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The effects of prosperity indices and land use indicators of an urban conurbation on the occurrence of hexabromocyclododecanes and tetrabromobisphenol A in surface soil in South China☆

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ABSTRACT

Hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) are legacy brominated flame retardants which are still produced and used in China. In this study, 187 surface soils from the Pearl River Delta (PRD) urban conurbation in China were collected, and the effects of urban conurbation development on the concentrations, distributions and human exposure risk of HBCDs and TBBPA were investigated. The concentration ranges of Σ_3HBCD (sum of α-, β-, and γ-HBCD) and TBBPA in soil were below the limit of quantification (<LOQ) to 300 ng g^{-1} dry weight (dw) and < LOQ to 53.1 ng g^{-1} dw, respectively. Concentration levels of HBCDs and TBBPA in the PRD were affected both by distributions of land-use type and by the location of the city. Soils from residential areas contained the highest concentrations of Σ_3HBCD (median: 1.75 ng g^{-1} dw) and TBBPA (1.92 ng g^{-1} dw) among all land-use types. In addition, soils from the central PRD had higher Σ_3HBCD and TBBPA levels (0.46 and 0.90 ng g^{-1} dw) than those from the surrounding areas (0.17 and 0.07 ng g^{-1} dw). The concentrations of Σ_3HBCD and TBBPA were highly correlated with urbanization level, population density, regional GDP and per capita income in all cities studied ($p < 0.01$), which indicates that the prosperity of the urban conurbation may play an important role in soil contamination of HBCDs and TBBPA in the PRD. Children living in residential areas had the highest estimated daily intakes of Σ_3HBCD (7.09 pg kg^{-1} d^{-1}) and TBBPA (7.76 pg kg^{-1} d^{-1}), suggesting that people living in residential areas have a relatively higher exposure risk of HBCDs and TBBPA. This is a comprehensive study to report the effects of prosperity indices and land use indicators of an urban conurbation on the occurrence of HBCDs and TBBPA in soil in China.

1. Introduction

Polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs) and tetrabromobisphenol A (TBBPA) are traditional brominated flame retardants (BFRs) which are incorporated into a variety of materials to resist burning. Since the restriction on the production and use of penta-BDEs and octa-BDEs by the Stockholm Convention in 2009, HBCDs and TBBPA have become very important BFRs (Law et al., 2014; Li et al., 2016; Liu et al., 2016). HBCDs are mainly used in expanded polystyrene (EPS) and extruded polystyrene (XPS) insulation boards, plastic materials, building materials, electric products and textiles (The Voluntary Emissions of Control Action Programme, 2014; United Nations Environment Programme, 2015). China is the largest producer and consumer of HBCDs in the world, producing 500 to 18,000 tons of HBCDs during 2001–2011, which represented almost 60% of global HBCD production at that time (Li et al., 2016). Given that HBCDs bioaccumulate, undergo long-range transport and are toxic, they were listed in Annex A of the Stockholm Convention on Persistent Organic Pollutants in May 2013 (Covaci et al., 2006; Zhang et al., 2016). However, the Chinese government was given an exemption for HBCD production, use, import and export for EPS and XPS production purposes from 2016 to 2021 (Ministry of

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Environmental Protection of China, 2016). TBBPA is mainly used in epoxy, polycarbonate and phenolic resins in printed circuit boards, as well as in plastic products such as acrylonitrile-butadiene-styrene and phenolic resins (Law et al., 2006; Screening Assessment Report, 2013). In 2003, the total global market demand for TBBPA was 120,000 tons, with demand dramatically increasing to 170,000 tons only a year later (Mäkinen et al., 2009). About 80% of TBBPA in the world is consumed in Asia, especially in China from the manufacture of circuit boards and electronic components (Birnbaum and Staskal, 2004; Malkoske et al., 2016). Animal studies have demonstrated that exposure to TBBPA is possibly detrimental to human health because it is an effective human transduction protein binding agent *in vitro*, and was 10 times more potent than natural ligand thyroxin (Meerts et al., 2000). However, there are still no relevant laws or regulations on restricting TBBPA production or use in China.

Soil, not only a major reservoir of hydrophobic organic contaminants but also a secondary emission source for some contaminates in the atmosphere, can reflect the pollution status of HBCDs and TBBPA in the environment over time (Cao et al., 2018). The occurrence of HBCDs and TBBPA in soil from both unintentional emission in the production and manufacture of BFRs as well as from release and disposal of consumer products in China have been reported previously. However, these studies mainly focused on specific sampling sites (waste dumping sites or electronic recycling facilities) or on hot spot areas (BFR-manufacturing regions or industrial areas) (Cao et al., 2018; Liu et al., 2016). Comparatively less work has been done to evaluate the contamination levels of HBCDs and TBBPA in regional soil as well as the relationship between the distribution of HBCDs and TBBPA in soil and human activities (Zhang et al., 2016). To be exact, there is a knowledge gap in understanding soil HBCD and TBBPA pollution at a large regional scale, especially in regions experiencing accelerating urbanization that may greatly affect the surrounding environment.

China has experienced unprecedented urbanization over the past few decades. A report conducted by the World Bank Group pointed out that China contributed to more than two thirds of the total urban land and at least 80% of the new urban land added in East Asia from 2000 to 2010 (World Bank Group, 2015). Nowadays, urban conurbations are a new type of urbanization in China (Fang, 2014). The Central Work Conference on Urbanization held by the Chinese government in 2013 demonstrated that urban conurbations are the main bodies of urbanization now being constructed in China (The Central Work Conference on Urbanization, 2013). The Pearl River Delta (PRD) urban conurbation is one of the national-level urban conurbations located in South China. By the end of 2010, the urbanization level in the PRD reached up to 60% (Statistical Bureau of Guangdong Province Guangdong Statistical yearbook, 2011). Faced with extensive transformation of the industrial structure and increasingly intensive socioeconomic activities, the PRD is an ideal site for assessing the occurrence, distribution and the influence of rapid urbanization on soil contamination by HBCDs and TBBPA on a regional scale. The results are to be of great value for evaluating the impacts of urban development on the environment.

