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Composition profiles of halogenated flame-retardants in the surface soils and in-situ cypress leaves from two chemical industrial parks

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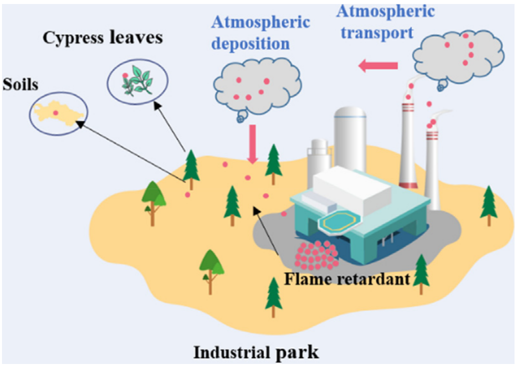
HIGHLIGHTS

- Times of higher PBDEs and DBDPE were found than most other regions.
- Significant correlations between soils and leaves only for several PBDE congeners
- Soil was not the important source of flame retardants in leaves.
- Air and particle were the main source of flame retardants in leaves.
- High pollution was related to the manufacture and operating activities.

GRAPHICAL ABSTRACT



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ABSTRACT

There is limited information available regarding the investigation on typical organic pollutants between the soil and in-situ grown plant leaves. This study is to reveal whether the pollution characteristics of soil and leaves can reflect the long-term and short-term pollution situation, and to find the differences between halogenated flame-retardants in the surface soils and in-situ cypress leaves. Polybrominated diphenyl ethers (PBDEs), dechlorane plus (DP), and decabromodiphenyl ethane (DBDPE) in were investigated in two different industrial parks, which were located at the largest brominated flame-retardant-manufacturing center in Weifang, China. These chemicals were frequently detected with high median concentrations of PBDEs (1.22×10^3 ng/g) and DBDPE (227 ng/g) in the soil samples, and DBDPE (881 ng/g) and PBDEs (461 ng/g) in the in-situ cypress leaves. The DP concentration was 1–4 orders of magnitude lower than the other two chemicals in both the matrices. Different composition profiles of the chemicals in soil and cypress leaves were observed. The PBDEs and DBDPE were found to be the predominant species in soils and cypress leaves, respectively. In comparison, the LG industrial parks had higher concentrations of PBDEs and DBDPE in both the soils and cypress leaves. No significant correlations were observed for these chemicals between the soil and leaf samples, although significant correlations ($p < 0.05$) were observed for several PBDE congeners among all samples from the industrial parks and a separate industrial park. The results indicated that the soil was not the important source of these chemicals in leaves. A large proportion of DBDPE was preferentially present in cypress leaves, which revealed the situation of recent pollution. The results deepen the understanding of chemical distribution characteristics among different environmental matrices in soils and leaves.

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1. Introduction

Flame-retardants are used as substrates in daily necessities. They are also used to delay the fire ignition time to acquire extra escape-time in emergencies. Common organic halogenated flame-retardants including polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD), and dechlorane plus (DP) are often subjected to such uses as described above (Fan et al., 2020; Ge et al., 2022; Li et al., 2012; Yu et al., 2009). However, non-bonding with materials or excessive addition of the flame-retardants inevitably results in leakages during the lifespan of chemical-containing products (Morgan, 2019). Continuous accumulation of these chemicals in the environment can lead to severe pollution of water, soils, air, dust, and biota, as well as increase in the human health risks due to exposure to these chemicals (Cai et al., 2022; Fan et al., 2020; Li et al., 2015; Liu et al., 2020; Zhu et al., 2014). Therefore, some flame-retardants including HBCD and PBDEs have been listed as the priority-controlled chemicals due to high toxicity (UNEP, 2009, 2017, 2019). Naturally, the demand for novel alternative flame-retardants such as decabromodiphenyl ethane (DBDPE) is expectedly increasing in recent years (De la Torre et al., 2020; Morgan, 2019).

Industrial activities, such as e-waste dismantling or burning, sewage treatment, and plastic or industrial flame-retardant production are important sources of chemicals during the operation or large-scale production or continuous release (Li et al., 2019a; Xu et al., 2017). The investigations to reveal specific pollution characteristics are important and many studies have focused on site pollution by these flame-retardants (Li et al., 2015, 2019b, 2021; Ge et al., 2020; Xu et al., 2017, 2019). Most flame-retardants such as PBDEs, DP, and HBCD are persistent and difficult to degrade in the environmental matrices, such as soil, sediments, and air. Soil is regarded as a main reservoir of these toxic compounds by dry and wet deposition of atmospheric particles (Newton et al., 2014). For instance, the predicted half-life of BDE209 (a deca-BDE congener) reaches up to 28 years in agricultural soils (Andrade et al., 2010). Meanwhile, soil is also considered as a secondary pollution and exposure source of these toxic compounds to other environmental matrices such as water, atmosphere, and plants (Cetin and Odabasi, 2007; Yang et al., 2019).

Plants are not only directly affected by soil contaminants through passive or active root absorption, but also receive chemicals through aerial deposition (Collins et al., 2006; Su et al., 2007; Zhang et al., 2021). For example, pine needles have been used as biomonitor or indicator for air pollution, such as that caused by PBDEs, DP, DBDPE, and HBCD (Jia et al., 2019; Li et al., 2019b; Wang et al., 2021). Previously, numerous studies have focused on the bioaccumulation of flame-retardants in leaves of plants (Chen et al., 2011; Fan et al., 2020; Li et al., 2019b; Jia et al., 2019; Qiu et al., 2019; Wang et al., 2020). However, only a handful of these studies have elaborated the contamination level correlations of soils with plant leaves (Li et al., 2012, 2019b), which need to be further explored to better understand the correlations of chemicals between soils and leaves.

In the present study, the relationship of PBDEs, DP, and DBDPE between the soils and leaves is investigated. Moreover, whether the compositions of these chemicals in the two matrices can reflect long-term and short-term pollution situation or not is also explored. It is considered in the study that soil has weak mobility, and leaves will fall and deposited particles on leaves can be washed by rain. Cypress is the most widely distributed tree in two typical chemical-based industrial parks in Weifang, Shandong, which hosts the largest brominated flame-retardant (BFR)-manufacturing center of China (Zhu et al., 2014). Therefore, the surface soil and in-situ cypress leaf samples were collected for these parks and compared. The concentrations of PBDEs, DP, and DBDPE were determined, and the composition profiles of the target contaminants and the correlations of soils with cypress leaves were analyzed. The present results deepen the understanding of chemical distribution characteristics among different environmental matrices, the sources of the chemicals in soils and leaves, as well as the long-term and short-term indicators of the environmental pollution.

