Hexabromocyclododecane and tetrabromobisphenol A in tree bark from different functional areas of Shanghai, China: levels and spatial distributions†

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The concentrations and spatial distributions of hexabromocyclododecane (HBCDD) and tetrabromobisphenol A (TBBPA) were measured in tree bark from different functional areas of Shanghai. ∑HBCDD (sum of α-, β-, and γ-HBCDD) concentrations ranged from 1.2 × 10^2 to 6.6 × 10^3 ng g⁻¹ lw (median 5.7 × 10² ng g⁻¹ lw) and TBBPA concentrations ranged from 48 to 7.2 × 10⁴ ng g⁻¹ lw (median 2.8 × 10² ng g⁻¹ lw). The concentrations of ∑HBCDD and TBBPA all followed the order of industrial areas > commercial areas > residential areas. The mean percentage of α-+HBCDD in bark samples (44%) from Shanghai was higher than that in technical HBCDD products, but comparable with that in air. The concentrations of TBBPA and individual HBCDD diastereoisomers between industrial areas and commercial areas were correlated. Based on the concentrations of HBCDD in the bark, the corresponding atmospheric HBCDD concentrations were estimated. Compared with the published data for HBCDD in urban air, the estimated atmospheric HBCDD concentrations in Shanghai had a relatively high level, and more attention should be paid to the pollution status of HBCDD in Shanghai.

1. Introduction

Hexabromocyclododecane (HBCDD or HBCD) and tetrabromobisphenol A (TBBPA) are two types of brominated flame retardants (BFRs) widely utilized to reduce the flammability of consumer products for a long time around the world.1,2 Although HBCDD has 16 diastereoisomers in theory, technical grade HBCDD is mainly comprised of three diastereoisomers: α-HBCDD, β-HBCDD and γ-HBCDD.3 The primary application of HBCDD is in expanded and extruded polystyrene (EPS and XPS) foam insulation boards widely employed in the building and construction sector.4,5 HBCDD is also used in polymer dispersions for textiles and in high impact polystyrene (HIPS) for electrical and electronic parts.6,5 Increasing attention has been paid to the environmental fate and toxicity of HBCDD due to its widespread applications.5–9 It has been proven to have persistence in the environment,8,9 toxicity to humans and wildlife,10–12 bioaccumulative tendency,13–18 and long-range transport potency.19,20 On 9th May 2013, HBCDD was listed in Annex A (decision SC-6/13) as a persistent organic pollutant (POP) by the Conference of the Parties (COP) of the United Nations Environment Program (UNEP) Stockholm Convention on POPs.21 The amendment came into force for most parties on 26 November 2014, and the date for China was 26 December 2016.22

HBCDD and TBBPA are two widely used typical brominated flame retardants worldwide and have received increasing attention. Although many studies for HBCDD and TBBPA have been carried out in industrialized cities or around point-source sites, few investigations were conducted on their distribution and migration inside cities. Tree bark has been used as a passive atmospheric sampler to analyze persistent organic pollutants for many years. In the present study, the contamination of HBCDD and TBBPA in tree bark from different functional areas of Shanghai, China was investigated, which could reveal the usage and migration of HBCDD and TBBPA within the city.
Unlike HBCDD, TBBPA is mainly (about 70–90%) used as a reactive BFR in epoxy, polycarbonate and phenolic resins in electrical and electronic equipment, and only 10–20% of TBBPA is used as an additive BFR in plastics. Until now, it has been detected in various abiotic (e.g., air, indoor dust, water, and sediment) and biota samples (e.g., fish, plants, and birds), even in human blood and breast milk. However, many prior studies have reported that TBBPA has cytotoxicity, hepatotoxicity, nephrotoxicity, neurotoxicity, immunotoxicity and endocrine-disrupting effects. In addition, TBBPA can be debrominated to bisphenol A (BPA), a known endocrine disruptor. In April 2016, the US state of Washington prohibited children’s products and residential upholstered furniture containing more than 0.1% of HBCDD and TBBPA from entering the market. But until now, no restrictive regulations have been imposed on the usage of TBBPA in China.