To achieve the above-mentioned objectives, three HBCDs (α-, β-, and γ-HBCD) and TBBPA were measured in 187 surface soil samples collected from the PRD. The purpose of this study was to explore the effects of large-scale urban development on the occurrence of HBCDs and TBBPA in soil, and to evaluate potential health risks of human exposure. This is a comprehensive study on HBCD and TBBPA pollution in soil on an urban conurbation scale in China, and it is significant for evaluating the effects of ongoing urbanization on the spread of organic contaminants.

2. Materials and methods

2.1. Chemicals and reagents

Three HBCD isomers, α-HBCD (≥99%), β-HBCD (≥99%) and γ-HBCD (≥99%), were purchased from Cambridge Isotope Laboratories (Andover, MA), and TBBPA (≥98%) was purchased from Sigma-Aldrich (St. Louis, MO). Four isotopically labeled compounds (D_{18}-α-HBCD (≥99%), $^{13}C_{12}$-β-HBCD (≥99%), D_{18}-γ-HBCD (≥99%) and $^{13}C_{12}$-TBBPA (≥99%)) were used as internal standard and were purchased from Cambridge Isotope Laboratories and Sigma-Aldrich, respectively. HPLC grade acetone, methanol, ethyl acetate and Milli-Q water (18 MΩ cm) were purchased from Thermo Fisher Scientific (Waltham, MA).

2.2. Sampling

The sampling campaign was conducted from December 2009 to March 2010. All fifteen cities belonging to the PRD (Guangzhou (GZ), Shenzhen (SZ), Zhuhai (ZH), Foshan (FS), Dongguan (DG), Zhongshan (ZS), Huizhou (HZ), Jiangmen (JM), Zhaoqing (ZQ), Shanwei (SW), Qingyuan (QY), Yunfu (YF), Heyuan (HY), Shaoguan (SG) and Yangjiang (YJ)) were included for field sampling. This sampling covered approximately 72,000 km^2 and encompassed six land-use types, i.e., residency, industry, landfill, agriculture, forestry, and drinking water source (Fig. 1). To elucidate the spatial patterns of HBCDs and TBBPA in soil and their correlations with socioeconomic development, the

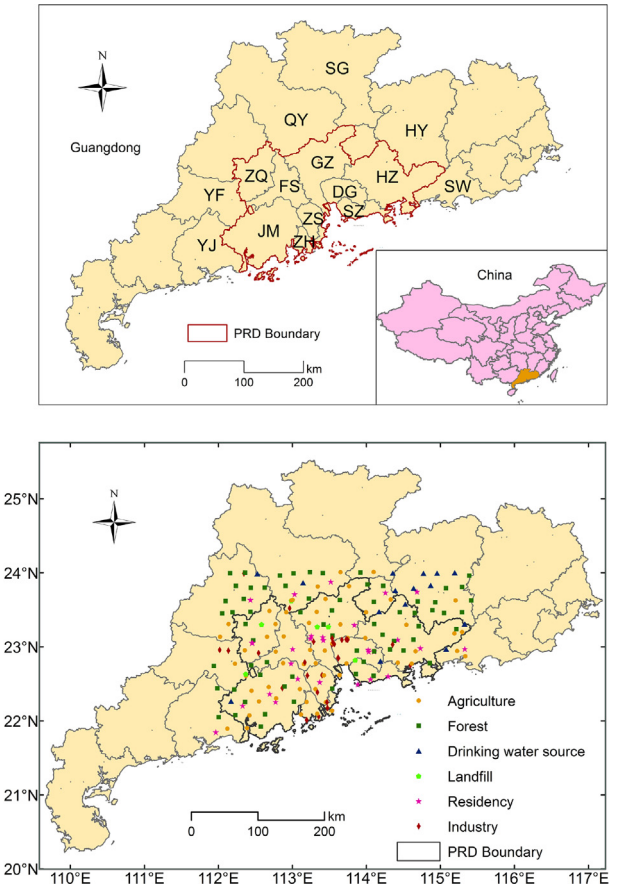

Fig. 1. Sampling sites in the PRD urban conurbations (GZ, FS, DG, ZS, ZH, SZ, ZQ, QY, JM, HZ, YJ, YF, HY, SW and SG are acronyms of district names, i.e., Guangzhou, Foshan, Dongguan, Zhongshan, Zhuhai, Shenzhen, Zhaoqing, Qingyuan, Jiangmen, Huizhou, Yangjiang, Yunfu, Heyuan, Shanwei and Shaoguan).

cities within the sampling region were divided into two groups based on the geographic locality and urbanization level, i.e., the collection of GZ, SZ, ZH, FS, DG and ZS was defined as the central PRD, and the combination of other cities (HZ, JM, ZQ, SW, QY, YF, HY, SG and YJ) was defined as the surrounding area. In 2010, the urbanization levels of cities in the central PRD were in the range of 80%–100% while the levels of cities in the surrounding PRD were in the range of 37%–65% (Statistical Bureau of Guangdong Province Guangdong Statistical yearbook, 2011). Sample collection followed the procedure proposed by the United States Environmental Protection Agency (USEPA, 1986, 2002). The sampling area was gridded according to longitude and latitude. The grid length was 12.9 km. A total of 187 surface soil samples (0–5 cm) were collected, in which 146 soils were collected at the centers of a hexagon grid based on equilateral triangles and 41 soils were randomly collected in residential, industrial and landfill areas to increase the sampling density. At each sampling site, at least three sub-samples were collected within an approximate area of 100 m^2 and composited into one sample. All soil samples were freeze-dried, homogenized and assorted with an 80-mesh stainless steel sieve (mesh size: 0.18 mm). They were stored in a 250 or 500 mL pre-cleaned brown bottle at −20 °C until analysis. Detailed information on the locations and descriptions of each soil sample are summarized in Table S1 (Supplemental Materials; "S" indicates texts, tables and figures in the Supplemental Materials afterwards).