2. Experimental

2.1. Reagents and materials

Twenty PBDE congeners (BDE17, 28, 47, 66, 71, 85, 99, 100, 138,153, 154, 183, 190, 196, 197, 203, 206, 207, 208, and 209), DP (*syn*-DP and *anti*-DP), and DBDPE were purchased from AccuStandard (New Haven, CT, USA). Internal standard ^{13}C-PCB-208 and recovery standard ^{13}C-PCB-141 were also purchased from AccuStandard (New Haven, CT, USA). Methanol, dichloromethane, *n*-hexane, isooctane, and ethyl acetate (high- performance liquid chromatography; HPLC grade) were obtained from CNW Technologies (Dusseldorf, Germany).

Pesticide grade Florisil (60–100 mesh) and empty solid phase extraction (SPE) cartridges (12 mL) were purchased from CNW Technologies (Dusseldorf, Germany) and Biocomma (Shenzhen, China), respectively. Anhydrous sodium sulfate and alumina (100–200 mesh) were purchased from Sinopharm Chemical Reagent (Shanghai, China), which were baked at 450 °C for 12 h and deactivated with 3 % ultrapure water before further use. Silica (80–100 mesh) was purchased from Puke (Qingdao, China), which was extracted using methanol and dichloromethane for 24 h, respectively, followed by deactivation using 3 % ultrapure water before further use. Copper sheets (CNW Technologies, Dusseldorf, Germany) for desulfurization were activated using hydrochloric acid removing oxide film.

2.2. Sampling and sample preparation

A total of 31 surface soil and 30 cypress leaf samples were collected in August 2020 from Weifang, Shandong, China (see Supplementary Information (SI); Table S1). Among these, 11 and 18 grid-distributed soil samples were collected from LG (3.7 km × 6.3 km) and BH (3.5 km × 5.0 km) chemical industrial park, respectively, which are the two important industrial parks in the BFR-manufacturing center. The two reference soil samples were also collected (Fig. S1). Meanwhile, according to the individual soil samples, 30 cypress leaf samples were collected from in-situ grown cypress at the height of 1 m. Each leaf sample consisted of the mixture of subsamples from three trees. Only one reference cypress leaf sample was collected because no cypress grew in one of the reference sites. Both the soil (each soil sample was a mixture of five subsamples) and the cypress leaf samples were wrapped in aluminum foil in an ice-box and immediately transported to the laboratory. After lyophilization, the soil and cypress leaf samples were grounded and crushed to fine powders. The samples were passed through a 100-mesh and the final powders were stored in brown bottles at −20 °C until further use.

2.3. Analytical protocols

For soil samples, a slightly modified method reported by Ge et al. (2020) and using ethyl acetate in the extracting agent was used. Briefly speaking, 1 g sample was spiked with ^{13}C-PCB141, and mixed with a 10 mL mixture of ethyl acetate, dichloromethane, and *n*-hexane (1:2:2, *v*/v) using a Teflon centrifuge tube. After vortexed (1 min), ultrasonic extraction (10 min) was conducted for three times, and the organic phase was collected after centrifugation (10 min, 4000 rpm). Copper scraps were added overnight to the combined supernatants to remove sulfur. Then, the extracts were concentrated into 1 mL and pass through an SPE cartridge (2 g Florisil). A 10 mL ethyl acetate and dichloromethane mixed solvent (1:1, *v*/v) was used to elute PBDEs, DP, and DBDPE. The eluates were dried under a gentle nitrogen stream, spiked with ^{13}C-PCB208 and resolved in 50 μL isooctane. All samples were stored at −20 °C before instrumental analysis.

For cypress leaf samples, methods reported by Wang et al. (2020) were used for PBDEs, DP, and DBDPE. Briefly speaking, the present study used less mass of leaf sample and added ethyl acetate in the extracting agent as well as used a larger elution volume. In order to obtain the halogenated flame-retardants, a 0.2 g leaf sample was added in a Teflon centrifuge tube and treated with the same extraction and concentration procedures as described above. The concentrated extracts (l mL) were purified using sulfuric acid (0.5 mL) to remove lipid and pigment. Then, 3 mL *n*-hexane was used for transfer and rinsing, and to separate the organic phase from sulfuric acid. Furthermore, the samples were passed through a multi-layer silica/alumina column assembled according to Yu et al. (2011). PBDEs, DP, and DBDPE were eluted using 80 mL dichloromethane and *n*-hexane (1:1, *v*/v), spiked with ^{13}C-PCB208 as internal standard after being concentrated, and resolved in 50 μL isooctane. All samples were stored at −20 °C before instrumental analysis.

2.4. Instrumental analysis

A gas chromatograph coupled with a mass spectrometer under negative chemical ionization mode (7890B/5977B, Agilent, USA) was used for the determination of PBDEs, DP, and DBDPE. The chemical separation was achieved using a DB-5HT capillary column (15 m × 0.25 mm × 0.1 μm). The initial oven temperature was set at 110 °C (held for 1 min). The temperature was raised to 270 °C at the heating rate of 16 °C/min, and finally increased to 300 °C at the heating rate of 20 °C/min (held there for 15 min). A 1 μL sample was injected and vaporized at the inlet at 270 °C. The carrier gas (high purity helium; 99.999 %) was used at a constant flow rate of 1 mL/min. The qualitative and quantitative ions of each chemical are presented in Table S2.

2.5. Quality assurance and quality control

Each batch of 10 samples, a matrix blank and a spiked matrix sample were analyzed. The recoveries of PBDEs, DP, DBDPE, and ^{13}C-PCB141 were 78.8 % ± 15.8 %–133.7 % ± 2.3 %, 103.8 % ± 12.7 %–112.9 % ± 6.6 %, 83.4 % ± 4.6 %, and 115.6 % ± 10.9 % for soil samples and 71.6 % ± 1.4 %–131.7 % ± 14.9 %, 98.3 % ± 10.3 %–108.3 % ± 8.9 %, 77.3 % ± 3.3 %, and 89.9 % ± 16.4 % for cypress leaf samples, respectively. The detailed recovery of each chemical is listed in Table S2. The internal standard method was used for the quantification of target chemicals. The R^2 values of calibrations used for quantification were > 0.99. The limit of detection (LOD) and the limit of quantitation (LOQ) for each compound were defined as the concentration corresponding to the threefold and the tenfold of the signal-to-noise ratio, respectively. Both the LOD and LOQ values are listed in Table S2. Trace levels of the target chemicals in matrix blank were < LOD–0.59 ng/g in soils and < LOD–0.93 ng/g in cypress leaves, whereas the concentration in samples was corrected by blanks and not by the recoveries.

2.6. Statistical analysis

Data analysis was performed on SPSS 13 (IBM, USA). Any concentration lower than the LOD was denoted as not detected, while it was replaced with 1/4 LOQ when it fell between the LOD and LOQ with a detection frequency of <50 %, or else 1/2 of LOQ (GB17378.2 − 2007, 2007). The difference between any two variables was confirmed by Mann-Whitney *U* test due to the abnormally distributed data. To access the correlation of a compound between the soil and cypress leaf, spearman correlation was applied. The significance was set at $p < 0.05$. The composition profiles were drawn using Origin 9.0 (OriginLab Corp., Northampton, MA, USA). Surfer 12 (Golden Software, USA) with “Kriging gridding method” was used for calculating the spatial distribution of chemicals.

