



Spatial distribution and implications to sources of halogenated flame retardants in riverine sediments of Taizhou, an intense e-waste recycling area in eastern China



Shanshan Zhou^a, Jie Fu^{a, c}, Huan He^{b, *}, Jianjie Fu^c, Qiaozhi Tang^d, Minfeng Dong^a, Yongqiang Pan^a, An Li^{e, a}, Weiping Liu^d, Limin Zhang^b

^a College of Environment, Zhejiang University of Technology, Hangzhou 310032, China

^b School of Environment, Nanjing Normal University, Nanjing, 210023, China

^c State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

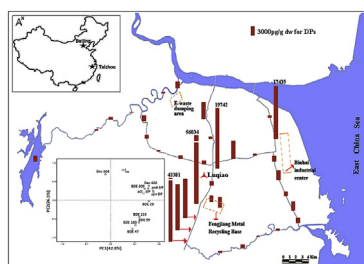
^d Ministry of Education Key Laboratory of Environmental Remediation & Ecosystem Health, College of Environmental and Research Sciences, Zhejiang University, Hangzhou 310058, China

^e School of Public Health, University of Illinois at Chicago, Chicago, IL 60612, United States

HIGHLIGHTS

- Residues of DPs were similar to the median of levels reported globally.
- Dec 604 stemmed from agrochemicals, while others from the use of flame retardants.
- Degradation of PBDEs and DP was evident.
- Distribution of DPs was influenced by a combination of diffuse and point sources.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 3 May 2017

Received in revised form

23 June 2017

Accepted 24 June 2017

Available online 26 June 2017

Handling Editor: Myrto Petreas

Keywords:

Dechlorane Plus
Flame retardants
e-waste recycle
Source apportionment
Sediment

ABSTRACT

Concentrations and spatial distribution pattern of organohalogen flame retardants were investigated in the riverine surface sediments from Taizhou, an intensive e-waste recycling region in China. The analytes were *syn*- and *anti*- Dechlorane Plus (DP), Dechloranes 602, 603, and 604, a DP monoadduct, two dechlorinated DPs and 8 congeners of polybrominated diphenyl ethers (PBDEs). The concentrations of Σ_8 PBDEs, Σ DP, Σ Dec600s, and Σ DP-degradates ranged from <100 to 172,000, 100 to 55,000, not detectable (nd) to 1600, and nd to 2800 pg/g dry weight, respectively. BDE-209 and DP, both have been manufactured in China, had similar spatial distribution patterns in the study area, featured by distinctly recognizable hotspots some of which are in proximity to known e-waste dumping or metal recycling facilities. Such patterns were largely shared by Dec602 and dechlorinated DP, although their concentration levels were much lower. These major flame retardants significantly correlate with each other, and cluster together in the loading plot of principle component analysis. In contrast, most non-deca PBDE congeners do not correlate with DPs. Dec604 stood out having distinctly different spatial distribution pattern, which could be linked to historical use of mirex. Organic matter content of the sediment was not

* Corresponding author.

E-mail address: huanhe@njnu.edu.cn (H. He).

the dominant factor in determining the spatial pattern of pollution by halogenated flame retardants in the rivers of this study.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Dechlorane Plus (DP) is a highly chlorinated norbornene-based flame retardant used in electrical wire and cable coatings, computer and televisions connectors, and plastic roofing materials (OxyChem, 2011). DP was suggested as a potential substitute to decabromodiphenyl ether (deca-BDE) in some applications (European Commission, 2007). It is a high production volume (HPV) chemical in the United States (U.S. EPA, 2008). Other dechlorane series compounds, such as Dechlorane 602 (Dec602), Dechlorane 603 (Dec603), and Dechlorane 604 (Dec604) were also patented as flame retardants (FRs) in the 1970s (Shen et al., 2010, 2011a, 2011b). After the first detection of DP and Dec 600s (Dec602, 603, and 604) in the environment (Hoh et al., 2006; Shen et al., 2010), their occurrence has been reported all over the world (Sverko et al., 2008; Wang et al., 2016). DP analogs such as Dechlorane Plus monoadduct (DPMA), DP degradation products like undecachloropentacyclooctadecadiene (Cl₁₁-DP) and decachloropentacyclooctadecadiene (Cl₁₀-DP) have also been detected in the environment (Sverko et al., 2008; Wang et al., 2016).

Electrical and electronic equipment, such as cell phones, televisions, and computers, is one of the largest categories of consumer products containing flame retardants. Such equipment eventually becomes electronic waste (e-waste) and would be dismantled to recover useful components. Emissions from e-waste recycling activities have been identified as an important source of flame retardants to the ambient environment, and found to increase the health risk of local residents (Wang et al., 2016). For example, elevated DP levels have been found in abiota, biota, and human samples collecting from e-waste recycling regions (Ben et al., 2013; Chen et al., 2011; Li et al., 2014; Mo et al., 2013; Ren et al., 2009; Yu et al., 2010; Zheng et al., 2010).