2.3. Sample preparation and analysis

After equilibration at room temperature, each soil sample (~1 g) was transferred into a 12-mL glass tube and spiked with 0.5 mL of an internal standard mixture at 20 ng mL^{-1}. The sample was equilibrated for 2 h and placed in a fume hood covered with aluminum foil overnight for solvent evaporation. Subsequently, 3 mL of ethyl acetate was added to the sample, which was then ultrasonically extracted for 20 min. The extract was shaken vigorously for 40 min and centrifuged at 4000 (× g) for 10 min. The organic fraction was collected into another clean glass tube. The extraction was repeated twice. Three organic fractions were combined and spiked with 1 mL of Milli-Q water. The extract was vortexed for 30 s and centrifuged at 4000 (× g) for 10 min. The organic layer was collected and evaporated to near dryness under a gentle stream of high-purity N_2 and taken up with 0.5 mL of methanol.

All target compounds were quantified by a Shimadzu LC-30A liquid chromatography system and an AB Sciex 5500 triple quadrupole mass spectrometer. A Betasil C18 column (100 mm × 2.1 mm i.d., 3.5 μm particle size; Thermo Electron, Waltham, MA) was used to achieve the chromatographic separation. Multiple reaction monitoring (MRM) in the negative ionization mode was applied. The interface heater temperature is 250 °C and the IonSpray Voltage is −4500. The mobile phase was Milli-Q water (A) and methanol (B), with the gradient as follows: 0.0–1.0 min, 10% B; 1.0–3.0 min, 60% B; 3.0–5.0 min, 90% B; 5.0–6.5 min, 99% B, 6.5–10 min, 99% B, 10.5–13 min, 10% B. The injection volume was 3 μL and the flow rate was 0.3 mL min^{-1}. Detailed information on the instrumental parameters is shown in Table S2.

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

Soil samples were randomly grouped into four batches to finish sample preparation. One field blank, two method blanks, two matrix spiked samples and two pairs of matrix-spiked samples/duplicates were processed for each batch. The average recoveries of α-HBCD, β-HBCD, γ-HBCD and TBBPA in matrix-spiked samples were 76 ± 11% (mean ± SD), 105 ± 5%, 97 ± 7% and 106 ± 12%, respectively. D_{18}-α-HBCD, $^{13}C_{12}$-β-HBCD, D_{18}-γ-HBCD and $^{13}C_{12}$-TBBPA were used as internal standards, and their average recoveries in soil samples were 60 ± 18%, 62 ± 21%, 65 ± 22% and 33 ± 10%, respectively. Though $^{13}C_{12}$-TBBPA presented low absolute recoveries, the average recovery of TBBPA in matrix spiked samples was 106 ± 12% when corrected with $^{13}C_{12}$-TBBPA. In procedural blanks, trace concentrations were found for α-HBCD (0.03 ng g^{-1}), β-HBCD (0.02 ng g^{-1}), γ-HBCD (0.02 ng g^{-1}) and TBBPA (0.01 ng g^{-1}). The LODs, defined as a signal-to-noise (S/N) ratio of 3:1, were 0.005, 0.003, 0.003 and 0.002 ng for α-, β-, γ-HBCD and TBBPA, respectively. Concentrations of analytes reported in the present study were corrected with the recoveries of $^{13}C_{12}$-α-HBCD, $^{13}C_{12}$-β-HBCD, $^{13}C_{12}$-γ-HBCD and $^{13}C_{12}$-TBBPA and were subtracted with the trace concentrations in procedural blanks. All concentrations of target analytes were reported on a dry weight basis.

2.5. Daily exposure assessment

The estimated daily intakes (EDIs) of HBCDs and TBBPA through soil ingestion, inhalation and dermal absorption pathways were evaluated. Residents lived in the PRD were divided into three groups: children (≤10 years), adolescents (11–18 years) and adults (≥19 years). The estimation equations are based on those developed by the USEPA (1989, 2011, 2012, 2014):

$$EDI_{ingestion} = (C \times CF_1 \times IR_{ingestion} \times EF \times ED)/(BW \times AT) \quad (1)$$

$$EDI_{inhalation} = (C \times CF_2 \times IR_{inhalation} \times EF \times ED)/(PEF \times BW \times AT) \quad (2)$$

$$EDI_{dermal} = (C \times CF_1 \times EF \times ED \times ABS \times SA \times AF)/(BW \times AT) \quad (3)$$

where $EDI_{ingestion}$, EDI_{dermal} and $EDI_{inhalation}$ are human exposure to HBCDs and TBBPA from ingestion, dermal and inhalation pathways via soil (ng kg^{-1} d^{-1}); C is the concentration of HBCDs and TBBPA in soil (ng g^{-1}); $IR_{ingestion}$ and $IR_{inhalation}$ are the soil ingestion rate (mg day^{-1}) and inhalation rate (m^3 day^{-1}); EF is the exposure frequency (day $year^{-1}$); ED is the exposure duration (year); BW is the body weight (kg); AT is the average lifespan (day); PEF is the particle emission factor (m^3 kg^{-1}); ABS is the absorption fraction (unitless); SA is the exposure area of the soil (cm^2); AF is the adherence factor for soil (mg cm^{-2}); CF_1 and CF_2 are the conversion factor of 0.001 g mg^{-1} and 1000 g kg^{-1}. The values of the above-mentioned parameters are presented in Table S3.

2.6. Data analysis

ArcGIS Version 10.3 (ESRI, Redlands, CA, USA) was applied to show the spatial distributions of target analytes. The Ordinary Kriging interpolation method was adopted. SPSS Software (Version 22) was applied to perform the statistical analyses. Comparisons of individual compound concentrations among different land-use types and geographical regions were conducted using non-parametric tests (Kruskal-Wallis test) followed by Tamhane's T2 Post-hoc test. Pearson correlation analysis was used for the analysis of relationship between two sets of data with normal distributions; otherwise, Spearman's rank correlation analysis was used. The data distribution was automatically fitted by the simulation function in SPSS. Statistical significance was set at $p < 0.05$. Monte Carlo simulation was applied to evaluate EDIs of HBCDs and TBBPA using the software Crystal Ball 11.1. For each parameter, 10,000 runs were conducted to test convergence and stability. Correlation coefficients (r) between each input (parameter) and the output (EDI) were used to determine the most influential parameter.

