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Levels and distribution of polybrominated diphenyl ethers in Three Gorges Reservoir, China

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) were investigated in water, sediments, suspended sediments and biofilms in Three Gorges Reservoir (TGR), China. Results showed that dissolved bioavailable PBDEs in water of TGR collected with semipermeable membrane device (SPMD)-based virtual organisms (VOs) were very low in the range of n.d. to 811 pg/g lipid and the detected compounds were mainly low molecular BDEs such as BDE-15, 17, 28, 47, 49, 66, 99 and 100. The PBDE levels in the sediment core collected near the dam were also very low in the range of 84–300 pg/g dw and the detected compounds were mainly large molecular BDEs such as BDE-196, 197, 206, 207 and 208. In suspended sediments and biofilms, the levels of PBDEs ranged from 298 to 52,843 pg/g dw and the detected compounds were also mainly large molecular BDEs such as BDE- 196, 197, 201, 203, 206, 207, 208 and 209. The dominant compound was BDE-209 which accounted for more than 90% of the total BDEs. Therefore, large molecular BDEs tended to be attached on fine particles. The vertical profile of BDEs on suspended sediments (SS) showed that SSs in the middle depth of water contained high level of BDE-209. The phenomenon indicated that most of BDE-209 did not settle into the sediment in front of the dam, instead transported further to downstream.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are widely utilized fire retardants embedded in textiles, plastics, electrical components, paints, foam, rubber, and other casing material [1]. They are halogenated organic compounds which are hydrophobic, bioaccumulative, and persistent [2]. Due to their toxicity of reproductive, immunologic, and neurologic disruptive nature [3], these compounds have been extensively investigated in many environmental matrices. A stable or increasing trend of concentration found in these matrices has caused great concern [4,5].

The Three Gorges Area (TGA) has been rice and orange fields for several centuries with a populous area of 55,800 km^2. Economically, the people (16 million) in TGA depend on the Three Gorges Reservoir (TGR) as a source of fresh drinking water and fishing as a source of favorite food in the local diet. The Three Gorges Dam (TGD) constructed on the Yangtze River in China is the largest hydro-electricity project in the world which created the TGR with an area of 1080 km^2. The closing of the TGD has resulted in drastic environmental alterations, for example, water flow becomes much slower which influences contaminants transport and fate in the water system. So far, the information on the contamination of PBDEs in TGR is limited. Available references include reports of Zhao et al. [6] on investigating PBDEs in surface sediments from

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TGR and Wolf et al. [7] for determining water concentration of PBDEs in TGR. However, no information is available on sediment cores, suspended sediments and biofilms in TGR. To better understand the environmental behavior of these compounds in the reservoir and their potential risk, it is essential to investigate their distribution, congener profiles, transportation and inventories in the different matrices in TGR.

The objectives of this study were to determine occurrence and congener profiles of PBDE in water, sediment cores, suspended sediments and biofilms from Three Gorges Reservoir and to evaluate the level, distribution and transportation of PBDEs in TGR. Triolein containing semipermeable membrane device (SPMD) were used as biovirtual organism (VO) to collect PBDE congeners in the water column. Biofilm was the biofouling grown on the surface of SPMD membranes. Sediment core and suspended sediment (SS) were collected in front of the dam to investigate the vertical distribution profile of PBDEs in the area.

2. Methods and materials

2.1. VO samplers and deployment in TGR

The SPMD-based VO samplers were prepared in the manner described in our previous paper [8]. Briefly, the semipermeable membranes were prepared using lay-flat polyethylene tubing (from VWR Ismaning, Germany; 2.5 cm wide and 65 μm thick). The tubing was cut into 29 cm pieces and 700 μL of triolein (Sigma, Munich, Germany, 99%) were pipetted into each piece of tubing before sealing the ends. For chemical analysis, the triolein was spiked with 16 ^{13}C-labeled PAHs (Cambridge Isotope Laboratories, USA) as performance reference compounds (PRC) [8]. The prepared VOs were stored in heat treated 10 mL glass vials with aluminum foil sealed at −28 °C and kept cooled during transportation until deployment.