Half of the world’s population live in urban areas and the proportion is up to 80% for most industrialized countries. However, urban pollution, especially urban air pollution, is becoming an increasingly serious problem and attracting more and more attention. One of the conventional ways to monitor semi-volatile organic compounds (SVOCs) in the atmosphere is by using an active sampler with a pump to draw the air through a filter and an adsorbent at a defined flow rate. Although the active sampling approach has been proved to have accurate, relevant and fine temporal resolution, the sampling station is expensive to establish and maintain. Compared with the active sampling approach, the passive sampling technique, an alternative method, does not require pumps and energy supply, and it can be conducted with minimal costs for sampling over large areas as needed. Tree bark has been used worldwide as a natural passive air sampler to measure atmospheric pollutants over the past few decades. It can accumulate contaminants for a long period of time (probably 3–5 years for trees without exfoliating bark). However, limited information is available on the occurrence of HBCDD and TBBPA in tree bark from urban areas. Industrial areas, commercial areas and residential areas are three typical urban functional areas closely related to human life and have attracted the attention of many environmental science researchers. But until now, no research has been carried out on the relationship of HBCDD (or TBBPA) among these functional areas.

Shanghai is the one of the largest cities in the world. Thriving business has attracted a large influx of population accompanied by a large number of industrial activities which have made Shanghai a typical city suffering from environmental pollution. Nevertheless, only the research conducted in 2006 was focused on the occurrence of HBCDD in air from Shanghai. As for TBBPA, the study was limited to printed circuit board (PCB) plants. No research has been carried out on HBCDD and TBBPA in bark from urban areas until now. In order to contribute to filling this data gap and refresh our understanding, the present study was conducted to (i) systematically investigate HBCDD and TBBPA in bark collected from different functional areas of Shanghai; (ii) study the diastereoisomer profiles of HBCDD in bark; (iii) study the interrelationship among individual HBCDD and TBBPA in tree bark from the same/different functional areas, and (iv) estimate the corresponding atmospheric HBCDD concentrations from the measured concentrations of HBCDD diastereoisomers in bark samples.

2. Materials and methods

2.1. Sampling information

Information on the tree bark samples analyzed in this study is given in Fig. 1. The tree bark samples were collected in December 2016 from three different categories of urban functional areas of Shanghai (industrial areas, n = 12; commercial areas, n = 8; residential areas, n = 9). Camphor (Cinnamomum camphora) was chosen as the target species due to its wide distribution and easy access, and it was also regarded as a better passive sampler than other tree species (such as Sycomore, Paulownia and Magnolia denudata). For each sampling site, bark was collected from five individual trees using a chisel (washed with ethanol before each use). Bark was taken from four different sides of each tree at a height of 1.5 m above the ground level. The cambium was not chiseled in order to avoid permanent damage to the tree. All bark samples were wrapped in pre-cleaned aluminum foil, sealed in plastic bags (HBCDD-free and TBBPA-free), shipped to the laboratory at Shanghai University and kept at −18 °C until analysis.

2.2. Chemicals and materials

α-, β-, γ-HBCDD and TBBPA were purchased from Accustandard, Inc. (New Haven, USA). 13C-labeled γ-HBCDD, d18-labeled γ-HBCDD and d10-labeled TBBPA were obtained from Cambridge Isotope Laboratories, Inc. (Andover, USA), Wellington Laboratories, Inc. (Guelph, Canada) and Dr Ehrenstorfer (Augsburg, Germany), respectively. The HPLC grade acetone, methanol and acetonitrile were purchased from Merck (Darmstadt, Germany). Hexane in HPLC quality was purchased from CNW (CNW, Germany). NH3·H2O, Na2SO4 and H2SO4 were supplied by Sinopharm (Shanghai, China).

2.3. Sample extraction and cleanup

For each site, about 1 g freeze-dried bark sub-samples from each tree were cut into small pieces and a compositied sample (about 5 g) was created. A method reported by Odabasi et al. was modified for this research. In brief, the compositied sample was spiked with 10 ng of 13C-labeled γ-HBCDD and d10-labeled TBBPA as recovery standards and soaked in 30 ml of hexane/acetone (1 : 1, v/v) for 48 hours. Then they were extracted by ultrasonic extraction for 30 min. After removing the organic phase, the extraction was repeated twice. The combined extracts were evaporated to about 2 ml by rotary evaporation, then 20 ml of hexane was added and the mixture was evaporated to about 2 ml once again; this process was repeated twice. After the extract was transferred into a 10 ml volumetric tube, 10% of the extract was taken for lipid content analysis. The lipid content was determined gravimetrically by evaporating the solvent. The rest of the extract (90%) was transferred into a 50 ml centrifuge tube and treated with 15 ml

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of concentrated H₂SO₄ to remove the lipids. After vortex shaking, the mixture was separated by centrifugation. The upper hexane layer was recovered, the acid residue was washed twice with 5 ml of hexane each time, and the upper hexane layers were combined and concentrated to 1 ml. The extract was loaded onto a silica column (500 mg, CNW, Germany) and then eluted with 6 ml of acetone (containing 0.5% NH₃·H₂O, v/v). The eluent was further concentrated and solvent exchanged to methanol, and then d₁⁸-labeled γ-HBCDD was added prior to LC-MS/MS analysis.