3. Results and discussion

3.1. Concentrations of HBCDs and TBBPA

All target analytes were found in ~90% of surface soil, suggesting their ubiquitous contamination in the soil of the PRD (Table 1). The concentrations of Σ_3HBCD (sum of α-, β-, and γ-HBCD) were in the range of < LOQ to 300 ng g^{-1} with a median value of 0.20 ng g^{-1}. An extremely high value of Σ_3HBCD (300 ng g^{-1}) was observed, which was at least one order of magnitude higher than others. This was unexpected, as the soil sample was collected in a residential area in the center of HZ, and to our knowledge, no factory associated with the production or use of HBCDs existed in the surroundings. The levels of Σ_3HBCD in our study were comparable with those reported in soil from western China (0.43–15.2 ng g^{-1}) and Korea (0.95–27.35 ng g^{-1}), but lower than those in soil from East China (<LOD–249 ng g^{-1}) (Jo et al., 2017; Lu et al., 2018; Tang et al., 2014; Wu et al., 2016). However, concentrations of Σ_3HBCD in soil of the PRD were much higher than those of several Asian developing countries (Cambodia, India, Indonesia, Malaysia, and Vietnam), with levels from <LOQ to 1.4 ng g^{-1} (Eguchi et al., 2013; Meng et al., 2011).

For TBBPA, the concentration range was from <LOQ to 53.1 ng g^{-1} (median: 0.19 ng g^{-1}). The TBBPA levels in soil of the PRD were in the ranges reported in industrialized regions in East China (<LOQ–78.6 ng g^{-1}) and in Spain (3.4–32.2 ng g^{-1}), but higher than those reported in paddy fields in South China (0.85–2.23 ng g^{-1}), the Tibetan Plateau (0.05–0.47 pg g^{-1}) and agricultural soils in Spain (<LOQ–0.3 ng g^{-1}) (Huang et al., 2017; Sánchez-Brunete et al., 2009; Tang et al., 2014; Wang et al., 2015). China is a hot spot of TBBPA contamination due to its high volume of production and demand. Extremely high TBBPA contamination was occasionally reported in soil from BFR manufacturing region (1.64–7758 ng g^{-1}), e-waste recycling sites (84.0–646 ng g^{-1}) and garbage dumping sites (1360–1780 ng g^{-1}) (Wang et al., 2015; Yu and Hu, 2007; Zhu et al., 2014).

The concentrations of α-HBCD, β-HBCD, γ-HBCD and TBBPA were highly correlated with each other in soil of all land-use types except for landfill (among all compounds) and agriculture (between β-HBCD and TBBPA) (Table S4). The relationships indicated that HBCDs and TBBPA were always come together from similar sources, but situation was more complicated in soils of landfill, for which sources only rich with HBCDs or TBBPA may exist.

3.2. Impacts of urban prosperity on spatial distribution of HBCDs and TBBPA

Land-use types play an important role in the distributions of HBCDs and TBBPA in soil of the PRD. Concentrations of Σ_3HBCD and TBBPA in soils of residency (1.75 and 1.92 ng g^{-1}) were significantly higher than those in landfill (0.25 and 0.67 ng g^{-1}), agriculture (0.19 and 0.11 ng g^{-1}), forestry (0.19 and 0.10 ng g^{-1}) and drinking water source (0.18 and 0.06 ng g^{-1}) ($p < 0.05$). Previous studies of other Chinese cities (Ningbo, Shanghai and Chongqing) suggested that industrial areas were the most heavily polluted areas with HBCDs among all land-use types (Lu et al., 2018; Tang et al., 2014; Wu et al., 2016), which were inconsistent with our findings. In the PRD, soils from residential areas contained the highest levels of Σ_3HBCD and TBBPA, which were at least four times higher than those in industrial areas (0.43 and 0.30 ng g^{-1}). Similar trends were also found for HBCD diastereoisomers. Concentrations of γ-HBCD in soils of residency (0.84 ng g^{-1}) and industry (0.26 ng g^{-1}) were higher than those in other land-use types ($p < 0.05$) and α-HBCD in soils of residential sites (0.72 ng g^{-1}) were higher than those in other land-use types, including industrial sites (0.18 ng g^{-1}) ($p < 0.05$).

High levels of HBCDs and TBBPA in soil from residential areas in the PRD may be attributed to several reasons. The variation of soil composition is an important factor may affect the distribution of those chemicals in different soil types (Feng et al., 2012; He et al., 2013). The total organic carbon (TOC) content in soil of the PRD varied from 0.23% to 25.7%, with a mean value of 2.14%. Among all land-use types, soils from residential areas had the highest TOC content (2.57%), which was significantly higher than soils from other land-use types (1.26%, 1.58%, 1.48%, 1.86% and 1.89% for industry, landfill, agriculture, forestry, and drinking water source respectively) ($p < 0.05$). Highly positively correlations were observed between concentrations of Σ_3HBCD and TOC in soil of residency, agriculture and forestry ($p < 0.05$), and between concentration of TBBPA and TOC in soil of residency ($p < 0.01$). Furthermore, the Log K_{OW} values of α-, β-, γ-HBCD and TBBPA are 5.59, 5.53, 5.44 and 4.50, respectively (Goss et al., 2008). High Log K_{OW} values for HBCDs and TBBPA result in greater hydrophobicity and propensity soil organic material. Thus, relatively higher TOC content in soil may partly contributed to high contamination of HBCDs and TBBPA in soil from residential areas.

High levels of HBCDs and TBBPA in soil of residential area in the PRD may be also resulted from local discharges. Daily living activities associated with products containing HBCDs and TBBPA may have an important effect on the soil contaminations, in addition to industrial discharges. For HBCDs, these activities include discharge of wastewaters with flame retardants; landfill of EPS/XPS insulation boards, textile back-coatings, electric and electronic appliances; and atmospheric release and subsequent redeposition to soil. All of these could contribute to the observed contamination of HBCDs (Remberger et al., 2004; Zhang et al., 2016). TBBPA is a widely used additive in electronic/electrical applications in day-to-day life, so it could escape from such products (Birnbaum and Staskal, 2004). For example, obsolete television and computer casings are primary

Table 1
Concentrations of HBCDs and TBBPA (ng g^{-1}) in surface soil from the PRD urban conurbation, China.