3. Results and discussion

3.1. Occurrence and pollution profiles of flame-retardants in the soil and in-situ cypress leaves

The detection frequencies of the chemicals are listed in Table 1. In the soil samples, PBDEs were widely detected in the two industrial parks, especially for high brominated congeners. Both the DP and DBDPE were observed in >83.3 % of the soil samples. Compared with soil samples, similar occurrence characteristics of PBDEs, DP, and DBDPE were observed in the cypress leaves. These results indicated that the flame-retardants were widely distributed in the sampling sites.

The concentrations of the target pollutants in the soil samples are presented in Table 1 with a sequence of Σ_{20}PBDE > DBDPE > DP. Meanwhile, contamination levels of most targets in cypress leaves were higher than those in the soils. Flame-retardants were found to lie in the following descending order: DBDPE > Σ_{20}PBDEs > DP in cypress leaves (Table 1). Expectedly, the concentrations of the flame-retardants (except for DP) at the reference site were much lower than those from the two parks, with median concentrations of 474 ng/g (PBDEs) and 65.5 ng/g (DBDPE). Moreover, the concentrations of PBDEs and DBDPE at reference sites were relatively high as compared to that of DP (median: 0.21 ng/g), which might be due to the production of PBDEs and DBDPE in the parks.

For the two parks separately, PBDEs were also the most abundant compounds in soil samples, followed by DBDPE, while DP were 1–3 orders of magnitude lower than DBDPE (Table S3). The median concentrations of DBDPE in the soil samples in LG industrial park were significantly higher ($p < 0.05$) than those in the BH industrial park, which was mainly due to the higher DBDPE yield in the LG industrial park. However, for cypress leaves, DBDPE was obtained as the predominant chemical, followed by PBDEs. Furthermore, DP was 1–3 orders of magnitude lower than the PBDEs (Table S3). Significantly higher concentrations of PBDEs and DBDPE were observed in cypress leaves in the LG industrial park as compared to those in the BH industrial park ($p < 0.01$). There were higher levels of PBDEs and DBDPE because there were three large BFR manufactures of China with the two chemicals as the main products. However, the main products were DBDPE, tetrabromobisphenol A, and octabromodisulfide in the BH industrial park. As for DP, no significant differences were observed between the two industrial parks.

In the present study, Σ_{20}PBDEs in the soil samples were 1–2 orders of magnitude lower than those in the samples collected from the PBDE manufacturing factory in Weifang and Laizhou bay (Li et al., 2015), a plastic modification factory in Guangdong (Deng et al., 2016), and an e-waste dismantling area (Ge et al., 2020) (Table S4A). Such difference might be due to the existence of marine chemicals, agrochemicals, and pharmaceutical factories with low pollution in the presently studied parks, except for the heavily polluted flame-retardant production plants. Furthermore, in the present work, Σ_{20}PBDEs was comparable to those in the soils from e-waste-processing workshop sites of Vietnam (Matsukami et al., 2017) (Table S4A). However, the present PBDEs were 1–2 orders of magnitude higher than those from agricultural soils in Weifang (Zhu et al., 2014), industrial soils in Tianjin (Han et al., 2021), farmlands in Chengdu, China (Liao et al., 2020), soils from e-waste recycling plants from Australia (McGrath et al., 2018) and Pakistan (Iqbal et al., 2017), and soils from landfills in Brazil (Cristale et al., 2019) (Table S4A).

Regarding DBDPE, the median concentrations were about 4 times those of reported from the whole city of Shouguang, Weifang (Zhu et al., 2014), and 1–3 orders of magnitude higher than those in the soils from other regions of China (Table S4B). The results indicated that the production of DBDPE caused high pollution to soils in Weifang, China. Moreover, the concentration of DBDPE in the present study was in an order of magnitude of those in the soils from the e-waste recycling area of Australia and Pakistan, and soils from landfills in Brazil (Table S4B). As for DP, the concentrations were comparable to those in the surface soils from north China (Ma et al., 2014) and industrial area from south China (Yu et al., 2010) (Table S4C). However, DP concentrations were 1–4 orders of magnitude lower than those from e-waste dismantling areas (Ge et al., 2020; Iqbal et al., 2017; Matsukami et al., 2017) and DP manufacture area (Xu et al., 2017). This was due to the absence of DP-related industrial activity in the two study parks. The BFR production activity directly enhanced the pollution levels of PBDEs and DBDPE, while it had little impact on non-BFRs DP in the present case.

The levels of PBDEs in cypress leaves were consistent with those reported in plants around BFR manufactures in Weifang (Li et al., 2015), Laizhou bay (Jin et al., 2008), and Jiangsu, China (Li et al., 2018), and almost 1–3 orders of magnitude higher than those in the leaves of peanut

Table 1

Concentrations (ng/g, dry weight) of PBDEs, DP, and DBDPE in soils and paired cypress leaves in the industrial parks as well as reference sites.

