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.

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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 ($r^2 = 0.32\text{--}0.57$; $p < 0.05$) 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.

Keywords: Urbanization; Anthropogenic impact; Halogenated flame retardant; Pearl River Delta; Soil

“Capsule”: The anthropogenic impacts in a large urban center were examined by the spatial distribution of soil halogenated flame retardants.

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 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 co-exist 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/Freedomia-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., 2014; Luo et al., 2009b; 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 $\times$ 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 $\pm$ standard deviation) for the target analytes in spiked samples were from 59 $\pm$ 14% to 96 $\pm$ 15%. In addition, recoveries of the surrogate standards, i.e., BDE-51, BDE-115 and ¹³C-BDE-209 were 97 $\pm$ 16%, 108 $\pm$ 24% and 99 $\pm$ 27%, respectively, for all samples. With soil sample weights ranging from 14 to 29 g and the final extract volume of 50 μ L, the reporting limits (RLs) were in the ranges from 0.002–0.18 ng g⁻¹ for individual HFR congeners (Table 1).

2.5. Data analysis

All measured concentrations were blank corrected, but not surrogate standard recovery corrected, and were normalized to dry sample weight. Ordinary Kriging interpolation under ArcGIS Version 10.0 (ESRI, Redlands, USA) was used to map out the spatial distributions of soil HFR concentrations. Significant differences in concentrations and compositional profiles between/among different administrative districts and land-use types were examined with SPSS Version 13.0 (SPSS, Chicago, IL, USA) using one-way analysis of variance. Any

significant difference between two sets of samples with unequal variances from the present study and previous studies was determined by a Welch's *t*-test. Criterion of significance was defined as $p < 0.05$ in all statistical analyses.

3. Results and discussion

3.1. HFRs levels and comparison with global values

Concentrations of $\sum$ HFR (sum of 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) varied in the range of 0.66–6500 ng g⁻¹ with a mean (median) value of 290 (47) ng g⁻¹ (Table 1). Moreover, PBDEs were detectable with fairly high frequency, i.e., 64–100% for individual PBDEs. BDE-209 was detectable in all samples with a concentration range of 0.20–4400 and a mean value of 211 ng g⁻¹ (Table 1). By comparison, the concentrations of other BDE congeners were in the range of < RL–500 ng g⁻¹ with mean values of 0.06–11.9 ng g⁻¹, significantly lower than those of BDE-209 ($p < 0.05$). The concentrations of BDE homologues increased from di-BDE to hexa-BDE, declined substantially from hexa-BDE to hepta-BDE and rose again from hepta-BDE to deca-BDE (Fig. 2a). Results from a comparison of soil PBDEs levels worldwide (Table S1) indicated that the concentrations of soil $\sum$ BDE (sum of 25 PBDEs except for BDE-209) and BDE-209 in the present study were in the midpoint of the global ranges.

As replacements of PBDEs, novel HFRs, i.e., DBDPE, DP and HBB were detected frequently (61%–99%; Table 1). The concentration range (< RL–530 ng g⁻¹) and mean (29 ng g⁻¹) of DBDPE were higher than those of DP (< RL–83 and 3.2 ng g⁻¹) and HBB (< RL–720 and 3.4 ng g⁻¹) (Table 1). House dust from a rural region (an e-waste dismantling site) and an urban area (Guangzhou) also contained DBDPE as the predominant component of novel HFRs (Wang et al., 2010b). In addition, soil samples collected from Guiyu were also

enriched with DBDPE accounting for more than 50% of the sum concentrations of HBB, DBDPE, 1,2-bis(2,4,6-tribromophenoxy) ethane, 2-ethylhexyl-2,3,4,5-tetrabromobenzoate, bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate, and pentabromoethylbenzene (Wang et al., 2016). A comparison of available soil DBDPE and DP data worldwide suggested that soil contamination by DBDPE and DP was generally more serious in China than in the selected countries (Table S1). Particularly, the concentrations of DBDPE and DP in the PRD and surrounding areas were greater than those in some major cities of China, e.g., Harbin (Ma et al., 2011), Huai'an (Wang et al., 2010a) and Taizhou (Xiao et al., 2013). Although HBB in soil has not been investigated previously, it has been detected in other environmental media, e.g., dust (Wang et al., 2010b), leaf surface particles (Tian et al., 2013) and sediment (Wu et al., 2010), terrestrial bird eggs (Sun et al., 2014), plants (Tian et al., 2013) and aquatic species (Wu et al., 2010) in the PRD and surrounding areas. Therefore, HBB as a novel HFR should also be monitored in the future.