Sampling area	Sample number	α-HBCD		β-HBCD		γ-HBCD		Σ_3HBCD		TBBPA	
		median	range	median	range	median	range	median	range	median	range
Total	187	0.11	Nd[a]-125	Nd	Nd-52.8	0.07	Nd-123	0.20	Nd-300	0.19	Nd-53.1
The central PRD	45	0.13	Nd-5.89	0.02	Nd-3.18	0.29	Nd-16.3	0.46	Nd-22.6	0.90	0.06–32.3
The surrounding areas	142	0.10	Nd-125	0.02	Nd-52.8	0.06	Nd-123	0.19	Nd-300	0.07	Nd-53.1
Residency	29	0.72	0.09–125	0.20	Nd-52.8	0.84	0.05–123	1.75	0.18–300	1.92	0.06–49.8
Industry	24	0.18	Nd-1.69	0.04	Nd-1.18	0.26	Nd-5.65	0.43	Nd-7.51	0.30	Nd-53.1
Landfill	7	0.10	0.08–3.05	0.02	Nd-0.71	0.13	0.05–2.06	0.25	0.15–5.82	0.67	0.06–11.2
Agriculture	53	0.10	Nd-0.34	0.02	Nd-0.15	0.06	Nd-2.20	0.19	Nd-2.67	0.11	Nd-12.0
Forestry	59	0.10	Nd-2.56	0.02	Nd-2.33	0.06	Nd-16.3	0.19	Nd-20.6	0.10	Nd-32.3
Water source	15	0.10	Nd-0.12	0.02	Nd-0.84	0.06	Nd-0.12	0.18	Nd-0.23	0.06	Nd-7.03

[a] Nd: not detected.

sources of TBBPA (Sellström and Bo, 1995; Takigami et al., 2008). Consequently, relatively high levels of HBCDs and TBBPA in residential soil in the PRD indicated that anthropogenic activities have an important influence on the distribution of HBCDs and TBBPA in soil.

Geographical location also plays an important role for the distributions of HBCDs and TBBPA in soil of the PRD. The median concentrations of Σ_3HBCDs in soil of the central PRD and the surrounding areas were 0.46 and 0.19 ng g^{-1}, decreased from the central region to the surrounding region. Similar spatial distribution pattern was also found for TBBPA, with relatively high levels in the central PRD (0.90 ng g^{-1}) and low levels in the surrounding areas (0.07 ng g^{-1}) ($p < 0.01$). As shown in Fig. 2, significantly higher levels of HBCDs and TBBPA were found in cities located in the central PRD (DG, FS, GZ, SZ, ZH and ZS) than those in cities located in surrounding areas (JM, HZ, ZQ, HY, QY, SG, SW, YF and YJ) ($p < 0.01$). As we mentioned above, the cities located in the central PRD have high urbanization levels (80%–100%) while the cities located in the surrounding areas have relatively low urbanization levels (37%–65%). This is another line of evidence that urban prosperity affects the spatial distribution of HBCDs and TBBPA in the PRD.

3.3. Impacts of urban prosperity on diastereoisomers of HBCDs

The concentrations of α-HBCD, β-HBCD and γ-HBCD in soil of the PRD were in the range of < LOQ–125 ng g^{-1} (median: 0.11 ng g^{-1}), <LOQ–52.8 ng g^{-1} (<LOQ) and <LOQ–123 ng g^{-1} (0.07 ng g^{-1}), respectively. Both α-HBCD and γ-HBCD were predominant components accounting for 47% and 42% respectively of Σ_3HBCD concentration on average, which are different from the isomer compositions of commercial HBCD mixtures (10–13%, 1–12% and 75–89% for α-HBCD and γ-HBCD, respectively) (Covaci et al., 2006).

The diastereoisomer profiles of HBCDs in soils of different land-use types are shown in Fig. 3. The concentration ratios of γ-HBCD to Σ_3HBCD were, in decreasing order, industrial sites (52%, mean value) > residential sites (49%) > landfill (44%) > agricultural sites (41%) > forested sites (37%) > drinking water source (34%), with a gradual decreasing trend, although not significant but obvious, from industrial sites to drinking water sources. It is worthy to notice, on the contrary, the ratios of α-HBCD to Σ_3HBCD were in the order of industrial sites (38%) < residential sites (41%) < landfill (46%) < agricultural sites (49%) < forested sites (51%) < drinking water source (53%), with a gradual increase from industrial sites to drinking water sources. β-HBCD exhibited a small variation in concentration ratios (10%–13%) within the range reported in commercial HBCD mixtures. These results suggested that the compositions of HBCD diastereoisomers in soil of the PRD were closely related to anthropogenic activities. The proportion of γ-HBCD gradually decreased from areas with intensive human activity to areas with less human activity, while the proportion of α-HBCD presented an opposite trend. This could be double confirmed

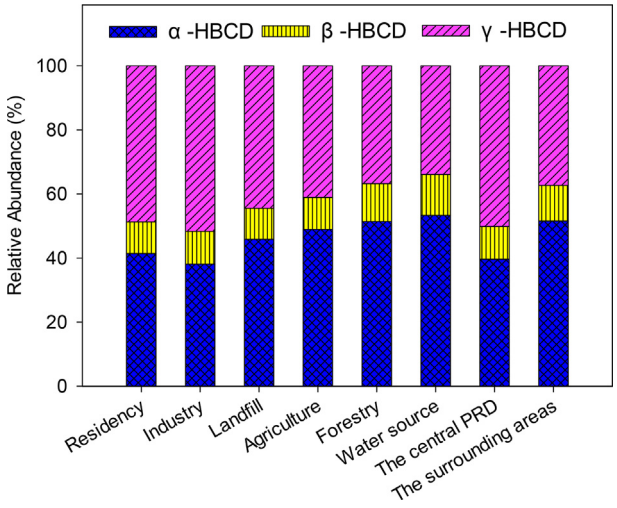

Fig. 3. Profiles of HBCDs in soil of different land-use types and regions.