	Industrial park (soil, n = 29)				Background (soil, n = 2)	Industrial park (cypress leaf, n = 29)				Background (cypress leaf, n = 1)
	Range	Median	Mean	DF		Range	Median	Mean	DF	
PBDEs										
BDE17	n.d.–43.2	0.18	2.11 ± 7.87	51.7 %	0.18	n.d.–9.29	1.59	2.24 ± 2.18	79.3 %	1.23
BDE28	n.d.–325	1.90	21.6 ± 64.4	93.1 %	0.46	n.d.–161	1.56	12.0 ± 35.2	62.1 %	0.79
BDE47	n.d.–85.0	0.25	3.30 ± 15.5	31.0 %	n.d	n.d.–44.2	2.81	7.01 ± 11.0	55.2 %	n.d.
BDE66	n.d.–314	0.32	12.0 ± 57.1	69.0 %	n.d	n.d.–48.2	1.11	6.95 ± 13.4	75.9 %	n.d.
BDE71	n.d.–2.07 × 10^4	46.2	920 ± 3.77 × 10^3	96.6 %	11.5	0.67–506	31.5	79.0 ± 110	100 %	1.18
BDE85	n.d.–169	0.22	16.5 ± 37.1	82.8 %	0.11	n.d.–1.82	0.20	0.42 ± 0.56	65.5 %	n.d.
BDE99	n.d–7.41 × 10^3	1.50	290 ± 1.35 × 10^3	72.4 %	3.39	1.86–69.0	14.7	23.4 ± 18.8	100 %	1.05
BDE100	n.d.–4.98	n.d.	0.39 ± 1.18	20.7 %	n.d.	n.d.–22.2	2.70	3.66 ± 4.85	82.8 %	n.d.
BDE138	n.d.–14.4	0.29	2.21 ± 3.75	51.7 %	0.15	3.57–1.23 × 10^3	81.5	168 ± 236	100 %	3.97
BDE153	0.12–35.0	1.12	3.96 ± 7.01	86.2 %	0.13	n.d.–24.9	0.35	2.02 ± 5.12	62.1 %	n.d.
BDE154	n.d.–351	20.6	41.7 ± 65.5	82.8 %	1.09	0.51–416	5.06	33.7 ± 78.3	96.6 %	3.14
BDE183	n.d.–69.2	0.88	6.55 ± 15.0	82.8 %	0.13	n.d.–23.0	0.39	1.93 ± 4.52	62.1 %	n.d.
BDE190	n.d.–1.10 × 10^3	n.d.	38.1 ± 200	17.2 %	n.d.	n.d.–38.9	n.d.	2.24 ± 7.22	34.5 %	n.d.
BDE196	n.d.–16.5	n.d.	1.32 ± 3.49	41.4 %	0.32	n.d.–7.71	2.04	1.60 ± 1.81	51.7 %	1.98
BDE197	n.d.–12.4	0.31	1.66 ± 3.33	55.2 %	0.31	n.d.–7.74	1.90	2.22 ± 1.54	86.2 %	1.64
BDE203	n.d.–2.17 × 10^3	55.6	187 ± 431	93.1 %	1.49.	n.d.–404	5.18	28.5 ± 79.5	79.3 %	n.d.
BDE206	n.d.–480	4.31	39.5 ± 97.5	96.6 %	5.46	n.d.–750	3.24	35.8 ± 137	96.6 %	2.73
BDE207	n.d.–192	8.50	29.7 ± 50.9	96.6 %	4.94	2.15–286	2.80	17.4 ± 52.6	100 %	2.20
BDE208	n.d.–108	2.86	12.4 ± 24.7	93.1 %	4.07	n.d.–5.92	2.20	2.02 ± 1.27	79.3 %	2.11
BDE209	6.44–6.28 × 10^4	374	4.93 × 10^3 ± 1.30 × 10^4	100 %	400	14.7–2.01 × 10^4	42.9	1.27 × 10^3 ± 3.95 × 10^3	100 %	15.8
ΣTri-hepta BDE	0.42–2.96 × 10^4	119	1.36 × 10^3 ± 5.37 × 10^3	96.6 %	17.10	12.7–1.39 × 10^3	209	342 ± 319	100 %	11.4
ΣOcta- BDE	n.d.–2.16 × 10^3	55.6	190 ± 431	100 %	2.11	n.d.–412	8.51	29.4 ± 76.7	100 %	3.61
ΣNona- BDE	0.55–738	16.9	82 ± 164	100 %	14.5	4.66–1.04 × 10^3	8.45	55.3 ± 188	96.6 %	7.04
ΣPBDEs	7.41–6.39 × 10^4	1.22 × 10^3	6.56 × 10^3 ± 1.38 × 10^4	100 %	474	38.6–2.07 × 10^4	461	1.70 × 10^3 ± 4.11 × 10^3	100 %	37.9
DBDPE										
DBDPE	n.d.–3.36 × 10^3	227	426 ± 668	86.2 %	65.5	294–4.51 × 10^5	881	1.87 × 10^4 ± 8.18 × 10^4	100 %	228
DP										
Syn-DP	n.d.–21.3	0.12	0.96 ± 3.86	86.2 %	0.06	n.d.–8.94	5.87	5.23 ± 2.17	86.2 %	5.79
Anti-DP	n.d.–1.21	0.15	0.26 ± 0.27	96.%	0.15	5.48–5.72	5.52	5.54 ± 0.05	100 %	5.49
ΣDP	0.12–22.2	0.28	1.22 ± 3.98	100 %	0.21	5.48–14.5	11.4	10.8 ± 2.17	100 %	11.3

For PBDEs, the sum of thirteen tri- to hepta- BDE, three octa-BDE, and three nona-BDE was expressed as ΣTri-hepta-BDE, ΣOcta-BDE, and ΣNona-BDE, respectively.

and corn cultivated near e-waste recycling area (Fan et al., 2020), mangrove plants from Shenzhen, China (Hu et al., 2020), and leaves from Germany (Dreyer et al., 2021) (Table S4A). As for DBDPE, it was 2–5 orders of magnitude higher than other studies in corn and peanut leaves in the e-waste area (Fan et al., 2020), pine needles in Shanghai, China (Jia et al., 2019), mangrove plant leaves in Shenzhen, China (Hu et al., 2020), and leaves in Germany (Dreyer et al., 2021) (Table S4B). Currently, the DBDPE in plants of the BFR manufacturing area was hardly of any concern in spite of the obviously high pollution. Although DP indicated lowest concentration among the targeted pollutants, the levels in the present study were much higher than those in pines needles from Shanghai, China (Jia et al., 2019), mangrove leaves in Shenzhen, China (Hu et al., 2020), leaves from Germany (Dreyer et al., 2021), and leaves of *typha angustifolia* from a large-scale constructed wetland in Singapore (Wang and Kelly, 2017) (Table S4C). The DP levels were slightly higher than those in the leaves of peanut and corn from e-waste area (Fan et al., 2020), and were consistent with those in the pine needles as well as eucalyptus leaves from an e-waste site of Qingyuan, China (Chen et al., 2011) (Table S4C). Different soil samples from the two industrial parks indicated severe pollution of PBDEs and DBDPE, suggesting that these could influence the soil quality. Both the PBDEs and DBDPE in cypress leaves showed the same level of pollution in the flame-retardant manufacturing area and were much higher than those in the e-waste recycling area, thus calling for more attention.

3.2. Pattern comparison of targeted pollutants in soil and in-situ cypress leaves

The composition profiles of chemicals from environmental samples could provide useful information regarding the chemical sources, behaviors, and environmental fates. In all the soil samples, the predominant flame-retardant was PBDEs (80.7 %–91.0 %), followed by DBDPE (9.0 %–19.3 %), and DP according to the median concentrations (Fig. S2). The similar pattern of flame-retardant composition in several farmland soils in Shouguang, Weifang was also reported by Zhu et al. (2014) with the PBDE concentration being several times that of the DBDPE. Higher concentration of these two chemicals and higher percentage of PBDEs was observed in the present study because of the long-term pollution from the BFR manufacturing area. Soil is an environmental matrix reflecting long-term accumulation of chemicals due to its weak mobility. The results suggested that such composition patterns might contribute to massive and extensive production of PBDEs in this area. Furthermore, BDE209 was gradually eliminated since 2020 with only a few exemptions in several commercial usages in China. To the best of our knowledge, some large flame-retardant manufacturer plants had changed their products from PBDEs to DBDPE in the industrial parks, which was due to the trend of phasing out technical Deca-BDE (the main component was BDE209) in China.