2.4. Sample analysis
Quantitative analysis of HBCDD was performed on an Agilent 1260 series high-performance liquid chromatograph (HPLC) coupled to a 6460 triple-quadrupole mass spectrometer (Agilent Technologies, Palo Alto, CA). The HPLC and mass spectrometer operating conditions described by Wu et al. were modified for this study. Briefly, a Poroshell 120 EC-C18 reversed-phase column (3 x 100 mm, 2.7 μm, Agilent) was used for the separation of α, β, γ-HBCDD and TBBPA. HPLC was operated in gradient mode. The mobile phase consisted of eluent A (methanol/acetonitrile, 1 : 1, v/v) and eluent B (water) at a flow rate of 0.4 ml min⁻¹. The gradient started at 80/20 A/B held for 1 min, increased to 90/10 A/B at 3 min and held for 1 min, then ran to 100/0 A/B at 4.8 min and kept for 3.2 min, followed by a linear decrease to 80/20 A/B within 0.1 min and held for 5 min.

The mass spectrometer operating in electrospray ionization (ESI) negative ion mode with multiple reaction monitoring (MRM) was used for the quantitative determination of ¹³C-labeled γ-HBCDD, d₁⁸-labeled γ-HBCDD, d₁₀-labeled TBBPA, native HBCDD diastereoisomers, and TBBPA based on m/z 652.6 → 79.0, 657.7 → 79.0, 552.7 → 79.0, 640.7 → 79.0 and 542.8 → 79.0, respectively. α, β, and γ-HBCDD were quantified by the internal standard method and the quantification of TBBPA was performed using an external standard method.

2.5. Quality assurance/quality control
One blank without HBCDD and TBBPA was included in each batch of 5 extracted samples. Blanks consisted of 5 g of Na₂SO₄, which was spiked with the same amount of surrogates. The instrumental limit of detection (ILOD) defined as 3 times the signal-to-noise (S/N) ratio was 1.4, 0.36, 0.9 and 1.2 pg for α, β, γ-HBCDD and TBBPA, respectively; the instrumental limit of quantification (ILQO) defined as 10 times the S/N ratio was 4.7, 1.2, 3.0 and 4.1 pg for α, β, γ-HBCDD and TBBPA, respectively. For each target compound, blank spiking experiments were conducted at two spiked levels: 10 ng (n = 3) and 100 ng (n = 3). The recoveries (mean ± standard deviation) for the spiked α, β, γ-HBCDD and TBBPA were 89 ± 5%, 95 ± 10%, 93 ± 6% and 72 ± 5%, respectively. The relative standard deviations (RSDs) were within 5–10% for all compounds between the duplicate samples. The recoveries of surrogates ¹³C-γ-HBCDD and d₁₀-TBBPA ranged from 68% to 108% and 58% to 87%, respectively. No ¹³C-labeled α- and β-HBCDD were found in all bark samples.

The reported concentrations were surrogate recovery corrected.

2.6. Statistical analyses
Statistical analyses of the data (tests for normality of distribution, ANOVA, Spearman correlation analysis and canonical correlation analysis) were performed with SPSS version 20.0 (IBM, USA). p < 0.05 was considered to indicate statistical significance. Iso-potential maps for the concentrations of the target compounds were plotted using Surfer 12.0 (Golden software, USA). The kriging interpolation technique was applied for the spatial distribution of target compounds among the measured points.