3.2. Spatial distribution patterns of HFRs

Concentrations of $\sum$ HFR in the land-use types of residency, industry and landfill were higher than those in agriculture, forestry and drinking water source (Fig. S3a). However, there were no significant differences for concentrations of $\sum$ HFR among residency, industry and landfill or agriculture, forestry and drinking water source ($p > 0.05$; Table S2). Moreover, the patterns of $\sum$ HFR in different land-use types were consistent with the distributions of $\sum$ BDE and BDE-209 (Fig. S3b and S3c), but a little different from that of the sum of DP, DBDPE and HBB with concentrations significantly lower in drinking water source than those in other land-use types (Fig. S3d). The current findings were also different from those of linear alkylbenzenes (LABs), polycyclic aromatic hydrocarbons (PAHs) and insecticides determined in the same samples. For example, the concentrations of LABs were

higher in industry, agriculture and residency than in other land-use types (Wei et al., 2014a), whereas those of PAHs were not significantly different among the six land-use types (Wei et al., 2014b). In addition, legacy insecticides, i.e., organochlorine pesticides (OCPs) were mainly distributed in landfill, industry and residency while current-used insecticides, such as organophosphate and pyrethroid were concentrated in landfill, agriculture and residency (Wei et al., 2015). The disparity among different types of contaminants may be attributed to different sources and redistribution processes of these contaminants. LABs were largely from sewage discharge (Wei et al., 2014a) and PAHs were from combustion of coal and refined petroleum (Wei et al., 2014b). Insecticides were applied to agricultural areas for protecting crops against insects and urbanized areas for mosquito control (Wei et al., 2015).

Spatially, Σ HFR concentrations were greater in the central PRD, i.e., Guangzhou, Foshan, Zhongshan, Dongguan and Shenzhen, than in the PRD's surrounding areas (Fig. 3). The spatial distribution patterns of Σ BDE, BDE-209 and DBDPE were consistent with those of Σ HFR (Figs. S4 and S5). Moreover, the mean contribution of BDE-209 to total PBDEs in the central PRD (81%) was higher than those in the PRD's periphery (68%), the East (59%) and West regions (65%) ($p < 0.05$; Fig. S6), while non-significant difference was observed on the relative abundance patterns of other brominated PBDEs (Fig. S6). These results suggested that the replacement rate of electronic products in the central PRD may be higher than those in the PRD's surrounding areas (Statistical Bureau of Guangdong Province, 2011). However, the contaminated sites with relatively higher DP levels were mainly located on Zhaoqing, Heyuan and Huizhou (Fig. S5a). This difference may be due to the fact that DP has been used as an alternative HFR in recent years and many manufacturing plants in the central PRD have been relocated to the western and eastern parts of the PRD with lower levels of urbanization and industrialization (Yang and Mao, 2014).