However, based on the median concentrations, there were different flame-retardant composition patterns in the cypress leaves with the most abundant chemical being the DBDPEs (64.4 %–83.8 %), followed by PBDEs (16.0 %–34.1 %) (Fig. S2). Similarly, DP accounted for the lowest proportion in the cypress leaves. The production of PBDEs was gradually replaced by DBDPE in the region, which is the main reason why DBDPE is the dominant chemical in the cypress leaves. Cypress leaves change every 3–5 years and rainfall also contributes to the reduction of pollutants from leaves. It could be inferred that the cypress leaves exhibit a short-term exposure to pollution and reflect short-term contamination. The deposition of organic pollutants from atmosphere to plants is an important pathway to enter the terrestrial plants (Salamova and Hites, 2013). It has been suggested that organic chemicals with log K_{OA} (octanol-air partition coefficient) of >6 and log K_{AW} (water-air partition coefficient) of > −6 could deposit into the plants mainly from the atmosphere (Cousins and Mackay, 2001). Furthermore, it has been reported that the atmospheric uptake of chemicals into the plants with log K_{OA} of >9 was dominant with particle-bound deposition determined using the model calculations (Cousins and Mackay, 2001). The log K_{OA} values of the targeted flame-retardants were within the ranges of 9.27–19.77 (Table S5), suggesting that their aerial deposition into cypress leaves might be a major source, though further research is needed to verify this. For instance, Hu et al. (2020) suggested that foliar uptake of DBDPE in the mangrove leaves was the main pathway of its accumulation. Qiu et al. (2019) reported that atmospheric sedimentation might contribute to elevated levels of DP and PBDEs in the mangrove leaves. As mentioned earlier, the factories changed the production of technical Deca-BDE to DBDPE, which would result in a sharp increase in the output of DBDPE and the transportation of released pollution through atmosphere, suggesting higher DBDPE levels in the cypress leaf samples. Furthermore, it is also possible that the specific bioaccumulation of DBDPE in leaves may be due to higher log K_{OA} value of DBDPE (19.77), which was much higher than that of BDE209 (15.26) (Hu et al., 2020).

For the different types of targets, based on median concentrations, the composition profiles of these chemicals in soils and cypress leaves are shown in Fig. 1. As for the PBDE congeners in soils, BDE209 was found to be the most predominant PBDEs, occupying 95.9 % and 44.4 % of the total PBDEs in LG and BH industrial parks, respectively (Fig. 1A). Such phenomena are in accordance with the fact that BDE209 was the most widely produced and used technical product in China (Han et al., 2021; Li et al.,

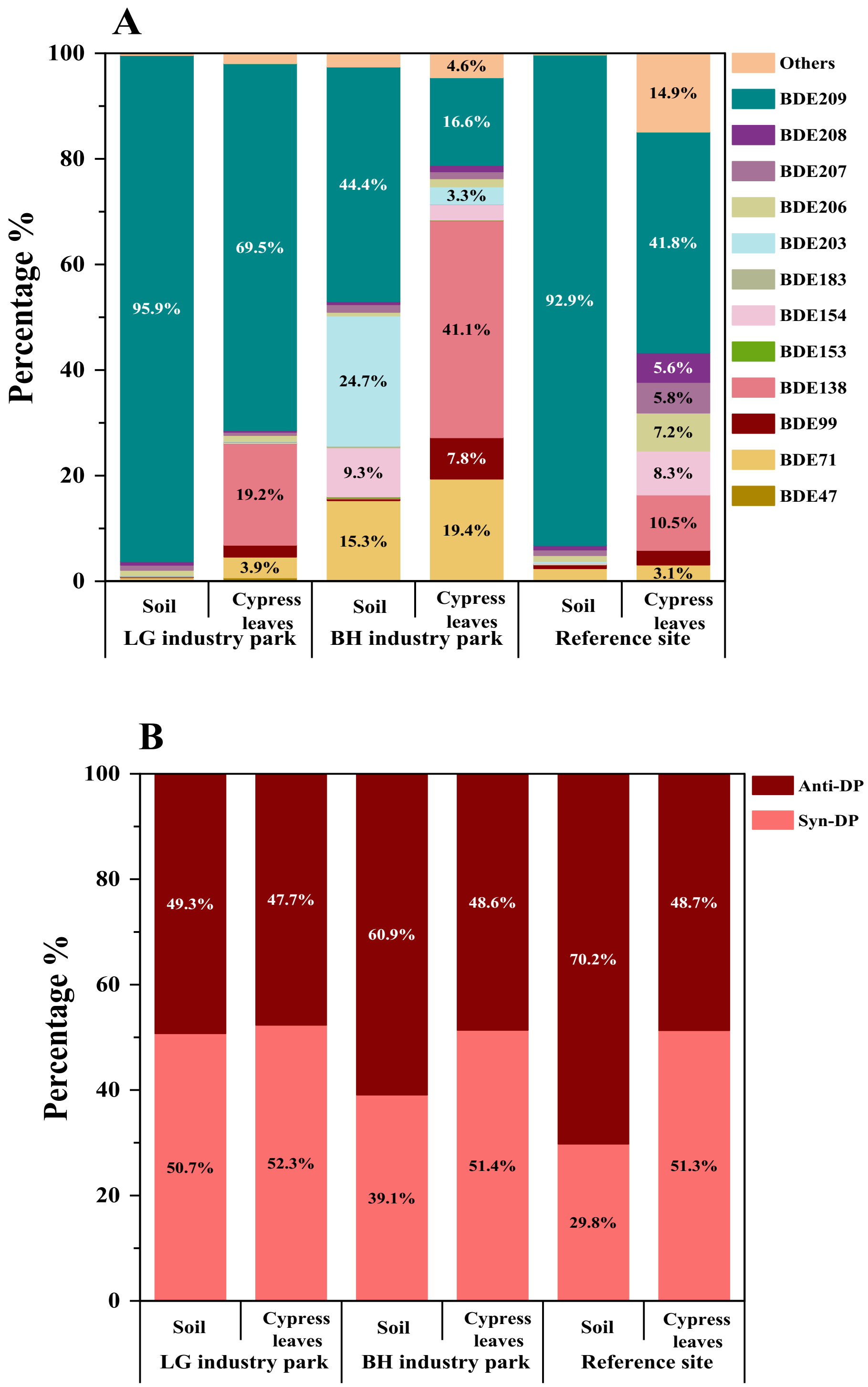

Fig. 1. The composition profiles of PBDEs (A), and DP (B) in soil and cypress leaf samples in LG and BH industrial parks and reference sites.

2015). Comparatively, less BDE209 (44.4 %) and increased percentage for lower brominated congeners were found in the BH industrial park (Fig. 1A). Furthermore, larger contributions were also observed for the lower brominated congeners in the cypress leaves as compared to those in the soil samples. The phenomenon might be due to the following reasons: (1) the longer manufacturing history of BH industrial park (set up in 2005) than the LG industrial park (established in 2010), which could lead to the degradation of PBDEs in the environment; (2) commercial Penta-BDE and Octa-BDE were banned in 2009, whereas BH industrial park produced low-brominated products in the initial stage, while LG industrial park did not; (3) less brominated PBDE congeners being preferentially accumulated and translocated from soil to root, stem and leaves, while BDE209 did not follow this pathway (Han et al., 2021; Hu et al., 2020; Wang et al., 2016).