3. Results and discussion
3.1. Concentrations and spatial distributions of HBCDD and TBBPA
The concentrations and spatial distributions of ΣHBCDD (sum of the three HBCDD diastereoisomers, α, β, and γ-HBCDD), α, β, γ-HBCDD and TBBPA in tree bark samples are shown in Fig. 1, S1, S2, S3 and S4 (see ESI†). The ΣHBCDD concentrations ranged from 1.2 x 10⁻³ to 6.6 x 10⁻¹ lipids g⁻¹, with a median concentration of 5.7 x 10⁻² ng g⁻¹ lw (Table S1†). The ΣHBCDD concentrations in bark from this study were higher than those from Beijing (China, mean 410 ng g⁻¹ lw), Norway (average 1.30 ng g⁻¹ lw), Indonesia (average 1.39 ng g⁻¹ lw), Taiwan (average 1.45 ng g⁻¹ lw), South Africa (average 0.66 ng g⁻¹ lw), Nepal (average 0.35 ng g⁻¹ lw), Canada (Downdsvie, average 21.3 ng g⁻¹ lw; Fraserdale, average 0.84 ng g⁻¹ lw; Whistler, average 0.27 ng g⁻¹ lw), Czech Republic (average 1.65 ng g⁻¹ lw), Ireland (ND), Iceland (average 0.62 ng g⁻¹ lw) and United States (Tula, average 0.76 ng g⁻¹ lw, ref. 59; St. Louis, range 118–138 ng g⁻¹ lw, ref. 56). In addition, Zhu et al. reported that the ΣHBCDD concentration in pine bark in the vicinity of an EPS material manufacturing plant from Tianjin (China) was 165 ng g⁻¹ dry weight.

The levels of TBBPA ranged from 48 to 7.2 x 10⁻² ng g⁻¹ lw with a median level of 2.8 x 10⁻² ng g⁻¹ lw. The TBBPA levels were not compared with other studies because there were no reports about TBBPA concentrations in tree bark in urban areas to our knowledge.

ΣHBCDD concentrations in bark from industrial areas, commercial areas and residential areas were 2.8 x 10⁻²–6.6 x 10⁻¹, 1.4 x 10⁻²–2.4 x 10⁻¹, and 1.2 x 10⁻²–1.1 x 10⁻³ ng g⁻¹ lw with a median of 1.1 x 10⁻¹, 6.4 x 10⁻², and 2.8 x 10⁻² ng g⁻¹ lw, respectively. The ΣHBCDD concentrations in bark in descending order was industrial areas > commercial areas > residential areas. The result was consistent with previous studies on HBCDD in the air from Shanghai. Yang et al. also found that HBCDD concentrations in soil from industrial areas were higher than those from residential areas in Ningbo (China). The highest concentration of ΣHBCDD was observed at site I6, followed by site I3, and both the sites were located in industrial areas. There were some building material production plants, auto parts manufacturing companies, electrical and electronic manufacturing plants, packaging material production companies, and logistics companies situated in these areas. These could be the source of HBCDD in the tree bark. Li et al. also found that HBCDD concentrations in soil from industrial areas were higher than those from residential areas in Ningbo (China). The highest concentration of ΣHBCDD was observed at site I6, followed by site I3, and both the sites were located in industrial areas. There were some building material production plants, auto parts manufacturing companies, electrical and electronic manufacturing plants, packaging material production companies, and logistics companies situated in these areas. These could be the source of HBCDD in the tree bark. Li et al. also found that HBCDD concentrations in soil from industrial areas were higher than those from residential areas in Ningbo (China). The highest concentration of ΣHBCDD was observed at site I6, followed by site I3, and both the sites were located in industrial areas. There were some building material production plants, auto parts manufacturing companies, electrical and electronic manufacturing plants, packaging material production companies, and logistics companies situated in these areas. These could be the source of HBCDD in the tree bark. Li et al. also found that HBCDD concentrations in soil from industrial areas were higher than those from residential areas in Ningbo (China). The highest concentration of ΣHBCDD was observed at site I6, followed by site I3, and both the sites were located in industrial areas. There were some building material production plants, auto parts manufacturing companies, electrical and electronic manufacturing plants, packaging material production companies, and logistics companies situated in these areas. These could be the source of HBCDD in the tree bark. Li et al. also found that HBCDD concentrations in soil from industrial areas were higher than those from residential areas in Ningbo (China). The highest concentration of ΣHBCDD was observed at site I6, followed by site I3, and both the sites were located in industrial areas. There were some building material production plants, auto parts manufacturing companies, electrical and electronic manufacturing plants, packaging material production companies, and logistics companies situated in these areas. These could be the source of HBCDD in the tree bark. Li et al. also found that HBCDD concentrations in soil from industrial areas were higher than those from residential areas in Ningbo (China). The highest concentration of ΣHBCDD was observed at site I6, followed by site I3, and both the sites were located in industrial areas. There were some building material production plants, auto parts manufacturing companies, electrical and electronic manufacturing plants, packaging material production companies, and logistics companies situated in these areas. These could be the source of HBCDD in the tree bark. Li et al.
reported that the emission of HBCDD from industrial uses in manufacturing FR products would reach the peak around 2015. It should be noted that the ΣHBCDD concentration in bark in site C3 is at a relatively high level compared with those in the sampling sites around site C3. One possible reason might be due to the fact that there were some super high-rise buildings located in this region. According to the code for fire protection design of buildings (GB50016-2014) and the fire prevention regulation for civil building exterior thermal insulation systems and exterior wall decoration (2009/09/25), for the buildings ≥100 m, the requirements for the combustion performance of external wall thermal insulation materials have enhanced. These policies have led to an increasing demand for thermal insulation. In China, EPS/XPS accounted for 80% of market shares of the thermal insulation.63