Taizhou is a medium-sized city in China, located at the central coastal section of Zhejiang Province. By the end of 2014, Taizhou had a total population of 5.97 million. It has been one of the largest e-waste recycling areas in the world since the 1980s (Chi et al., 2011). E-waste recycling operations are mainly in the towns of Luqiao and Wenling in southern Taizhou (Li et al., 2014). Each year, approximately 2.2 million metric tons of e-waste is processed in Taizhou (Chan et al., 2007). Unregulated primitive manner of the operations and dumping of the residual waste has resulted in severe contamination of the local environment (Fu et al., 2011; Ma et al., 2009, 2011). Several studies have revealed the existence of DP, Dec602, and *anti*-Cl₁₁-DP in the living beings from Taizhou (Ben et al., 2013, 2014; Li et al., 2014; Wu et al., 2016). DP was also detected in the air (Sun et al., 2017) and in the floor particles of several e-waste recycling workshops in Taizhou (Zeng et al., 2016). However, little is known on the occurrence, spatial distribution, and sources of DP and its structurally related compounds in Taizhou's water environment.

In the present study, the concentrations of 8 DPs, including *syn*-DP, *anti*-DP, Dec602, Dec603, Dec604, DPMA, *anti*-Cl₁₀-DP and *anti*-Cl₁₁-DP in sediment samples from five main rivers in Taizhou were measured. Concentrations of selected congeners (BDEs 28, 47, 100, 99, 154, 153, 183, and 209) of polybrominated diphenyl ethers (PBDEs) were also measured to examine the correlations among flame retardants. The spatial distribution and the site-specific

contaminant patterns were analyzed to reveal potential sources of the targeted chemicals in the study area.

2. Materials and methods

2.1. Site description and sampling

Thirty-four surface sediment samples were collected during July 22–25, 2013, from five rivers, which run through the urban, industrialized, rural, or e-waste recycling areas of Taizhou and finally enter the East China Sea (ECS). A sampling map is shown in Fig. 1A, and site information is provided in Table S1 of Supplementary Material (SM). Sampling sites were chosen from the upstream to the downstream of each river within the study area, with 3–5 km apart between sites. Additional description of the rivers and sampling sites is provided in SM.

The top 5 cm of the sediments were taken with a stainless steel grab sampler and stored in stainless steel containers during transport under chilled conditions. All samples were freeze-dried, homogenized, passed through a 60 mesh sieve and kept at –20 °C before further analysis. Subsamples were analyzed for organic matter fraction (*f*_{OM}) using previously established method (Zhou et al., 2014), and the results are provided in Table S1.

2.2. Chemical analysis

Chemical information and details of laboratory procedures are given in Supplementary Material. A brief description is given below.

For each sample, 10 g freezing-dried sediment was spiked with surrogate standards (¹³C-PCB141 and ¹³C-PCB208), and Soxhlet-extracted. Anhydrous sodium sulfate and activated copper were added for removing water and elemental sulfur, respectively. The extract was concentrated by a rotary evaporator and the solvent was exchanged to 1–2 mL hexane. Cleanup of the extracts was conducted by the use of a glass column packed with Florisil, and target compounds were eluted with 40 mL of hexane:DCM (4:1). After volume reduction and solvent exchange to isoctane, internal standard ¹³C-PCB202 was added before instrumental analyses.

All samples were quantitatively analyzed using an Agilent 7890/5973 gas chromatography – mass spectrometry (GC–MS) (Agilent Technologies, Santa Clara, California) with electron capture negative ionization. The GC was equipped with a DB-5HT capillary column (15 m × 0.25 mm × 0.10 μm; J&W Scientific). Identification of the compounds was performed by comparing their retention times and mass spectra with those of the standards. For each analyte, quantification was achieved via selected ion monitoring of the molecular ion with the most intensive isotopic abundance, and by use of a calibration curve based on the internal standard. All concentrations were normalized to dry weight (dw) and were not adjusted using surrogate recovery.

2.3. Quality control (QC)

For every set of 15 samples, a solvent blank and a procedure blank were run to check for interference and cross-contamination. The concentrations of *anti*-DP in all blanks were less than 0.5 pg/g dw, while those of other analytes were below their respective

Download English Version:

<https://daneshyari.com/en/article/5746232>

Download Persian Version:

<https://daneshyari.com/article/5746232>

[Daneshyari.com](https://daneshyari.com)