For DP, the f_{anti} values [(f_{anti} = *anti*-DP/(*anti*-DP + *syn*-DP)] are shown in Fig. 1B. The present data observed in both the soils and cypress leaves were slightly lower than that in commercial products, which was 0.65 or 0.75 (Xian et al., 2011). In the soil samples of the industrial parks, the lower f_{anti} value (LG: 0.49; BH: 0.61) meant that DP might not originate from raw commercial products (Wang et al., 2016), but might be due to unstable *anti*-DP suffering from photolytic or thermal transformation in the environment (Ge et al., 2020; Jia et al., 2019). The results from the present study were lower than those in the soil samples from Shandong, Shanxi, and Hebei, where the f_{anti} values were approximately 0.65 (Ma et al., 2014). As for the cypress leaves, low f_{anti} value (0.49, median) was found in the present study. Similarly, low f_{anti} values were also observed in mangrove leaves (Qiu et al., 2019) and vegetables cultivated in an e-waste area (Wang et al., 2016). Considering the high $r_{l\text{-}s}$ value (the ratio of the concentration of a chemical in cypress leaves to that in the soils from the same sampling site), the DP in leaves mainly originated from leaf-air exchange. In addition, the relatively lower $r_{l\text{-}s}$ value of *anti*-DP (37.4 vs. 50.7, median) (Table 2) might suggest that the biotransformation of *anti*-DP was due to its instability in the plant leaves (Hoh et al., 2006; Qiu et al., 2019). More specifically, the -CH_2 group on the cyclooctane structure in *anti*-DP was less masked by chlorine atoms than the *syn*-DP, which resulted in a higher reactivity and sensitivity of *anti*-DP. On the other hand, *syn*-DP had a higher dipole moment and larger van der Waals volume, which made it less susceptible in plants (Hoh et al., 2006).

3.3. Relevance of the chemicals between soils and cypress leaves

In this study, significance relevance ($p < 0.05$) between soils and in-situ cypress leaves could only be observed for several PBDE congeners in all the samples from the two industrial parks or individual industrial park separately (Table 3). Interestingly, the $r_{l\text{-}s}$ of these chemicals were less than unity (median: 0.21–0.66), which meant that their concentrations in leaves were less than in soils, except for BDE196 (2.54) (Table 2). Chemicals in leaves were the comprehensive result of complex absorption and metabolism in plants. Further research is needed to explore whether $r_{l\text{-}s}$ value of less than one can reveal the important role of root uptake from soils in cypress leaves or not. As relatively lower brominated congeners, BDE153 and BDE154 might exhibit the prioritized bioaccumulation from soil to roots, and translocation from roots to stem or from stem to leaves for some plants as reported by Hu et al. (2020) and Wang et al. (2020). As for BDE209, the particle deposition and foliar uptake from air might be an important pathway (Wang et al., 2014). However, the references also suggested that root passive uptake of BDE209 in rice plants (Chow et al., 2015) and congeners with high log K_{OW} values tended to be accumulated in the root lipids (Yao et al., 2021), and contributed to high concentration of BDE209, thus further transporting from soil to leaf and exhibiting strong relationship between them. These phenomena were also reported in the field study of plants grown in the wetland of Singapore (Wang and Kelly, 2017).

On the contrary, DBDPE in cypress leaves had no correlation with those in the soil samples from industrial parks or the individual industrial park separately (Table 3). Liu et al. (2020) found DBDPE was the dominant halogenated flame-retardants in air and 95 % of them existed in particulates,

Table 2

The $r_{l\text{-}s}$ values of PBDEs, DBDPE, and DP in industrial parks.

	Industrial parks			LG industrial park			BH industrial park		
Compounds	Range	Median	Mean	Range	Median	Mean	Range	Median	Mean
PBDEs									
BDE17	0.73–15.9	2.73	6.23	8.70–11.9	10.3	10.3	0.73–15.9	2.71	5.33
BDE28	0.11–7.75	2.39	3.00	0.13–4.35	1.66	1.81	0.11–7.75	2.81	3.49
BDE47	4.22–37.0	26.5	23.8	4.22–37.0	22.6	21.6	32.8	32.8	32.8
BDE66	0.72–144	3.32	22.1	0.72–144	9.14	38.6	0.84–8.57	0.96	3.33
BDE71	0.06–33.9	0.82	4.46	0.10–33.9	4.72	9.80	0.06–6.62	0.72	1.13
BDE85	0.31–3.56	0.92	1.18	0.49–3.56	0.92	1.32	0.31	0.31	0.31
BDE99	0.11–67.0	2.49	11.0	0.16–67.0	2.94	15.1	0.11–25.3	2.63	6.85
BDE100	0.85–39.5	3.28	11.7	0.85–39.5	20.2	20.2	3.17–3.38	3.28	3.28
BDE138	4.70–1.07 × 10^3	38.3	140	38.3–1.07 × 10^3	142.2	275.8	4.70–208	11.2	48.7
BDE153	0.07–55.4	0.39	4.72	0.16–55.4	0.31	9.50	0.07–1.56	0.39	0.62
BDE154	0.05–23.0	0.66	1.95	0.09–23.0	0.58	3.67	0.05–2.92	0.81	1.02
BDE183	0.08–30.7	0.55	2.82	0.19–30.7	0.55	5.63	0.08–2.39	0.50	0.71
BDE190	3.30–15.4	5.34	8.01	3.30–15.4	9.34	9.34	5.34	5.34	5.34
BDE196	0.47–17.3	2.54	5.23	0.47–9.36	2.25	3.88	17.3	17.3	17.3
BDE197	0.13–11.2	2.04	3.21	0.21–11.2	1.66	3.58	0.13–5.01	3.25	2.54
BDE203	0.06–4.42	0.23	0.68	0.08–4.42	0.93	1.36	0.06–0.77	0.16	0.28
BDE206	0.06–15.5	1.06	1.44	0.06–15.5	0.47	2.06	0.15–1.85	1.08	1.01
BDE207	0.05–2.19	0.38	0.60	0.05–2.19	0.32	0.64	0.12–1.57	0.48	0.58
BDE208	0.05–2.71	0.90	1.00	0.05–1.51	0.23	0.54	0.36–2.71	0.91	1.23
BDE209	0.06–27.6	0.21	1.55	0.06–27.6	0.35	3.11	0.06–3.05	0.19	0.51
ΣTri-hepta BDE	0.11–1.67 × 10^3	1.65	64.3	0.59–1.67 × 10^3	9.1	161.1	0.11–4.71	1.01	1.68
ΣOcta- BDE	0.06–11.3	0.54	1.63	0.35–11.3	1.38	2.98	0.06–2.03	0.13	0.41
ΣNona- BDE	0.06–33.1	0.59	1.84	0.06–33.1	0.41	3.59	0.10–1.90	0.72	0.77
ΣPBDEs	0.07–121	0.53	5.13	0.08–121	0.50	12.6	0.07–3.34	0.56	0.75
DBDPE									
DBDPE	0.48–665	7.03	37.5	1.19–665	9.53	79.7	0.48–74.9	3.74	9.31
DP									
Syn-DP	0.29–170	50.7	57.7	0.29–80.9	45.4	45.2	4.24–170	54.7	65.4
Anti-DP	4.72–57.5	37.4	34.7	6.46–50.9	38.9	34.1	4.72–57.5	36.3	35.2
ΣDP	0.52–92.3	42.4	40.3	0.52–54.4	29.6	30.8	6.67–92.3	43.9	46.4

It should note that the sites of chemicals were not detected in soils or cypress leaves were excluded.