The TBBPA concentrations in bark in industrial areas, commercial areas and residential areas were 1.5 × 10^2–7.2 × 10^3, 71.56 × 10^2, and 48–2.8 × 10^2 ng g−1 lw with a median of 6.0 × 10^2, 2.9 × 10^2, and 1.3 × 10^2 ng g−1 lw, respectively. Like HBCDD, the TBBPA concentrations in bark in descending order was also industrial areas > commercial areas > residential areas. Different from HBCDD, the highest concentration of TBBPA was detected at site I10 located in the industrial areas with many companies manufacturing acrylonitrile-butadiene-styrene (ABS) engineering plastics and PCBs. The possible explanation for the difference was that TBBPA is usually used as an additive and reactive brominated flame retardant in ABS and PCBs, respectively.63 These results suggested that the production and use of TBBPA-containing materials might be one of the primary sources of TBBPA in tree bark from Shanghai.

3.2. Diastereoisomer profiles of HBCDD in tree bark

The average composition profiles of HBCDD diastereoisomers in all bark samples from Shanghai were 44% α-HBCDD (range 20–62%), 18% β-HBCDD (range 10–34%) and 38% γ-HBCDD (range 12–70%). The portions of α-HBCDD in the composition profiles of the bark samples were rather high compared with the commercial technical HBCDD product which consisted mainly of 10–13% α-HBCDD, 1–12% β-HBCDD and 75–89% γ-HBCDD.64

To date, few studies have focused on the diastereoisomer profiles of HBCDD in bark.65 Hu et al.45 reported that the ratio of α-HBCDD, β-HBCDD and γ-HBCDD in bark from Beijing was 24%, 13% and 63%, respectively. Zhu et al.66 found that the HBCDD diastereoisomer profiles in pine bark samples from the vicinity of an EPS manufacturing plant of Tianjin were similar to those in commercial EPS products (18.2%, 9.40%, and 72.4% for α-, β-, and γ-HBCDD, respectively) and that HBCDD in pine bark mainly originated from the surrounding environment. Bark can accumulate POPs from the vapor and particle phases of the ambient air.61,64 Compared with Beijing, the portion of α-HBCDD in the air of Shanghai was higher.53,54 However, a higher portion of α-HBCDD was also found in other environmental media (soil,65,66 sediment,65,66 road dust,57 and sewage sludge57) from Shanghai (Fig. 2).

The mean portion of α-HBCDD in industrial areas (45%) was comparable with those in residential areas (44%) and commercial areas (42%). Similar findings were also found in β-HBCDD and γ-HBCDD. ANOVA analysis reveals that no significant difference was found in the portion of each HBCDD diastereoisomer in bark among different functional areas. However, these results were contradictory to previous research. Li et al.31 reported that the atmospheric percentage of α-HBCDD from industrial areas was significantly lower than those from residential regions and commercial centers in Shanghai. Similar results were also found in the soil samples from Ningbo (China), and the portion of α-HBCDD in soil from industrial areas was lower than that from residential areas.64 One of the possible reasons for the higher portion of α-HBCDD in industrial areas in our study was the wide use of color steel sandwich
Fig. 2 HBCDD diastereoisomer profiles in different environmental media from Shanghai. Data for HBCDD in bark were from this study. Data for HBCDD in air, soil 1, soil 2, road dust, sediment 1, sediment 2 and sewage sludge were from the studies of Li et al., Meng et al., Wu et al. (2016), Wu et al. (2016), Wu et al. (2014), Tang et al., and Xiang et al. respectively. The ‘product’ meant the ‘technical HBCDD product’ and the related data were from the study of Cruz et al.