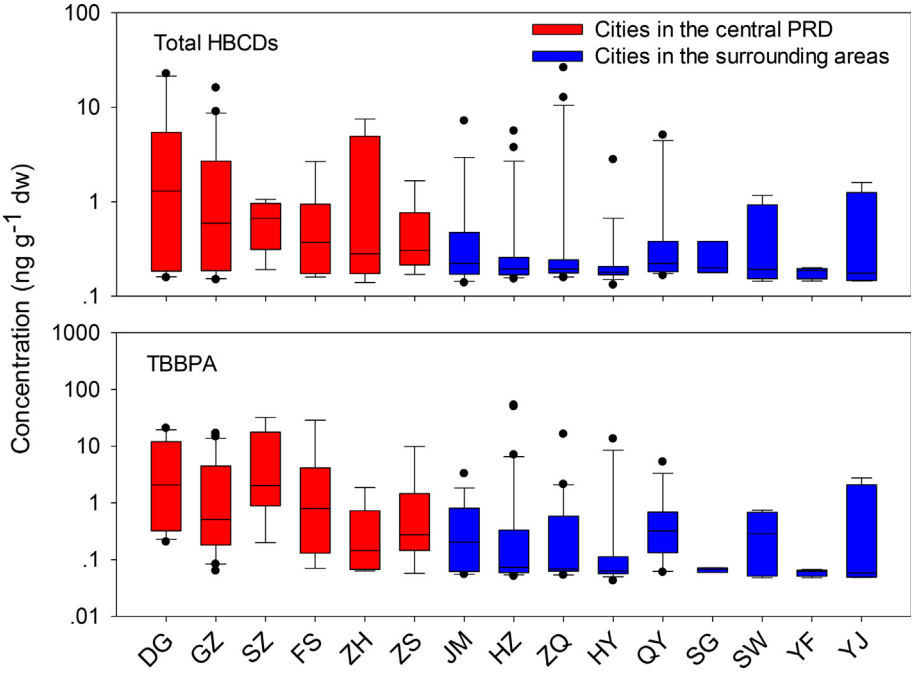

Fig. 2. Concentrations of HBCDs and TBBPA in soil of different cities in the PRD urban conurbation.

by the facts that the ratios of γ-HBCD to Σ_3HBCD decreased from the central PRD (50%) to the surrounding areas (37%) ($p < 0.01$) and the ratios of α-HBCD increased from the central PRD (40%) to the surrounding areas (51%) ($p < 0.01$). The relatively high γ-HBCD ratios found in the central PRD might also be partly resulting from the inhomogeneous distribution of industrial sampling sites between the center PRD and the surrounding areas (Fig. 1). Tang et al. also found that the ratios of γ-HBCD to Σ_3HBCD in soil samples in East China were in the order of industrial area > traffic area > waste dumpling site > residential area > farmland (Tang et al., 2014), which is similar to our results: the ratio of γ-HBCD gradually decreases from industrial area to areas where human activities are sparse.

Variations of HBCD diastereoisomers have been widely discussed (Gao et al., 2011; Tang et al., 2014). However, the mechanism responsible for the significant variations from γ-HBCD to α-HBCD remains not clear. It is generally considered that the rearrangement and decomposition of γ-HBCD due to high temperature operation during the manufacturing process (rearrangement occurs at 120–140 °C and decomposition occurs at 160–200 °C) and the photolytically mediated shift from γ-HBCD to α-HBCD are two of the main reasons leading to variation in HBCD diastereoisomer composition (Davis et al., 2005; Harrad et al., 2009; Köppen et al., 2008; Mattrel, 2008; Zhao et al., 2010). Previous studies also pointed out that atmospheric transportation and deposition may have great influence on HBCDs migration from sources to remote areas (Feng et al., 2012). Accordingly, the increasing ratios of α-HBCD to Σ_3HBCD from areas with high human activity to the surrounding areas in the PRD might suggest that soil HBCDs of agriculture, forestry and water land use sites were mainly transmitted from industries, residential areas and landfills, and the relatively consistent high ratios may have resulted from photolytically mediated shifts of γ-HBCD to α-HBCD, as well as differential volatilization and redeposition of the isomers and differential sorption/desorption in the process of atmospheric transmission within the PRD. In addition, microorganism in soil is another important factor that has to be considered to affect the transformation of HBCDs. For example, α-, β-, γ- and δ-HBCDs could be converted by the haloalkane dehalogenase LinB from *Sphingobium indicum* B90A, a bacterial strain of the *Sphingomonadacea* family that isolated from hexachlorocyclohexanes dump sites and β-HBCDs could also be transformed by the haloalkane dehalogenase LinA2 (Heeb et al., 2018; Heeb et al., 2019; Heeb et al., 2015; Heeb et al., 2012; Heeb et al., 2013). Some *Sphingomonadacea* strains, such as *Sphingobium chinhatense* stain IP26, also have the ability to transform HBCDs due to the high conservation of protein sequences related to LinA and LinB enzymes during evolution (Heeb et al., 2017). Therefore, the changes in concentration ratios of α/γ-HBCD to Σ_3HBCD in this study may be also influenced by the variation of microbial populations in soil of different areas in the PRD.