The spatial patterns of $\sum\text{HFR}$, as well as $\sum\text{BDE}$, BDE-209 and sum of DP, DBDPE and HBB appeared to be consistent with those of population density, gross domestic production (GDP) and level of urbanization, i.e., high $\sum\text{HFR}$ concentrations were congested in the central PRD with high population density, GDP and urbanization levels (Figs. 4a and S7). Moreover, the linear correlations between $\sum\text{HFR}$ concentrations and GDP ($r^2 = 0.44$, $p < 0.01$; Fig. 4b), population density ($r^2 = 0.32$, $p < 0.05$; Fig. 4c) and urbanization levels ($r^2 = 0.57$, $p < 0.01$; Fig. 4d) were similar and moderately significant. Similarly, concentrations of $\sum\text{BDE}$, BDE-209 and sum of DP, DBDPE and HBB were moderately correlated with social and economic factors (GDP, population density and urbanization levels; $r^2 = 0.32\text{--}0.61$, $p < 0.05$; Fig. S8), except the relations between GDP and concentrations of $\sum\text{BDE}$ ($r^2 = 0.13$, $p > 0.05$; Fig. S8a), and GDP and concentrations of sum of DP, DBDPE and HBB ($r^2 = 0.26$, $p > 0.05$; Fig. S8c). In general, the results indicated that social and economic factors appear to have dominated the spatial distributions of $\sum\text{HFR}$ concentrations in the PRD, which was also found in our previous study conducted in the coastal zone off southern China (Liu et al., 2014). On the other hand, there was only a weak correlation ($r^2 = 0.13$, $p < 0.001$; Fig. S9) between log-transformed $\sum\text{HFR}$ concentrations and log-transformed TOC contents. The same results were also observed between log-transformed individual HFR concentrations and log-transformed TOC contents with the r^2 values ranging from 0.01 to 0.24, indicating that TOC was not a governing factor for the spatial distribution of soil HFRs. It is interesting to note that $\sum\text{HFR}$ concentrations in the drinking water source were significantly correlated with log-transformed TOC contents ($r^2 = 0.50$, $p < 0.001$), but not for other land-use types ($r^2 = 0.07\text{--}0.34$). This was probably because the sampling areas in the drinking water source are away from urban centers and have low population density, so that HFRs in these areas may have been transported from other areas through the atmosphere. It was further corroborated by the lower fraction of BDE-209 in the drinking water source (68%) than in other land-use

types (71–83%; Fig. S6), as heavily brominated PBDEs were less likely to migrate through the atmosphere than lightly brominated PBDEs (Ruiz-Fernández et al., 2014).

3.3. Compositions of HFRs

BDE-209 was the predominant BDE congener, accounting for $72 \pm 18\%$ of the total BDE concentrations (Fig. S10), consistent with the results of previous studies on agricultural soils (Zou et al., 2007) and e-waste disposal soils in Guiyu of southern China (Leung et al., 2007). In addition, the relative abundances of BDE-206 and -207 were 1.4% and 4.3%, respectively, likely due to the degradation of BDE-209 in the environment (Gerecke et al., 2005). The main low brominated BDE congeners were BDE-47 and -99, which contributed 2.3% and 3.1% of the total BDE concentrations. La Guardia et al. (2006) revealed that BDE-47 and -99 were the major components of industrial products of Penta-BDE. However, the correlation between BDE-47 and -99 in the present study was weak ($r^2 = 0.24$, $p < 0.001$; Fig. S11a). Because BDE-47 and -99 in soils may undergo various physicochemical processes, their relative abundances may change (Xu et al., 2015). Moreover, Xu et al. (2015) found that the ratio of BDE-47 to (BDE-99 + BDE-100) deviated more from commercial Penta-BDE products in outdoor particles than in indoor samples. Aside from BDE-209, the abundance of BDE-153 was high (mean: 5%; Fig. S10), which is attributed to the abundant occurrence of BDE-153 in the technical products of Penta-BDE and Octa-BDE (La Guardia et al., 2006). In 2006, commercial products of Penta-BDE and Octa-BDE were officially banned by the Chinese government, but they were still used privately (Zhang et al., 2009).

Principal component analysis was used to analyze the sources of PBDEs, which obtained six components contributing to 85% of the total variance in the PBDE data (Table S3). The first component, accounting for 30% of the total variance, predominantly contained BDE-209, -208, -207, -206, -204, -196, -181 and -15, and is related to the usage of industrial

products of Deca-BDE (La Guardia et al., 2006). The second component, responsible for 13% of the total variance, was enriched with BDE-47, -99 and -100 from the usage of industrial products of Penta-BDE in outdoor particles. Overall, the results of principal component analysis and relative abundances of individual PBDEs indicated that PBDEs in soil of the PRD and surrounding areas may have been derived from the use of Penta- and Deca-BDE, as well as degradation of BDE-209.