The sampling sites spanned the whole reservoir from the upstream Chongqing to the great dam, covering more than 600 km long distance. The sampling sites were MP (Maoping), GJB (Guojiaba), BD1 (Badong), BD2 (Badong), DN1 (Wushan), DN2 (Wushan), FJ (Fengjie), XJ1(Yunyang), XJ2(Yunyang), WZ (Wanzhou), CS (Changshou), CQ (Chongqing) (Fig. 1). In late April to May 2008, the SPMDs were deployed for 7 d and 25 d at seven sites (MP, GJB, BD1, BD2, WZ, CS, CQ) in the TGR and in the same period in 2009, the SPMDs were deployed for 14 d and 25 d at the same seven sites. In the sampling campaign from late April to May in 2011, 5 sites were added for deploying SPMDs which were DN1, DN2, FJ and XJ1, XJ2.

The VOs were deployed in stainless steel cages and immersed into the water at about 1 m depth. Each cage contained 4 replicates of VOs. The samplers were mounted on boats or fastened to docks which were about 10–20 m from the river bank. The VOs for the determination of blanks were prepared together with the other VOs for sampling. VO blanks were transported to the sampling sites as well in clean airtight jars, not deployed. After retrieval, the VOs were transported to the laboratory in the corresponding glass jars protected from light and were kept in a freezer at −28 °C until processing.

2.2. Collection of sediment cores, suspended sediments and biofilms

Sediment cores were obtained with a stainless gravity sediment core sampler (100 cm in length and 25 cm in diameter) at MD (7 km away from the dam) in September 2012. The core was sliced into 10 cm fractions with a spatula from top to bottom layers. Suspended sediments (SS) were collected with multi-pore stainless boxes in September 2012 which were deployed in the water at the depths of 1, 11, 21, 31, 41, 51 and 61 m at the same site MD for one month. Biofilms were collected by scraping gently the biofoulings from the surface of the SPMDs which were deployed in TGR in May of 2009 and May of 2011.

2.3. Sample extraction and clean up

All organic solvents were of picograde quality and were obtained from LGC standards (Wesel, Germany). For later quantification, samples were spiked before extraction with a mixture of ^{13}C-labeled brominated flame retardants BFR-LCS (Wellington Laboratories, Canada) to monitor the extraction and cleanup procedures. All of the sediment samples, suspended sediments and biofilms were lyophilized. 1–5 g of the samples were extracted with Accelerated Solvent Extractor by 100 mL solvent mixture of hexane and acetone (1:1 v:v). The extraction method for VO was according to our previous study [8]. In brief, the VO was cut into small pieces and extracted in 100 mL cyclohexane overnight at 200 rpm on a left-right shaker. The volume of the extraction solution of VOs or particles was reduced to one drop around 1 mL using vacuum rotary evaporation. The residue was redissolved again with

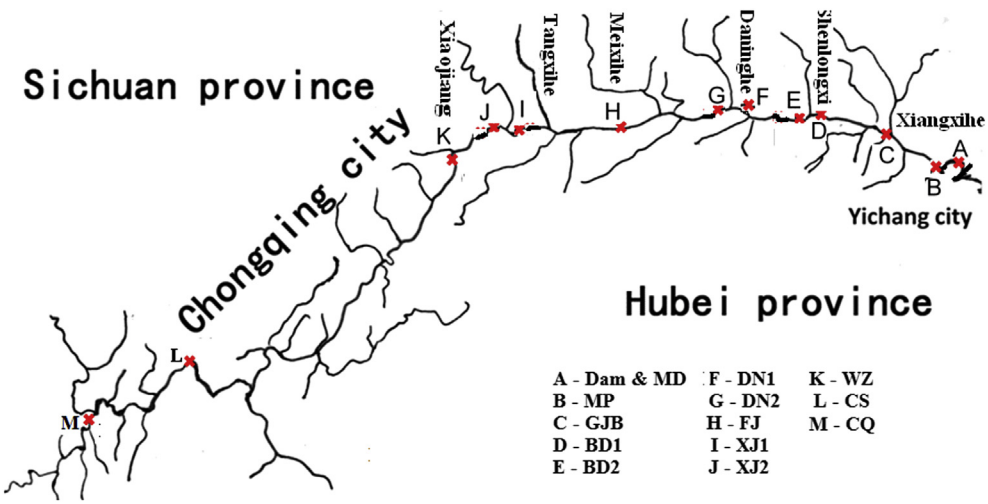

Fig. 1. Scheme of sampling sites in Three Gorges Reservoir.

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