Table 3

The Spearman's rank correlations of PBDEs, DBDPE, and DP between soils and paired cypress leaves in the industrial parks.

	Industrial parks		LG industrial park		BH industrial park	
Compounds	Coefficients	*p*-value	Coefficients	*p*-value	Coefficients	*p*-value
PBDEs						
BDE17	0.052	0.784	−0.224	0.508	0.251	0.315
BDE28	0.224	0.233	0.555	0.076	0.194	0.441
BDE47	0.109	0.567	0.010	0.978	−0.127	0.617
BDE66	0.102	0.592	0.116	0.735	−0.046	0.857
BDE71	−0.07	0.715	0.000	1.000	0.024	0.926
BDE85	0.008	0.968	0.203	0.549	0.427	0.077
BDE99	−0.002	0.992	0.303	0.365	−0.033	0.897
BDE100	0.042	0.825	0.169	0.619	0.042	0.869
BDE138	0.076	0.688	0.059	0.846	0.067	0.791
BDE153	**0.363***	0.048	0.465	0.150	0.182	0.469
BDE154	**0.486****	0.006	0.409	0.211	0.329	0.182
BDE183	0.076	0.688	0.393	0.232	0.123	0.626
BDE190	0.318	0.087	**0.721***	0.012	0.050	0.843
BDE196	**0.476****	0.008	−0.023	0.947	0.070	0.781
BDE197	0.117	0.538	0.303	0.365	−0.076	0.763
BDE203	**0.574****	0.001	**0.665***	0.026	**0.497***	0.036
BDE206	0.359	0.051	0.473	0.142	−0.197	0.433
BDE207	0.353	0.056	0.473	0.142	0.026	0.919
BDE208	−0.095	0.617	**−0.761****	0.006	0.230	0.359
BDE209	**0.582****	0.001	**0.627***	0.039	0.088	0.729
ΣTri-hepta BDE	0.297	0.110	0.355	0.2857	0.375	0.126
ΣOcta- BDE	**0.447***	0.013	0.456	0.159	0.377	0.123
ΣNona- BDE	**0.388***	0.034	0.445	0.170	−0.096	0.705
ΣPBDEs	**0.391***	0.033	0.373	0.259	0.172	0.494
DBDPE						
DBDPE	0.264	0.159	0.182	0.593	−0.359	0.143
DP						
Syn-DP	−0.159	0.402	**−0.642***	0.033	−0.182	0.496
Anti-DP	0.243	0.196	0.064	0.853	0.240	0.336
ΣDP	0.134	0.481	0.082	0.811	−0.007	0.977

* $p < 0.05$.

** $p < 0.01$.

nearby Laizhou bay. It has been reported that particle-bound deposition from atmosphere may be the dominant source of DBDPE in leaves (Cousins and Mackay, 2001; Hu et al., 2020), whereas plant leaves were used to monitor air pollution of DBDPE (Dreyer et al., 2018; Jia et al., 2019). Furthermore, DBDPE has high log K_{OA} value, making it hard to transport from soils to leaves. Moreover, the $r_{l\text{-}s}$ of DBDPE in industrial parks was 7.03 and 9.53 (median), which means that the concentration of DBDPE in soils was much less than that in leaves (Table 2). Therefore, the results from the present study indicated that soil was not the important source of DBDPE in leaves. However, whether air could be the main source of cypress leaves or not needs to be verified through air data in the future, although Hu et al. (2020) suggested that foliar uptake of DBDPE from air into the mangrove leaves was vital. However, based upon the results, it can be inferred that differences between plants could not be ignored (Dobslaw et al., 2021).

For DP, although no significant correlations were observed between all soil and cypress leaf samples from the industrial parks, a negative correlation ($p < 0.05$) was observed for *syn*-DP between them in the samples from LG industrial park (Table 3). The median $r_{l\text{-}s}$ values of DP in the LG and BH industrial parks were 29.6 and 43.9, respectively (Table 2). A significant positive correlation ($p < 0.05$) was observed for the DP in both the *eucalyptus* leaves and pine needles, and in the air samples from e-waste areas (Chen et al., 2011). Similar atmospheric sedimentation of DP in leaves was also reported by Qiu et al. (2019) and Wang and Kelly (2017). Therefore, the high $r_{l\text{-}s}$ values in the present study could not be explained by the root uptake from soils, while air-leaf exchange progress and particle deposition were also important factors.

Therefore, soil might not be the main contributor to the most target contaminants in cypress leaves, and air might be a more probable source, although this requires further verification by related atmospheric samples. However, the deposition of flame-retardants in plant leaves is a complex process, including root translocation to the shoots by transpiration stream, elimination in shoot, and leaves uptake (Yao et al., 2021). Therefore, it is suggested that more field experiments and real-time observations at the cellular level should be conducted.

3.4. Spatial distributions of the target pollutants in soils

Pollutants could be released from emission sources and transported to the surroundings through air (Ge et al., 2020; Yu et al., 2010). The spatial distribution of target pollutants in the industrial park soils is presented in Fig. 2. The levels of Σ_{20}PBDEs exhibited higher trends in those areas, which were near to the production source or building material factory with more usage of these chemicals as compared to others. Decreasing concentration of PBDEs with the increase in distance of the high polluted areas indicated the deposition of chemicals in soils. Similar results were also reported around BFR manufacturing plant area by Li et al. (2016). In the LG industrial park (Fig. 2A), the site with extremely high level of PBDEs was observed at the site between two large factories. One is a factory with annual BFR output of >10,000 tons, while another is a factory with the major product of technical Deca-BDE. The results indicated that relatively low PBDE level was observed in those sites, which were close to the factories producing agricultural chemical and pharmaceutical chemicals and were far from flame-retardant manufacturing zone. Unlike the LG industrial park, the BH industrial park also had more BFR plants, while their major products were found to be TBBPA, octabromide, and octabromosulfide, rather than the traditional BFRs. Lower PBDE levels were observed at the sites (Fig. 2E). As the predominant PBDE congener, the distribution of BDE209 in soils was close to Σ_{20}PBDEs, especially in the LG industrial park (Fig. 2B and F). Spatial distribution of DBDPE was analyzed and is shown in Fig. 2C and G. Due to the similar distribution of PBDEs and DBDPE in the LG industrial park (Fig. 2A and C), the results were found to be consistent with a previous study that reported that DBDPE was replacing the production of PBDEs (Zhu et al., 2014). High polluted sites were found around the DBDPE manufacturing factories, papermaking additive factories and building material factories (Fig. 2C and G). The results demonstrated that the factories associated with the production and use of PBDEs and DBDPE were found to be the main sources of chemicals in the areas.