Furthermore, the contributions of DBDPE or HBB were not significantly different in different districts ($p > 0.05$; Fig. S12), probably suggesting that the emission sources and fate of DBDPE or HBB were similar among different districts. Possible input sources include, but are not limited to, textiles, electronics, furniture and thermoplastics as investigated previously (La Guardia et al., 2013). The widespread use of the household appliances is obviously a result of economic prosperity in recent years. For example, the numbers of color television sets, washing machines, refrigerators and mobile phones were 119, 45.8, 49.1 and 82.4 per 100 rural families in 2010, as compared to 143, 97.7, 96.6 and 91.8 per 100 urban families in 2010 (China Statistical Yearbook, 2011). The ratios of *anti*-DP ($f_{anti-DP}$; $f_{anti-DP} = anti-DP / (anti-DP + syn-DP)$) were in the range of 0.18–1.00 (mean $\pm$ standard deviation: 0.73 ± 0.15), close to those in commercial products of DP (mean: 0.65–0.80) (Hoh et al., 2006; Tomy et al., 2007). i.e., DP in soils may have been resulted from DP-containing industrial products. The spatial distribution pattern of $f_{anti-DP}$ (Fig. S13) was consistent with that of DP concentrations (Fig. S5a). This finding was similar to those from the previous studies (Qi et al., 2010; Sverko et al., 2007; Wang et al., 2010a). In addition, log-transformed concentrations of BDE-209 and DBDPE were significantly correlated ($r^2 = 0.70$, $p < 0.001$; Fig. S11c), indicating that the behavior and fate of these two flame retardant compounds were similar and thereby DBDPE was the main substitute of Deca-BDE (La Guardia et al., 2012). However, the fraction of DBDPE ($DBDPE/(DBDPE+BDE-209)$) was greater than 0.5 in

9.2% of the samples only, which may indicate low replacement of BDE-209 by DBDPE in the PRD and surrounding areas. A recent study also found the fraction of DBDPE was lower than 0.5 in most soil samples collected in northern China (Lin et al., 2015).

3.4. Impacts of HFRs from e-waste disposal activities on surrounding areas

Shijiao and Longtang in Qingyuan are two of the largest e-waste dismantling areas around the world, with approximately 1.7 million tons of e-waste recycled annually (Luo et al., 2009a). In the present study, the mean $\sum$ HFR concentration in Qingyuan was 160 ng g^{-1} , and the sample containing the highest $\sum$ HFR concentration (700 ng g^{-1}) was collected at a location between several yards where e-waste recycling activities were actually conducted in Shijiao. The sum of PBDE concentrations in this sample was 630 ng g^{-1} , lower than those in abandoned dump soil of e-waste (25000 ng g^{-1}) (Yang et al., 2008) and soil in e-waste dismantling area in Longtang (2900 ng g^{-1}) (Li et al., 2011) ($p < 0.05$), but higher than that in soil near an e-waste recycling region (mean: 275 ng g^{-1} ; $p < 0.05$) (Luo et al., 2009a).

In an attempt to examine the transport of PBDEs discharged from e-waste recycling activities, the mean concentration (28.1 ng g^{-1}) of PBDEs in the land type of drinking water sources was taken as a reference level. The highest concentration (630 ng g^{-1}) of total PBDEs in the soil sample mentioned above was 4.1–9.9 times those in three soil samples collected near the e-waste recycling region, which is less than 3 km from the waste recycling yards. Apparently soil HFR concentrations gradually decreased with increasing distance from e-waste recycling sites. Furthermore, the concentrations of PBDEs declined to 18.3 ng g^{-1} , which were comparable to those in drinking water sources, at a distance less than 10 km from the e-waste recycling yards.

Luo et al. (2009b) found that the mean PBDE concentration in a sample collected at approximately 10 m from an e-waste recycling yard was 2689 ng g^{-1} , 64 times of mean

concentration (42.2 ng g^{-1}) of those in farmland soil samples collected at approximately 2 km downwind from the e-waste recycling yard. Li et al. (2011) also showed that the concentrations of total PBDEs and polychlorinated biphenyls in soil close to Longtang e-waste recycling yards were 2908 and 1891 ng g^{-1} , respectively, and decreased to 4.66 and 449 ng g^{-1} at 2.5 km away from the e-waste recycling yards. Moreover, DP concentrations decreased by a factor of 5000 within 20 km from the e-waste recycling region of Qingyuan (Yu et al., 2010). Zhao et al. (2009) suggested that the transport patterns of lightly and heavily brominated PBDEs were similar at a short-range scale. All these findings support the notion that HFRs released from e-waste recycling activities may largely remain in surrounding areas.