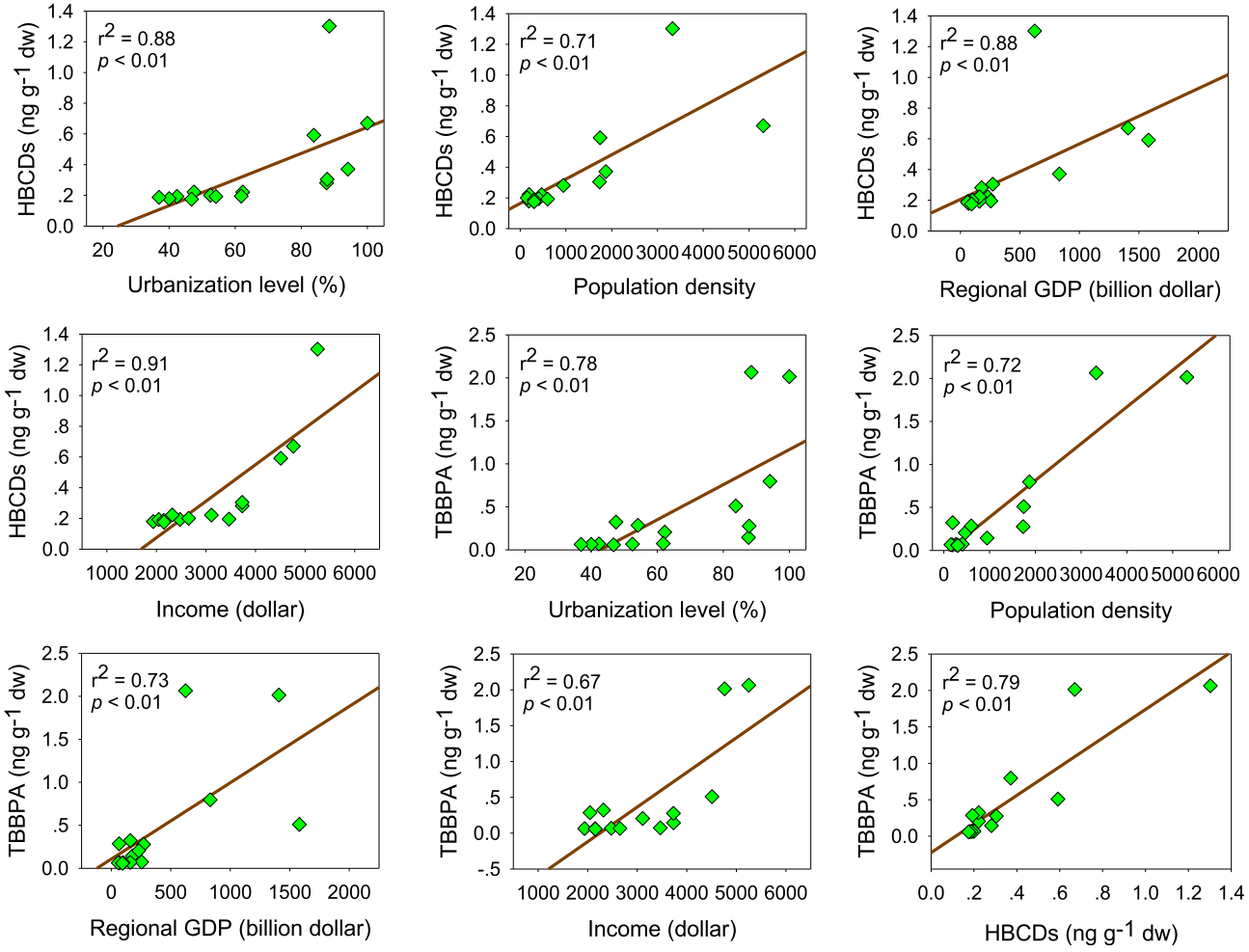

Fig. 4. Correlations between urban prosperity indicators and soil HBCDs and TBBPA levels in the PRD urban conurbations.

3.4. Correlations between urban prosperity and occurrence of HBCDs and TBBPA

To further discuss the relations between accelerating urbanization and HBCDs and TBBPA contamination in soil, correlation analysis between several urban prosperity indicators and the occurrence of HBCDs and TBBPA was conducted (Table S5). It is interesting to observe that the levels of Σ_3HBCD and TBBPA were not only significantly correlated with each other, but were highly correlated with urbanization level, population density, regional gross domestic product (GDP) and per capita income in all cities in the PRD ($p < 0.01$) (Fig. 4). These observations further demonstrated that in the PRD, urban prosperity played an important role in the contaminations of HBCDs and TBBPA in soil. Urban prosperity indicators such as urbanization level, population density, regional GDP and per capita income might be considered as the factors indicating the distributions of HBCDs and TBBPA in soil. The principal components analysis (PCA) was applied to concentrations of Σ_3HBCD and TBBPA and these prosperity indicators. Only one factor, accounting for ~80% of the total variance, was obtained, suggesting the levels of Σ_3HBCD and TBBPA in soil and these prosperity indicators were covariant with each other.

3.5. Assessment of potential health risk from soil HBCDs and TBBPA

The total EDIs of Σ_3HBCD and TBBPA via soil in different age groups were 0.83 and 0.77 pg kg^{-1} d^{-1} in children, 0.25 and 0.24 pg kg^{-1} d^{-1} in adolescents, and 0.37 and 0.34 pg kg^{-1} d^{-1} in adults (Table 2). Residents in the PRD were exposed to approximately the same levels of Σ_3HBCD and TBBPA via soil. Ingestion was the major pathway for HBCDs and TBBPA exposure from soil. The EDIs of Σ_3HBCD and TBBPA in three age groups from ingestion were all at least three orders of magnitude higher than those from dermal absorption. This is consistent with previous studies which suggested that, compared to inhalation and dermal absorption, ingestion appears to be the most significant route of exposure to HBCDs and TBBPA via soil (Lu et al., 2018). Wu et al. (2016) calculated the EDIs of HBCDs in different ages of population (infants, toddlers, children, teenagers and adults) and showed that, except for adult, the total EDIs of HBCDs via soil decreased with age (Wu et al., 2016). In our study, children were more vulnerable to soil TBBPA and HBCD intake, followed by adults and adolescences. The EDIs of Σ_3HBCD and TBBPA in children through ingestion, inhalation and dermal absorption pathways were all at least 2–3 times higher than those in adolescents and adults. This may be resulted from very frequent hand-to-mouth activities, which make it easier for children to ingest pollutants from soil. Relatively lower body weight as well as different calculation equations and parameters were also important factors leading to higher HBCDs and TBBPA exposure in children.

For residents living in different areas, the total EDIs of Σ_3HBCD in all age groups were in the order of residencies > industries > landfill > agriculture ≈ forestry ≈ drinking water sources, while the EDIs of TBBPA were in the order of residencies > landfill > industry > agriculture ≈ forestry ≈ drinking water sources. People living in residential area had the highest soil HBCD and TBBPA intake doses, which were at least four times greater than those in industrial and landfill areas, suggesting that

Table 2
Estimated daily intakes (pg kg^{-1} d^{-1}) of HBCDs and TBBPA via soil.