However, there was a completely different distribution of DP with the two BFRs above, confirming its special source. The result of DP in the soil samples of the LG industrial park are given in Fig. 2D. The concentration of DP in the site of LG6 was about 20 times higher than the other sites, but still 3 orders of magnitude lower than the soils around the DP manufacturing area (Wang et al., 2010). As is well known, DP flame-retardant has widely been added in industrial polymers (thermoplastic materials) as a flame-retardant, such as plastic roofing materials, cables, electrical wires, computers connectors and electronics (Wang et al., 2010). The higher concentration in the LG6 site might be due to the wide usage and improper disposal of DP products in urban activities as compared to other sites. In the soil samples of the BH industrial park (Fig. 2H), all sites showed the same low level of DP, suggesting that DP might have come from daily use in urban activities and underwent natural environmental transportation process. However, except for the critical factor of pollutant sources, the existence of pollutants in soils associated with other complex factors such as soil structure and properties needs further research in the future (Xiong et al., 2021).

4. Conclusions

This study researched the different pollution characteristics of three kinds of halogenated flame-retardants, in surface soils and in-situ cypress leaves from the two BFR manufacturing industrial parks. The target chemicals were widely detected and the concentrations of PBDEs and DBDPE were relatively higher than those in the samples from other cities in China. LG industrial park had more serious pollution by PBDEs and

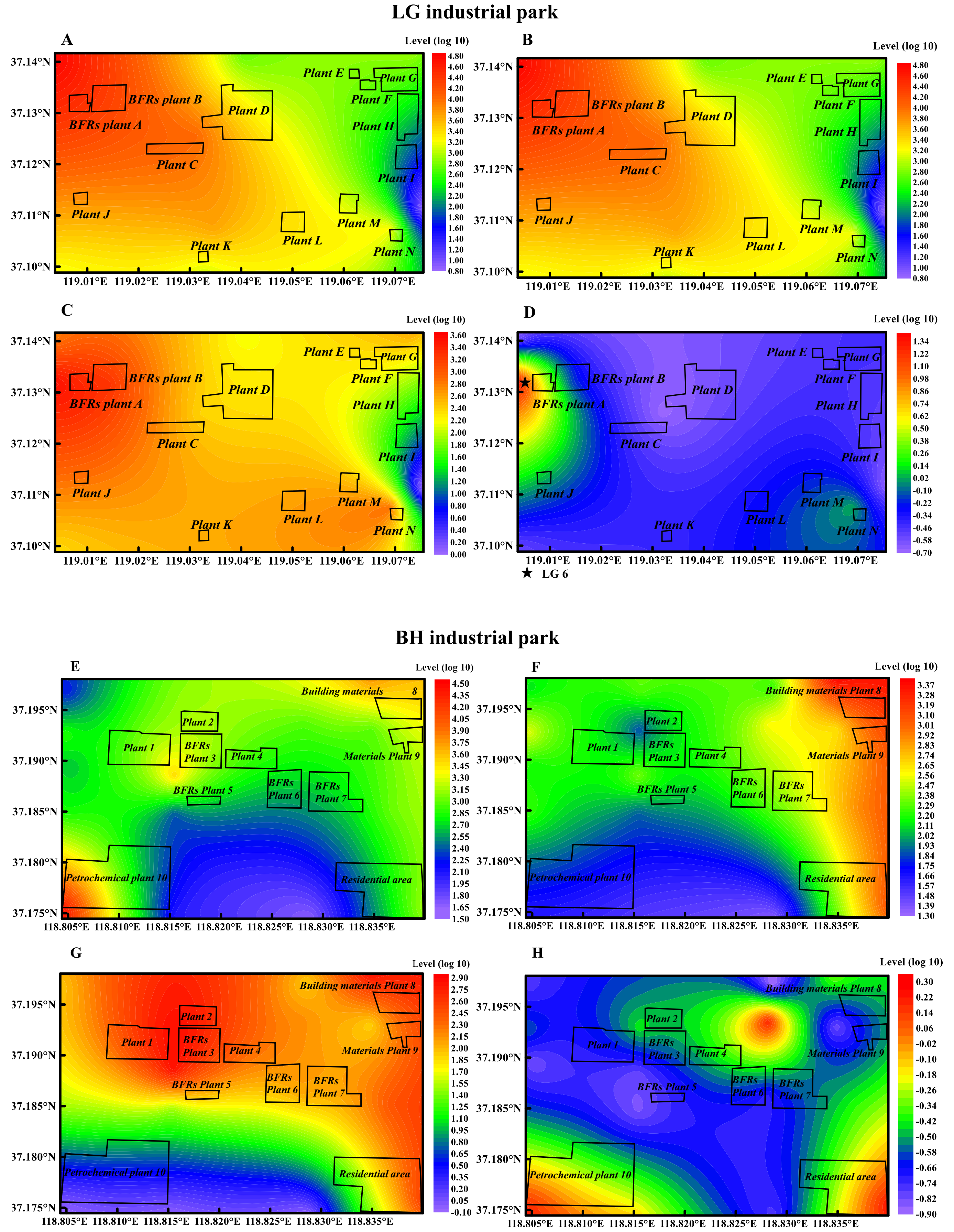

Fig. 2. The spatial distribution of Σ_{20}PBDEs (A, E), BDE209 (B, F), DBDPE (C, G), and DP (D, H) in the soils of LG and BH industrial parks.

DBDPE than the BH industrial park. Higher levels of chemicals were related to the manufacturing and operational activities of BFRs. Different composition profiles of the chemicals in soil and cypress leaf samples were observed. PBDEs and DBDPE were found to be the predominant species of BFRs in soils and cypress leaves, respectively. The long-term production history and extensive production of PBDEs resulted in high pollution in the study area, which needs more attention. Except for several PBDE congeners, no significant positive correlations were observed for these chemicals between the soils and the leaves. The $r_{l\text{-}s}$ values were higher than unity, suggesting that soil might not be the main contributor of the chemicals in cypress leaves. A large proportion of DBDPE was preferentially exhibited in cypress leaves, which revealed that the recent pollution was due to the replacing of PBDEs by DBDPE. The transformation, metabolic fate, and systematical source analysis are also important factors for studying flame-retardants in the future.

CRediT authorship contribution statement

Yingxin Yu: Design, formal analysis, writing - original draft.
Meijuan Lu: Methodology, data analysis, writing.
Xiang Ge: Methodology.
Shengtao Ma: Data curation.
Hongli Liu: Methodology.
Guiying Li: Methodology, review & editing.
Taicheng An: Supervision, writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.157129.

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