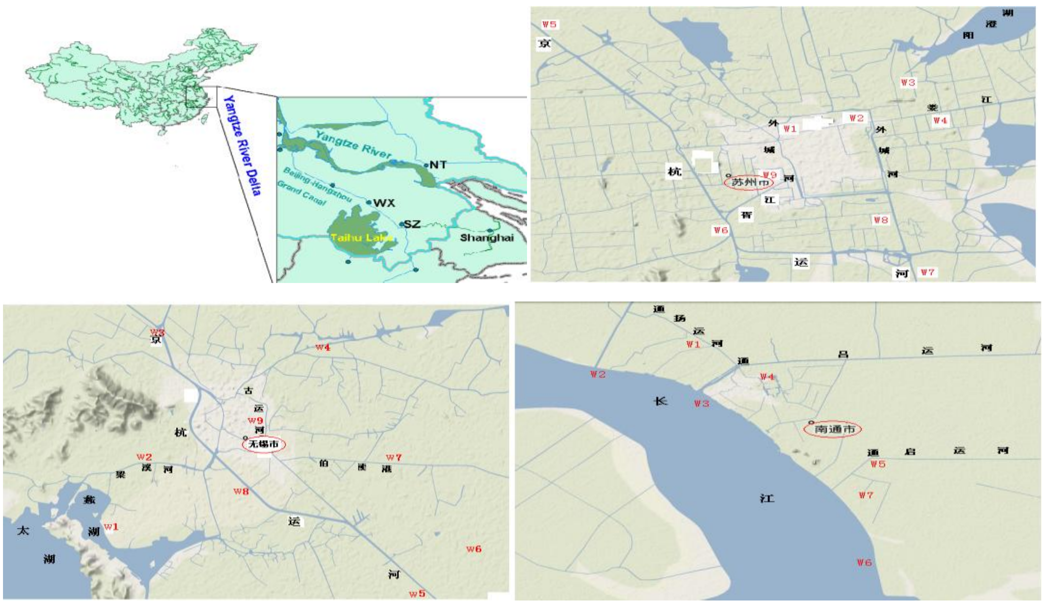

Fig.1 sediment sampling sites at the middle and lower reaches of Yangtsi River Delta region

Materials and methods

Sampling:

25 surface sediment samples were collected from the Beijing-Hangzhou Grand Canal, Yangtze River or brooks in three cities of Nantong, Wuxi and Suzhou, from June to July, 2009 (see Fig.1). Using a stainless steel grab sampler, the sediment cores were scooped to glass bottles with a lid in which a Teflon film embed. Samples were transported to laboratory on ice and frozen at -20℃ before analysis.

Sample preparation:

The sediments were freeze-dried, grounded and sieved. After extraction by Acceleration Solvent Extractor (ASE 300, Dionex, USA) , the extract was concentrate and then spiked with carbon isotope labeled clean -up standards, i.e. 7 tri-hepta BDEs (labeled BDE 28, 47, 99, 100, 153, 154, 183, MBDE-MFXs, Willington lab, Canada) and labeled BDE-209. (EC-5003, Cambridge Isotope Lab., USA).A Sulfuric acid treatment was carried out before the multilayer Silica column cleanup procedure., the column was packed with Florisil, Sulfuric acid Silica, Potassium Hydroxide Silica and activated neutral Silica, 25% dichloromethane in Hexane is used as elution solvent.

Instrumental Analysis:

39 tri-hepta PBDEs (BDE-AAP-A-15X, Accustandard Inc., USA) were determined by Agilent 7890/5975C GC/MS in EI mode (Agilent Corp. USA) in the pulse injection mode, using a 30m×0.25μm i.d.×0.25μm film thickness DB-5MS capillary column (J&W Corp. USA). An internal standard method is employed using the clean-up standard as the internal standard for quantitative measurement as well.

BDE-209 were analyzed with the isotope dilution method using QP-2010 plus GC-NCI-MS (Shimadzu Corp. Japan) in the pulse injection mode, using a 15m×0.25μm i.d.×0.10μm film thickness ZB-5HT capillary column (Restek Corp. USA).

Results and discussion:

PBDEs in the surface sediment of SZ, WX, and NT

The total tri-hepta brominated bdes and bde 209 concentrations in the surface sediment of SZ, WX, and NT were given in Table 1. We also made data comparison in China and around the world (Table 1). PBDEs in the surface sediment of SZ, WX, and NT were comparable to data in literatures. The major congeners detected in the surface sediment were BDE-28,-47,-49,154,183 and 209. Bde-209 was the most predominant congener and account for over 90% PBDEs mass concentration for all samples. The summary of PBDEs concentrations in sediment list Table 1.

In general YRD have lower PBDEs concentration in sediment than in Zhujiang River and Dongjiang River located in Peal River Delta[2], another famous region with highly concentrated manufactories in China, Such difference may be attributed to the discrepancy of manufactory enterprises in two regions. In this study PBDEs levels in YRD sediment are found higher than in sediments of Yangtze River and its estuary[3], It could be partially caused by the different sedimentation properties at sampling sites, In Yangtze River the large stream volume may hinder suspended particle deposition.