4. Conclusions

The present study indicated that the soil of the central PRD contained the greatest concentrations of HFRs, whereas soil of the PRD's surrounding areas included the least abundant HFRs. BDE-209 was the predominant compound, obviously derived from the huge amounts of technical Deca-BDE products used in the study regions. Moderate correlations were found between HFR concentrations and certain socioeconomic factors, such as population density, GDP and level of urbanization, indicating that anthropogenic sources moderately impacted the spatial patterns of soil HFR concentrations. Additionally, concentrations of HFRs discharged from e-waste recycling areas tended to sharply decrease with increasing distance from the sites of discharge, indicating a confined impact of e-waste recycling and disposal on the surrounding environments. Overall, health risk of HFRs in metropolis with intense human activities should be further concerned in future studies.

Acknowledgments

This work was financially supported by the National Science Foundation of China (Nos. 41390240 and 41329002) and Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (No. SKLOG2015A01). This is contribution No. IS-XXXX from GIGCAS.

Appendix. Supplementary data

Supplementary material associated with this article can be found, in the online version, at

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Table 1. Concentrations (range, median, mean $\pm$ standard (SD); ng g⁻¹ dry weight), detection frequencies (DF; %) and reporting limits (RLs; ng g⁻¹ dry weight) of individual and total halogenated flame retardants (HFRs) in soil in the Pearl River Delta and surrounding areas, southern China.

Target	range	median	mean $\pm$ SD	DF	RLs
BDE-15	< RL-2.5	0.01	0.06 $\pm$ 0.26	65	0.002–0.004
BDE-17	< RL-22	0.02	0.19 $\pm$ 1.46	78	0.002–0.004
BDE-28	< RL-3.7	0.02	0.14 $\pm$ 0.44	74	0.002–0.004
BDE-47	< RL-30	0.39	1.05 $\pm$ 2.9	98	0.002–0.004
BDE-66	< RL-17.4	0.12	0.46 $\pm$ 1.34	78	0.002–0.004
BDE-71	< RL-500	0.10	2.7 $\pm$ 33	84	0.002–0.004
BDE-77	< RL-3.8	0.16	0.36 $\pm$ 0.60	90	0.002–0.004
BDE-85	< RL-16.6	0.13	0.59 $\pm$ 1.78	89	0.002–0.004
BDE-99	< RL-76	0.54	2.8 $\pm$ 8.8	94	0.003–0.005
BDE-100	< RL-44	0.30	1.01 $\pm$ 3.9	92	0.002–0.004
BDE-126	< RL-13.2	0.22	0.64 $\pm$ 1.47	88	0.002–0.004
BDE-138	< RL-27	0.14	0.90 $\pm$ 3.1	82	0.002–0.004
BDE-153	< RL-111	0.82	5.2 $\pm$ 13.6	93	0.002–0.004
BDE-154	< RL-28	0.11	0.77 $\pm$ 3.0	78	0.002–0.004
BDE-166	< RL-27	0.10	0.89 $\pm$ 3.1	83	0.002–0.004
BDE-181	< RL-129	0.09	2.2 $\pm$ 11.0	77	0.003–0.007
BDE-183	< RL-320	0.15	1.75 $\pm$ 21	86	0.003–0.007
BDE-190	< RL-37	0.02	0.53 $\pm$ 3.4	64	0.003–0.007
BDE-196	< RL-83	0.10	1.19 $\pm$ 6.6	82	0.007–0.014
BDE-203	< RL-92	0.25	1.51 $\pm$ 7.2	76	0.007–0.014
BDE-204	< RL-47	0.09	0.77 $\pm$ 3.7	80	0.007–0.014
BDE-206	< RL-142	0.40	3.9 $\pm$ 13.4	96	0.009–0.018
BDE-207	< RL-480	1.25	11.9 $\pm$ 43	95	0.009–0.018
BDE-208	< RL-85	0.18	2.0 $\pm$ 7.4	96	0.009–0.018
BDE-209	0.20–4400	26	211 $\pm$ 620	100	0.017–0.036
HBB	< RL-720	0.02	3.4 $\pm$ 48	61	0.017–0.036
<i>syn</i> -DP	< RL-28	0.17	0.89 $\pm$ 2.8	75	0.034–0.072
<i>anti</i> -DP	< RL-66	0.43	2.3 $\pm$ 6.3	90	0.034–0.072
DBDPE	< RL-530	8.2	29 $\pm$ 66	99	0.086–0.18
$\sum$ BDE ^{a,e}	0.17–1320	8.7	43 $\pm$ 133	100	0.09–0.18
$\sum$ BDE ^{b,e}	0.37–5700	34.5	250 $\pm$ 740	100	0.10–0.22
DP ^{c,e}	< RL-83	0.61	3.2 $\pm$ 8.6	90	0.07–0.14
$\sum$ HFR ^{d,e}	0.66–6500	47	290 $\pm$ 820	100	0.27–0.56

