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Characterization of anthropogenic impacts in a large urban center by examining the spatial distribution of halogenated flame retardants☆

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ABSTRACT

Anthropogenic impacts have continuously intensified in mega urban centers with increasing urbanization and growing population. The spatial distribution pattern of such impacts can be assessed with soil halogenated flame retardants (HFRs) as HFRs are mostly derived from the production and use of various consumer products. In the present study, soil samples were collected from the Pearl River Delta (PRD), a large urbanized region in southern China, and its surrounding areas and analyzed for a group of HFRs, i.e., polybrominated diphenyl ethers (PBDEs), decabromodiphenyl ethane, bis(hexachlorocyclopentadieno) cyclooctane (DP) and hexabromobenzene. The sum concentrations of HFRs and PBDEs were in the ranges of 0.66–6500 and 0.37–5700 (mean: 290 and 250) ng g^{-1} dry weight, respectively, around the middle level of the global range. BDE-209 was the predominant compound likely due to the huge amounts of usage and its persistence. The concentrations of HFRs were greater in the land-use types of residency, industry and landfill than in agriculture, forestry and drinking water source, and were also greater in the central PRD than in its surrounding areas. The concentrations of HFRs were moderately significantly ($r^2 = 0.32$–0.57; $p < 0.05$) correlated with urbanization levels, population densities and gross domestic productions in fifteen administrative districts. The spatial distribution of DP isomers appeared to be stereoselective as indicated by the similarity in the spatial patterns for the ratio of *anti*-DP versus the sum of DP isomers ($f_{anti\text{-}DP}$) and DP concentrations. Finally, the concentrations of HFRs sharply decreased with increasing distance from an e-waste recycling site, indicating that e-waste derived HFRs largely remained in local soil.

1. Introduction

Urbanization is an essentially irreversible process accompanied with industrialization that spurs the migration of rural residents to urban centers (Engelke, 2012). As a consequence, large urban centers have become sources of anthropogenic impacts on the environment. This trend is expected to continue, particularly in developing countries, as the level of urbanization in these countries remains relatively low as compared to developed countries. Urbanization has created a series of pollution issues, exerting long-term stress to the health of the eco-environment and human beings (Chen, 2007; Lin et al., 2014; Szolnoki et al., 2013). The imbalance of social and economic development, however, may have resulted in substantial disparity in terms of the spatial distribution of environmental contamination.

The situation in China, the largest emerging economy in the world, is quite alarming, as the urbanization process is still underway at a fast pace. One source estimated that the urbanization level rose from 19.4% in 1980 to 50% in 2010 (China Statistical Yearbook, 2011). The rising standard of living, largely thanks to the rapid economic growth in the last three decades, has created strong demand for a variety of consumer products, e.g., textiles, electronics, thermoplastics, and building materials. For example, the outputs of washing machines, refrigerators, color television sets and air-conditioners had been escalating since 1978, when the Reform and Open Policy was first implemented (Fig. S1 of the Supplementary Data; "S" represents figures and tables in the Supplementary Data thereafter). Accompanied with this production

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surge, the global demand for halogenated flame retardants (HFRs) used to reduce the flammability in consumer products has increased by 4.6% per year and projected to reach 2.8 million metric tons in 2018 (http://www.marketresearch.com/Freedonia-Group-Inc-v1247/Flame-Retardants-8783038/). Because HFRs may be released to the environment during the manufacture and use of HFRs-containing commercial products (Alaee et al., 2003), their residual levels in the environment may be a good indicator of industrial output and human population.

The major component of HFRs, polybrominated diphenyl ethers (PBDEs), have been gradually banned or restricted for use in many countries, e.g., Deca-BDE was banned in Europe in 2008 (Law et al., 2008), Penta-BDE and Octa-BDE were phased out in USA in 2008 (Ward et al., 2008), while they were also banned in China in 2007 (Ding et al., 2016). Alternative novel HFRs including decabromodiphenyl ethane (DBDPE), bis(hexachlorocyclopentadieno) cyclooctane (DP) and hexabromobenzene (HBB) that meet the fire and safety regulations were introduced to replace PBDEs (Covaci et al., 2011; Sverko et al., 2011). Due to their persistence, bioaccumulation and biomagnification, PBDEs and novel HFRs may coexist in the environment and pose a great threat to human health (Du et al., 2016; Law et al., 2008).

China is one of the most rapidly expanding HFR markets worldwide (http://www.marketresearch.com/Freedonia-Group-Inc-v1247/Flame-Retardants-8783038/), while the Pearl River Delta (PRD) located in southern China (Fig. 1) is an important manufacturing base of electronic/electrical products, textiles and building materials in the world. In addition, Qingyuan located in north of Guangzhou, the center of the PRD (Fig. S2), houses a large number of e-waste recycling facilities. Approximately 145 million pieces of obsolete electronic/electrical devices were processed in Qingyuan using mostly primitive techniques in 2002 (Martin et al., 2004). Therefore, it is not unexpected that samples of air, dust, sediment and birds collected from the PRD and surrounding areas contained high levels of HFRs (Li et al., 2014; Luo et al., 2009b, 2014; Peng et al., 2015; Shi et al., 2009; Sun et al., 2014; Yu et al., 2014). These previous findings hinted the feasibility of utilizing HFRs to assess anthropogenic impacts on a regional scale in the PRD.