Table 1: Total PBDEs concentration (ng/g) in the surface sediment of SZ, WX, and NT and comparison with data in China and around the world

Study area	ΣPBDEs*	BDE-209
Yangtzi River Delta region (this study)	3.48(0.33-16.0)	375(56.6-2059)
Nantong (n=7, this study)	1.69(0.33-4.06)	598(68.0-2059)
Suzhou (n=9, this study)	5.94(0.53-15.96)	327(101-535)
Wuxi (n=9, this study)	2.41(0.84-6.99)	249(56.6-624)
Peal River Delta		
Zhujiang River	12.9 (1.1- 49.3)	890 (26.3-3580)
Dongjiang River	27.3 (2.2- 94.7)	1440 (21.3 -7340)
Xijiang River	0.36 (0.1-0.6)	16.1 (1.9-77.4)
South China Sea	0.5 (0.04-4.5)	2.8 (0.4- 9.1)
Yangtze River Delta	ND-0.55	0.16-94.6
Rivers and estuaries, Japan	21–59	＜25–11600
Great Lake, USA	0.3-6.3	4-242
Singapore coastal marine	3.4-13.8	
Coastal location, South Korea	0.45–494	0.22–493
Sweden	8-50	68-7100
Spain	0.4-34.1	2.1-132

*: bde 209 not included

PBDEs congener profiles in the surface sediment of SZ, WX, and NT

BDE209 is the predominant congener, accounting for over 90% PBDEs mass concentration in all samples, it indicates commercial deca BDE product is the main PBDEs produced and in use in YRD, as reported in other region in China and most of Asian countries. We check the congener pattern except for BDE 209 of the surface sediment samples in SZ, WX, and NT, as shown in Figure 2. We also compare the pattern with that of the industrial product (Fig.3) reported in literature. Some similarity can be found.

Spatial profile of PBDEs concentration

The spatial distribution of bde 209 are showed in Figure 4. The high BDE 209 concentration in NT1 and NT7 samples make the average of Nantong sediment higher than Suzhou and Wuxi. NT7 is sampled at a brook close to a flame retardant material plant.

Figure 5 shows the spatial distribution of tri-hepta brominated BDEs. More and higher concentration of PBDE congeners (except for BDE-209) are found in Suzhou than in Nantong and Wuxi.

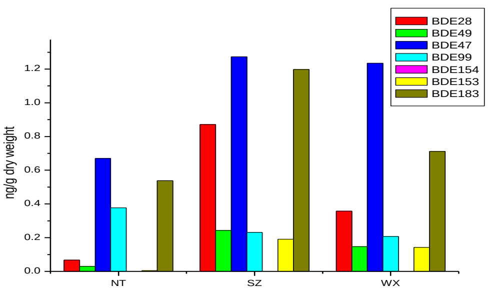

Figure 2 PBDEs congener pattern in the surface sediment of three cities,

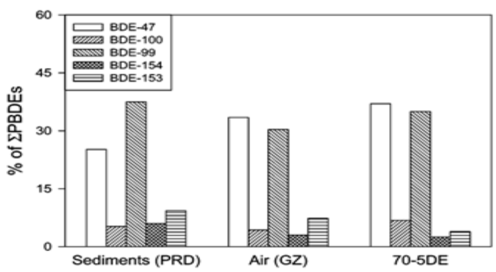

Figure 3 Congener pattern for commercial Penta BDE product

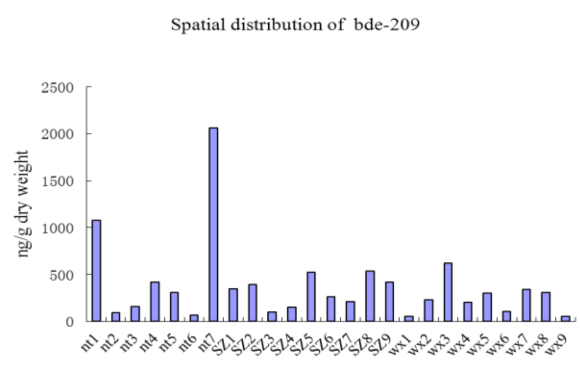

Figure 4 BDE 209 concentrations in the surface sediment

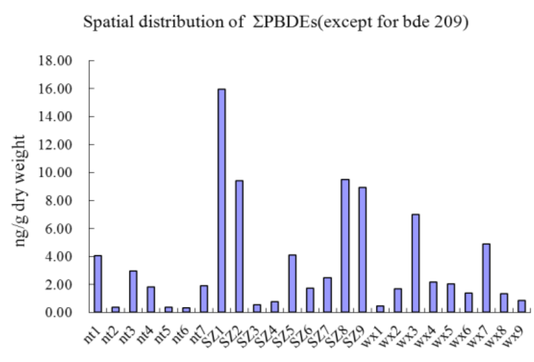

Figure5 Tri-hepta BDEs concentrations in the surface sediment

Relationship of PBDEs concentration and OC content in sediment samples

After normalize the BDE209 concentration with OC content for all samples, the concentration ranks change for some samples including NT1(Figure 6), it indicate the high BDE 209 mass concentration of NT1 probably due to its relative high OC content.

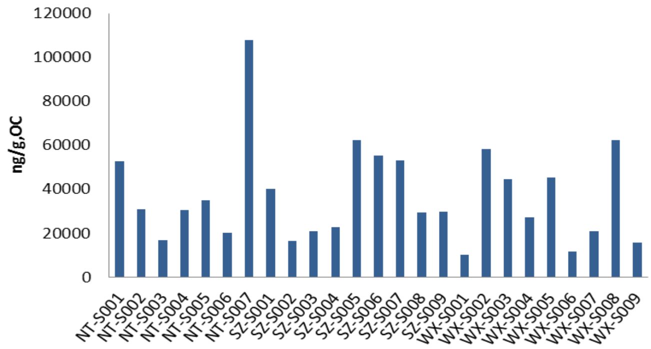

Figure 6 BDE 209 concentrations normalized by OC content

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