panels as building materials. The commonly used chemicals for these panels were EPS and XPS in China. The high temperature generated in the factory production process can lead to an increase in the portion of α-HBCDD. Many studies have shown that elevated temperatures could trigger the isomeric rearrangement during the manufacturing or processing of HBCDD-containing products (e.g. XPS was produced at 200 °C (ref. 71)), and γ-HBCDD can thermally isomerize to α-HBCDD. The mean α-HBCDD/γ-HBCDD ratio and variation were highest in the bark from commercial areas (mean 1.75 and range 0.29–4.69), followed by those from industrial areas (mean 1.39 and range 0.76–2.63) and residential areas (mean 1.23 and range 0.63–2.23). Further research studies need to be conducted on the specific reasons. Additionally, the α-HBCDD/γ-HBCDD ratio for all bark samples was higher than that in commercial EPS products (0.25). This suggested that HBCDD in tree bark from this study was mainly from past usage.

Although the technical HBCDD mixture was dominated by γ-HBCDD, the diastereoisomer profiles of HBCDD could be affected by many factors. In addition to thermal rearrangement, other factors can also contribute to the variation of HBCDD diastereoisomer profiles. Photoisomerization was also one of the reasons for the transformation of γ-HBCDD to α-HBCDD. Zhao et al. investigated HBCDD diastereoisomers by density functional theory (DFT) and time-dependent DFT calculations, and found that α-HBCDD was the most stable one. Gerecke et al. found that the environmental half-life of α-HBCDD was longer than that of γ-HBCDD. Besides, Koppen et al. found that γ-HBCDD can also thermally isomerize to β-HBCDD at a temperature of 160 °C with a lower conversion rate.

3.2.1. Interrelationships among individual HBCDD and TBBPA in tree bark from the same/different functional areas.

Though HBCDD and TBBPA were added in different consumer products, a correlation has been found between the concentrations of TBBPA and HBCDD in English lake water and Ningbo (China) soil. The results of Spearman correlation analysis of each HBCDD diastereoisomer, ∑HBCDD and TBBPA in tree bark samples from all sampling sites, residential areas, commercial areas and industrial areas are summarized in Tables S2, S3, S4 and S5 (see ESIF), respectively. α-, β-, and γ-HBCDD were significantly positively correlated with each other and ∑HBCDD in bark from all sampling sites, residential areas and industrial areas, indicating that the three diastereoisomers share similar potential sources in these areas. γ-HBCDD was not correlated with α- and β-HBCDD in tree bark from commercial areas; α-, β-, γ-HBCDD and ∑HBCDD were not correlated with TBBPA in tree bark from residential areas, commercial areas and industrial areas. These results suggested that these compounds in these areas may have different sources. However, with respect to all sampling sites, TBBPA was significantly positively correlated with α-, β-, γ-HBCDD and ∑HBCDD. This suggested that these contaminants had similar sources throughout the study area. We were unable to explain this diversity based on the current survey, and it also required continuous observation to be confirmed.

The simple supply chain for a product was raw materials processed into the final goods, then transported to distribution centers and ultimately to customers. HBCDD-containing products might follow a similar route of transfer. The results of Spearman correlation analysis of TBBPA in tree bark samples between residential areas, commercial areas and industrial areas are summarized in Table S6. TBBPA in tree bark from industrial areas was significantly positively correlated with that from commercial areas, indicating that TBBPA shares similar potential sources in these areas. Another possible reason was that TBBPA-containing products in commercial areas were manufactured from industrial areas. In other words, TBBPA migrated from the industrial areas to the commercial areas. Unlike TBBPA, HBCDD has three diastereoisomers (α-, β- and γ-HBCDD). The canonical correlation analysis was conducted via Bartlett’s chi-square test to investigate the interrelationships of individual HBCDD diastereoisomers between different functional areas. As for industrial areas and commercial areas, the first canonical correlation coefficient was 0.991, and the results passed the significance test (p < 0.05), indicating that the concentrations of individual HBCDD diastereoisomers between industrial areas and commercial areas were correlated. Interestingly, the result was consistent with TBBPA in tree bark from industrial areas and commercial areas. As for industrial areas and residential areas, commercial areas and residential areas, the results of the canonical correlation did not pass the significance test (p > 0.05), which suggested that the concentration of individual HBCDD diastereoisomers between these areas was uncorrelated. TBBPA also showed a similar result to HBCDD.