To this end, the present study was designed to determine the spatial pattern of HFRs in the PRD and its surrounding regions. Regional socioeconomic factors, such as population density, gross domestic production (GDP) and urbanization level, were also examined. Finally, concentrations of HFRs discharging from e-waste recycling site were compared with those at its surrounding areas to figure out the transport potential of derived HFRs from e-waste dismantling activities.

2. Materials and methods

2.1. Materials

Twenty-five target BDE congeners, including BDE-15, -17, -28, -47, -66, -71, -77, -85, -99, -100, -126, -138, -153, -154, -166, -181, -183, -190, -196, -203, -204, -206, -207, -208 and -209, and DP were purchased from AccuStandard (New Haven, CT, USA). Two other target standards, i.e., DBDPE and HBB, were obtained from Cambridge Isotope Laboratories (Andover, MA, USA) and Wellington Laboratories (Guelph, ON, Canada), respectively. The surrogate standards BDE-51, BDE-115 and ^{13}C-BDE-209 and internal standards BDE-69, ^{13}C-PCB-208 and ^{13}C-BDE-139 were supplied by Cambridge Isotope Laboratories. Hexane and dichloromethane of HPLC grade were acquired from Honeywell (Morristown, NJ, USA). In addition, acetone of analytical grade was obtained from Chemical Reagent Factory (Tianjin, China) and redistilled prior to use. Copper sheets were activated with diluted HCl, and washed with distilled water and acetone sequentially.

2.2. Sample design and sample collection

Two hundred and twenty-nine soil samples were collected from the PRD and surrounding areas, southern China between December 2009 and March 2010 (Wei et al., 2014b). The sampling region is divided into six land-use types, i.e., residency, industry, landfill, agriculture, forestry and drinking water source (Fig. 1). In addition, fifteen administrative districts within the sampling region are divided into four groups, e.g., the central PRD (Shenzhen, Dongguan, Guangzhou, Zhuhai, Zhongshan and Foshan), the PRD's periphery (Zhaoqing, Jiangmen, Qingyuan and Huizhou), the East (Shaoguan, Heyuan and Shanwei) and West (Yangjiang and Yunfu) regions (Fig. 1), in an attempt to elucidate the spatial patterns of soil HFRs contamination.

2.3. Sample extraction and instrument analysis

Each freeze-dried soil sample (~20 g) was Soxhlet-extracted with 170 mL of hexane:acetone:dichloromethane mixture (2:1:2 in volume) after surrogate standards (BDE-51, BDE-115 and ^{13}C-BDE-209) and copper sheets were added. The extract was concentrated and subject to purification/fractionation in a column (13 mm i.d.) consisting of silica gel and alumina, i.e., from bottom to top, with neutral alumina (6 cm, 3% deactivated), neutral silica gel (2 cm, 3% deactivated), 25% sodium hydroxide silica (5 cm), neutral silica gel (2 cm, 3% deactivated), 44% sulfuric acid silica (6 cm) and anhydrous sodium sulfate (1 cm). The fraction eluted with 80 mL of a hexane/dichloromethane mixture (1:1 in volume) was collected, concentrated and solvent exchanged with hexane. A known amount (2.5 ng) of internal standards (BDE-69, ^{13}C-PCB-208, ^{13}C-BDE-139) was added to each extract before GC/MS analysis.

Target HFRs (BDE-15, -17, -28, -47, -66, -71, -77, -85, -99, -100, -126, -138, -153, -154, -166, -181, -183, -190, -196, -203, -204, -206, -207, -208 and -209, DBDPE, DP and HBB) were quantified with a gas chromatograph coupled to a mass spectrometry (Shimadzu GC/MS-QP2010 Plus; Kyoto, Japan) in the negative chemical ionization mode and separated with a DB-5HT column (15 m × 0.25 mm i.d., 0.10 μm film thickness). Ultra-pure helium was used as the carrier gas at a flow rate of 1.5 mL min^{-1}. Extract volume of 1 μL was injected in the splitless/split mode at 290 °C. Ion source and transfer line temperatures were set at 250 and 280 °C, respectively. In addition, the oven temperature was initially held at 110 °C for 5 min, ramped to 200 °C at 40 °C min^{-1} (held for 4 min), increased to 260 °C at 10 °C min^{-1} (held for 1 min) and finally programmed to 315 °C at 15 °C min^{-1} and held for 12 min. The qualification and qualifier ions of target analytes were described previously (Zhang et al., 2013).

2.4. Quality assurance and quality control (QA/QC)

A procedural blank, spiked blank, matrix blank, matrix spiked sample and three sample replicates were processed as quality control samples for every batch of 17 field samples. Matrix blank and matrix spiked samples were randomly selected from extracted soil samples. The recoveries (mean ± standard deviation) for the target analytes in spiked samples were from 59 ± 14% to 96 ± 15%. In addition, recoveries of the surrogate standards, i.e., BDE-51, BDE-115 and ^{13}C-BDE-209 were 97 ± 16%, 108 ± 24% and 99 ± 27%, respectively, for all samples. With soil sample weights ranging from 14 to 29 g and the final extract volume of 50 μL, the reporting limits (RLs) were in the ranges from 0.002 to 0.18 ng g^{-1} for individual HFR congeners (Table 1).