^a Sum of BDE-15, -17, -28, -47, -66, -71, -77, -85, -99, -100, -126, -138, -153, -154, -166, -181, -183, -190, -196, -203, -204, -206, -207, and -208.

^b Sum of 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.

^c Sum of *syn*- and *anti*-DP.

^d Sum of 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, *syn*- and *anti*-DP, and HBB.

^e At least one analyte was detected with higher concentration than the RL in sample.

Figure captions

Fig. 1. Map of the sampling sites in the Pearl River Delta (PRD) and surrounding areas, including (a) four geographic regions marked with different colors: (I) West region (YJ and YF; in white); (II) the PRD's periphery (ZQ, QY, JM, and HZ; in light grey); (III) the central PRD (GZ, FS, DG, ZS, ZH, and SZ; in dark grey); and (IV) East region (HY, SW, and SG; in white) and (b) six land-use types, i.e., industry, agriculture, landfill, residency, forestry, and drinking water source. YJ, YF, ZQ, QY, JM, HZ, GZ, FS, DG, ZS, ZH, SZ, HY, SW, and SG are acronyms of district names, i.e., Yangjiang, Yunfu, Zhaoqing, Qingyuan, Jiangmen, Huizhou, Guangzhou, Foshan, Dongguan, Zhongshan, Zhuhai, Shenzhen, Heyuan, Shanwei, and Shaoguan, respectively.

Fig. 2. Sum concentrations of (a) BDE homologs and (b) classes of halogenated flame retardants. Di-BDE = BDE-15; tri-BDE = BDE-17 and -28; tetra-BDE = BDE-47, -66, -71 and -77; penta-BDE = BDE-85, -99, -100 and -126; hexa-BDE = BDE-138, -153, -154 and -166; hepta-BDE = BDE-181, -183 and -190; octa-BDE = BDE-196, -203 and -204; nona-BDE = BDE-206, -207 and -208; and deca-BDE = BDE-209. BDEs = BDE-15, -17, -28, -47, -66, -71, -77, -85, -99, -100, -126, -138, -153, -154, -166, -181, -183, -190, -196, -203, -204, -206, -207 and -208. Error bars adjacent to the bottom and upper parts of each box stand for the 10th and 90th percentiles, respectively, and horizontal lines from the bottom to the top of each box stand for the 25th, 50th and 75th percentiles. The dotted lines represent mean concentrations.

Fig. 3. Spatial distribution patterns of soil halogenated flame retardants (ng g^{-1} dry weight) in the study region (Fig. 1), which is the sum of 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, hexabromobenzene, bis(hexachlorocyclopentadieno)cyclooctane and decabromodiphenyl ethane. YJ, YF, ZQ, QY, JM, HZ, GZ, FS, DG, ZS, ZH, SZ, HY, SW and SG are acronyms of district names, i.e., Yangjiang, Yunfu, Zhaoqing, Qingyuan, Jiangmen, Huizhou, Guangzhou, Foshan, Dongguan, Zhongshan, Zhuhai, Shenzhen, Heyuan, Shanwei and Shaoguan, respectively.

Fig. 4. (a) Population density (in hundred person km^{-2}), gross domestic production (GDP; in ten billion RMB), urbanization levels (%) and concentrations of halogenated flame retardants (HFRs; in ten ng g^{-1} dry weight), as well as correlations between the concentrations of HFRs and (b) population densities, (c) GDP and (d) urbanization levels in different administrative districts in the Pearl River Delta and surrounding areas, southern China (Fig. 1).

(a) Districts and regions of sampling region

(b) Sampling location

Fig. 1

Fig.2

Fig. 3

Fig. 4