3.3. Estimation of HBCDD diastereoisomer concentrations in the atmosphere

Although tree bark is a good passive sampler, less research has been devoted to using tree bark to compare the levels of contaminant pollution in different regions. In order to eliminate this deficiency, many research studies have used the bark/air partitioning of the persistent organic pollution model.
combined with tree bark levels to estimate the concentrations of pollutants in the atmosphere. This method has been effective in predicting the atmospheric concentration of HBCDD,\(^6\) polybrominated diphenyl ethers,\(^7\) polychlorinated biphenyls,\(^8\) and organochlorine pesticides.\(^9\) The estimation equation for the bark/air partitioning of the POP model was expressed as below:

\[
K_{BA} = \frac{C_b}{C_A} = \{2\text{LipCont}\}^{0.61}K_{OA}^{0.52}\text{exp}(-0.964\Delta H_{vap} + 3.130(1/T - 1/302.05) \times 10^5/R) \times 10^{-6} + 210B(S_A)^{0.706}(P_{ptn}/1.54)^{0.706}(T_{sp})K_{OA})/(1 + B(T_{sp})K_{OA})
\]

where \(C_b\) is the concentration of HBCDD in the tree bark (pg m\(^{-3}\) air); \(C_A\) is the concentration of HBCDD in the atmosphere (pg m\(^{-3}\) air); LipCont is the lipid content of tree bark (g lipid m\(^{-3}\) bark); \(K_{OA}\) is the octanol-air partition coefficient of POPs; \(\Delta H_{vap}\) is the enthalpy of vaporization of the subcooled liquid; \(T\) is the temperature of the atmosphere (K); \(R\) is the gas constant of 8.3 Pa m\(^3\) mol\(^{-1}\) K\(^{-1}\); \(B\) is a constant (m\(^3\) \(\mu\)g\(^{-1}\)); \(S_A\) is the specific surface area of the tree bark (m\(^2\) m\(^{-3}\)); \(P_{ptn}\) represents precipitation values (mm); \(T_{SP}\) is the concentration of total suspended particles (\(\mu\)g m\(^{-3}\)).

The details of the parameters for the estimation equation are listed in Table S7.\(^+\) Since TBBPA would be overestimated,\(^10\) the concentrations of TBBPA in the air estimated by the model were beyond our consideration. According to the results, the atmospheric HBCDD concentrations of Shanghai ranged from 30 to 1.6 × 10\(^3\) pg m\(^{-3}\), with a median level of 1.4 × 10\(^2\) pg m\(^{-3}\). The results were higher than those detected in Shanghai in 2006. These were not surprising because the production and usage of HBCDD were increasing dramatically over the past decade.\(^10\) The trend of a rapid increase of the concentration of HBCDD in soil from Beijing was also found by Wang et al.\(^9\) In order to better understand the pollution level of HBCDD in the air from Shanghai, we summarized the published data for that in air from urban sampling sites in Table 1. As can be seen from Table 1, the concentrations of HBCDD in the atmosphere varied largely from different cities during different time periods. Before 2005, the concentrations of HBCDD in air from European cities were higher than those from China. However, in recent years, atmospheric HBCDD concentrations in urban areas from China appeared to be comparatively higher than those from Europe and America, especially in densely populated large cities. These variations might be influenced by the production and use of HBCDD. In 2001, 57% of the estimated world market demand for HBCDD was attributed to European consumption, and that for Asia was 23%; nevertheless, half of the Asian demand was accounted for by Japan.\(^9\) In 2007, Europe was still accounted for the biggest part of the global demand for HBCDD with a consumption of 11 600 t, while the production capacity of HBCDD in China was 7500 t.\(^8\) In 2011, the estimated production of HBCDD was 13 000 tonnes for the EU and the United States, and that was 18 000 tonnes for China.\(^21\) According to the previous study conducted by Salanova and Hites,\(^26\) the concentrations of HBCDD in tree bark were significantly correlated with population and Shanghai is the world’s largest city with an agglomeration of 23 million inhabitants.\(^3\) Besides, one of the possible reasons was that changes in China’s building energy conservation and fire safety policy promoted the use of EPS and XPS.\(^5\)\(^3\)\(^4\)