	$EDI_{ingestion}$		$EDI_{inhalation}$		EDI_{dermal}		EDI_{Total}	
	Σ_3HBCD	TBBPA	Σ_3HBCD	TBBPA	Σ_3HBCD	TBBPA	Σ_3HBCD	TBBPA
Total								
Children	0.70	0.65	1.13E-04	1.05E-04	0.12	0.12	0.83	0.77
Adolescence	0.21	0.20	4.33E-05	3.04E-05	0.04	0.04	0.25	0.24
Adult	0.33	0.31	3.27E-05	3.04E-05	0.03	0.03	0.37	0.34
Residency								
Children	6.03	6.59	9.70E-04	1.06E-03	1.06	1.16	7.09	7.76
Adolescence	1.80	1.97	3.70E-04	3.10E-04	0.38	0.42	2.18	2.39
Adult	2.86	3.13	2.80E-04	3.10E-04	0.27	0.30	3.13	3.43
Industry								
Children	1.46	1.03	2.35E-04	1.65E-04	0.26	0.18	1.72	1.21
Adolescence	0.44	0.31	9.00E-05	4.50E-05	0.09	0.07	0.53	0.37
Adult	0.69	0.49	7.00E-05	4.50E-05	0.07	0.05	0.76	0.54
Landfill								
Children	0.87	2.31	1.40E-04	3.70E-04	0.15	0.41	1.02	2.72
Adolescence	0.26	0.69	5.00E-05	1.10E-04	0.05	0.15	0.31	0.84
Adult	0.41	1.10	4.00E-05	1.10E-04	0.04	0.10	0.45	1.20
Agriculture								
Children	0.66	0.37	1.10E-04	6.00E-05	0.12	0.07	0.77	0.44
Adolescence	0.20	0.11	4.00E-05	2.00E-05	0.04	0.02	0.24	0.13
Adult	0.31	0.18	3.00E-05	2.00E-05	0.03	0.02	0.34	0.19
Forestry								
Children	0.65	0.36	1.10E-04	6.00E-05	0.12	0.06	0.77	0.42
Adolescence	0.20	0.11	4.00E-05	2.00E-05	0.04	0.02	0.24	0.13
Adult	0.31	0.17	3.00E-05	2.00E-05	0.03	0.02	0.34	0.19
Children	0.61	0.21	1.00E-04	3.00E-05	0.11	0.04	0.72	0.25
Adolescence	0.18	0.06	4.00E-05	1.00E-05	0.04	0.01	0.22	0.08
Adult	0.29	0.10	3.00E-05	1.00E-05	0.03	0.01	0.32	0.11
The central PRD								
Children	1.58	3.09	2.50E-04	5.00E-04	0.28	0.55	1.86	3.64
Adolescence	0.47	0.92	1.00E-04	1.40E-04	0.10	0.20	0.57	1.12
Adult	0.75	1.47	7.00E-05	1.40E-04	0.07	0.14	0.82	1.16
The surrounding areas								
Children	0.66	0.25	1.10E-04	4.00E-05	0.12	0.04	0.78	0.29
Adolescence	0.20	0.07	4.00E-05	1.00E-05	0.04	0.02	0.24	0.09
Adult	0.31	0.12	3.00E-05	1.00E-05	0.03	0.01	0.34	0.13

people living in the residential area in the PRD have a relatively higher exposure risk of HBCDs and TBBPA. The EDIs of Σ_3HBCD and TBBPA for residents living in the central PRD were also greater than that for residents living in the surrounding areas, especially for TBBPA. Residents living in the central PRD had one order of magnitude higher total EDIs of TBBPA than those living in the surrounding area, indicating that the central PRD, an area with more traffic, infrastructure as well as many other human activities, played an important role in human exposure to TBBPA. Compared to the reference doses (RfD) for HBCDs (200 ng $kg^{-1}day^{-1}$) and TBBPA (600,000 ng $kg^{-1}day^{-1}$), the EDIs of Σ_3HBCD and TBBPA in children, adolescents and adults in the present study were well below, indicating that the exposure risks of HBCDs and TBBPA in residents living in the PRD via soil is at a safe level (Besis et al., 2017). A sensitivity analysis was performed on the EDIs of HBCDs and TBBPA. For children, adolescents and adults, the greatest contributions to variance in total EDIs were the concentrations of HBCDs and TBBPA. They contributed >95% to the total variance of EDIs through ingestion, inhalation and dermal contact pathways for all age groups, while other parameters ($IR_{ingestion}$, $IR_{inhalation}$, *EF*, *BW*, *ABS*, *SA* and *AF*) contributed < 5.0%.

Dietary intake is the main route for human exposure to HBCDs and TBBPA (Cruz et al., 2015). The exposure of HBCDs and TBBPA via food consumption for Chinese population has been widely reported (Chonghuan et al., 2011; Labunska et al., 2015; Meng et al., 2012; Ruan et al., 2018, Wang et al., 2019, Zhang, et al., 2018). According to the 5th Chinese Total Diet Study carried out in 2011, the dietary exposure to HBCDs and TBBPA for general Chinese population via food consumption were 1.51 and 1.34 ng kg^{-1} d^{-1}, respectively (Shi et al., 2017). The EDIs of Σ_3HBCD and TBBPA in residents living in the PRD were orders of magnitude lower than that in general Chinese population via dietary intake, suggesting that the exposure of HBCDs and TBBPA via soil in the PRD is unable to raise significant health concerns.

4. Conclusions

This study reported the occurrence of HBCDs and TBBPA in surface soil of the PRD and investigated the relationships between their contaminations and urban prosperity. The results indicated that the structure, land use planning and urbanization degree have important effects on the concentrations and spatial distributions of HBCDs and TBBPA in soil. Urban prosperity indicators including urbanization level, population density, regional GDP and per capita income could reflect the contamination levels of HBCDs and TBBPA in soil to some extent. However, there are still some uncertainties should be noted. Soil samples analyzed in this study collected from the PRD distributed over 72,000 km^2 of land. Large scale sampling in the PRD might lead to information loss for spatial heterogeneity of HBCDs and TBBPA. Industrial activity associated with the production and application of HBCDs and TBBPA was another important factor to be considered in studies as heavily HBCDs and TBBPA industrial activities in specific areas may have significant effect on the levels and distributions of these chemicals and may, to a large extent, weaken or even mask the relationships between the prosperity of urban agglomeration and the contaminations of these chemicals. Therefore, these specific regions should be analyzed separately. However, despite its large urban population, China has an even larger non-urban population, which indicated that the urbanization process in China is unlikely to stop in the following decades and this process will have a long-lasting impact on the environment.

Conflicts of interest

The authors declared that they have no conflicts of interest to this work.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.06.128.

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