**Table 1** The occurrence of HBCDD in air from urban sampling sites from the published data

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Details</th>
<th>Sampling time (m(\text{y})-m(\text{y}))</th>
<th>Concentration (pg m(^{-3}))</th>
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<td>100 (average)</td>
<td>80</td>
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<tr>
<td>Istanbul, Turkey</td>
<td>Besiks</td>
<td>2(2012)-3(2012)</td>
<td>1200</td>
<td>81</td>
</tr>
<tr>
<td>Birmingham, UK</td>
<td></td>
<td>12(2007)</td>
<td>34–40 (mean 37)</td>
<td>24</td>
</tr>
<tr>
<td>Chicago, US</td>
<td></td>
<td>1(2003)-12(2003)</td>
<td>0.9–9.6 (mean 4.5)</td>
<td>82</td>
</tr>
<tr>
<td>Stockholm, Sweden</td>
<td>Huddiksvalls gatan 2</td>
<td>1(2001)</td>
<td>610</td>
<td>83</td>
</tr>
<tr>
<td>Stockholm, Sweden</td>
<td>Schoolyard of Na Latin</td>
<td>8–9(2000)</td>
<td>76</td>
<td>83</td>
</tr>
<tr>
<td>Guangzhou, China</td>
<td>Industrial areas</td>
<td>6(2004)</td>
<td>0.28–1.78</td>
<td>84</td>
</tr>
<tr>
<td>Guangzhou, China</td>
<td></td>
<td>6(2004)</td>
<td>2.20–3.92 (mean 3.09)</td>
<td>84</td>
</tr>
<tr>
<td>China</td>
<td>24 Urban sites across China</td>
<td>7–10(2005)</td>
<td>&lt;LOD-390 (mean 100)</td>
<td>85</td>
</tr>
<tr>
<td>Guangzhou, China</td>
<td>Tianhe district</td>
<td>11(2006)</td>
<td>1.2–1.8</td>
<td>86</td>
</tr>
<tr>
<td>Shanghai, China</td>
<td>Jiading district, Industrial areas</td>
<td>3(2006)</td>
<td>26.9–123 (mean 71.9)</td>
<td>51</td>
</tr>
<tr>
<td>Shanghai, China</td>
<td></td>
<td>2–3(2006)</td>
<td>3.21–66.1 (mean 25.6)</td>
<td>51</td>
</tr>
<tr>
<td>Harbin, China</td>
<td>Residential region</td>
<td>8(2007)-9(2008)</td>
<td>3.9–6700 (mean 150)</td>
<td>87</td>
</tr>
<tr>
<td>Beijing, China</td>
<td>Minzu University of China</td>
<td>10(2008)-7(2009)</td>
<td>20–1800 (mean 390)</td>
<td>45</td>
</tr>
<tr>
<td>China</td>
<td>11 Chinese large cities</td>
<td>6(2009)-6(2010)</td>
<td>17–300 (mean 73)</td>
<td>85</td>
</tr>
<tr>
<td>Harbin, China</td>
<td></td>
<td>8(2008)-7(2013)</td>
<td>&lt;LOD-3400 (mean 360)</td>
<td>88</td>
</tr>
<tr>
<td>Shanghai, China</td>
<td>Industrial areas</td>
<td>12(2015)-12(2016)</td>
<td>68–1.6 × 10(^2) (median 2.7 × 10(^2))</td>
<td>Estimated values in this study</td>
</tr>
<tr>
<td>Shanghai, China</td>
<td>Residential areas</td>
<td>12(2015)-12(2016)</td>
<td>30–2.7 × 10(^2) (median 67)</td>
<td>Estimated values in this study</td>
</tr>
<tr>
<td>Shanghai, China</td>
<td>Commercial areas</td>
<td>12(2015)-12(2016)</td>
<td>35–5.9 × 10(^2) (median 1.6 × 10(^2))</td>
<td>Estimated values in this study</td>
</tr>
</tbody>
</table>

\(\text{“m}\(\text{y}\)-m\(\text{y}\)” means “month\(y\)-month\(y\)”.

4. Conclusions

The present study is the first to report HBCDD and TBBPA concentrations in the tree bark from different urban functional
areas. The concentrations of HBCDD and TBBPA in bark from
industrial areas of Shanghai were relatively high compared with
those from commercial areas and residential areas. The di-
stereoisomer profiles of HBCDD in bark from industrial areas
were similar to those from commercial areas and residential
areas. The correlation was found in the concentrations of
TBBPA and individual HBCDD diastereoisomers between
industrial areas and commercial areas. In addition, the
concentrations of HBCDD in air were estimated by the bark/air
partitioning of the POP model. Compared with the data from
previous studies for the air from urban sampling sites, the
estimated atmospheric HBCDD concentrations in Shanghai
had a relatively high level. Further research should be con-
ducted on the confirmation of concentrations of HBCDD in air
from different functional areas of Shanghai, and the potential
health risk for the people working in industrial areas should be
given more attention.

Conflicts of interest
There are no conflicts to declare.

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