Uptake of halogenated organic compounds (HOCs) into peanut and corn during the whole life cycle grown in an agricultural field

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ARTICLE INFO

ABSTRACT

Here, we elucidated the uptake and translocation of numerous halogenated organic compounds (HOCs) into corn and peanut throughout their life cycle cultivated in an agricultural field of an electronic waste recycling area, where plants were simultaneously exposed to contaminants in soil and ambient air. The geometric mean concentrations of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) were 22.3 and 11.9 ng/g in peanut and 16.6 and 13.6 ng/g in corn, respectively. Decabromodiphenyl ethane (DBDPE, 6.07 ng/g) and dechlorane plus (DPs, 6.22 ng/g) also showed significant concentrations in peanuts. The plant uptake was initiated from root absorption at the emergence stage but it was subsequently surpassed by leaves absorption from the air since the late seedling stage or early reproductive stage. There was a rapid uptake of lower halogenated HOCs at the early vegetative stages in both species. However, robust uptake of highly halogenated compounds at the reproductive stages suggests a delayed accumulation of them by the plants. PBDE and PCB congener profiles suggest more noticeable tendency for inter-compartment translocation in peanut than in corn during the plant development. The DP and HBCD isomeric compositions in peanut (enriched with *syn*-DP and γ-HBCD) were different from those in the rhizosphere soils and air, suggesting a more stereoisomer-selective uptake and/or biotransformation in this species compared to corn. The bioaccumulation factors for root-soil and stem-root of these HOCs in most cases were <1. The tissue-distributions demonstrated that leaves serve as a significant reservoir of absorbed HOCs under the field conditions, whereas the low concentrations in peanut and corn kernels indicated translocation of most HOCs into this compartment was significantly hindered (especially for highly halogenated compounds).

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1. Introduction

Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and other halogenated flame retardants (HFRs) are a typical class of man-made chemicals that have been or are being used as additives in a variety of applications (Ali et al., 2012; Genisoglu et al., 2019). Although the production and use of some of these chemicals have been banned for decades or several years, they are still frequently found in the environment due to the persistence property (Li et al., 2006) and humans are continuously exposed to them in pathways.

Plant uptake of organic chemicals represents the first step for these substances to enter the terrestrial food web and plays an important role in human exposure to them (Nizzetto et al., 2008). The uptake can occur via transfer from soil into the roots, which has been shown to be a passive or active process (Collins et al., 2006), as well as atmospheric deposition to leaves including dry gaseous deposition for many semivolatile organic compounds (SOCs) (Su et al., 2007) and particle-bound deposition for SOCs with low vapor pressures (Moeckel et al., 2009; Su et al., 2007). Xenobiotics absorbed by plant roots or leaves can be translocated into other plant parts and induce significant phytotoxicity (Bakker et al., 2001;

Li et al., 2018; Luo et al., 2015; Wang et al., 2017). Translocation of organic chemicals from roots to fruits of tomato and cucumber has been found even for highly hydrophobic compounds (Zhang et al., 2015; Sun et al., 2019a). Recent studies of carrot uptake highlight the importance to consider metabolites of some organic chemicals in the risk assessment (Sun et al., 2015; Sun et al., 2018). Therefore, plants, especially those grown in heavily contaminated environments, may result in adverse health effects associated with food consumption.

The uptake of organic chemicals into plant is a function of physicochemical properties of the compounds, environmental conditions, and plant species (Huang et al., 2011; Zhang et al., 2015a). Numerous studies have been conducted on the plant uptake and translocation of organic pollutants, mainly through greenhouse cultivation, closed chamber, spiked soil, or hydroponics experiment. These controlled experiments can produce results that are specific and relevant with consistency. However, the simulated condition, plant growth, and plant accumulation behavior, may be different from those in the field. Moreover, experimental research usually involves short-term exposure duration and single exposure source (e.g., soil, air, or water) (Li et al., 2011; Wang et al., 2012; Zhao et al., 2012). To date, only a few studies reported the simultaneous uptake of pollutants from multi-environmental media (Mikes et al., 2009; Wang et al., 2015b). There is a lack of information on the translocation behavior in different plant compartments during the whole growth period.

This study was conducted in an abandoned electronic waste (e-waste) area, where a huge amount of e-waste was recycled using primitive methods (see more information in Supplementary Material). A wide range of toxic halogenated organic compounds (HOCs), including PCBs, PBDEs, and numerous HFRs, were released into the environment, leading to potentially long-term exposure and health risk of the workers and local residents (Grant et al., 2013). Corn and peanut were cultivated in an agricultural field, which were simultaneously exposed to contaminants in both the soil and air. The primary aims were i) to elucidate the processes of uptake, translocation, and accumulation of HOCs at different growth stages of plants grown under field conditions, ii) to investigate the changes in their concentrations, compositions, and tissue distribution over the entire life of plants, iii) and to assess and compared the uptake pathways of the two species that are concurrently exposed to contaminants from both soil and air.

2. Materials and methods

2.1. Plant cultivation and sampling

The field trial was carried out on an agricultural plot (approximately 3×8 m) located in a small village in Qingyuan, South China, which is about 200 m away from an abandoned e-waste recycling facility (Fig. S1). Two species, corn (Zea mays L., an annual monocotyledon plant) and peanut (Arachis hypogaea Linn., an annual herbaceous dicotyledonous plant), which are the common crops in the study area, were selected. Peanut and corn seeds were purchased from a local farmer's market, which were produced by two agricultural technology corporations.

The plants were cultivated under field conditions and in manners as local farms do. Information on plants growth stages and sample collection is summarized in Table 1. The first sampling was conducted on day 6 at the stage of emergence, and radicle and cotyledon of peanut and radicle and hypocotyl of corn were collected. The first pair of leaves and radicle were also collected for corn that was at the late sprout stage. At the stage of seedling, primary roots and leaves for corn and primary root, cotyledon, stem, and leaves for peanut were sampled on day 15. At the late

seedling stage (for peanut) and jointing stage (for corn), roots, stems, and leaves were collected on day 38 for both species. In addition to roots, stems, and leaves, ears (for corn only), immature/mature kernels were obtained from each stage of the budding, flowering and ripening of the plants (days 39–97). Corn stalks (including the stem and corresponding leaves) collected at four reproductive stages (days 53–97) were further divided into three segments from bottom to the top (lower, middle, and upper) to further understand the acropetal translocation of HOCs. The sampled plants were randomly selected in each sampling event from the original seed until the harvest, each of them was a composite of at least triple subsamples (Fig. S2).

Air, initial soils (prior to the planting, 0–10 cm), and rhizosphere soils were also collected. Two pairs of polyurethane foam (PUF) passive air samplers were deployed in the field (0.5 m above the ground) to collect gaseous HOCs (Ding et al., 2016). The PUF disks were replaced at each time the plant samples collected, and were sealed in zip-lock aluminum foil bags. Rhizosphere soils were gently removed from roots using a brush as far as possible. The samples were transported to the laboratory in a cooler.

2.2. Sample treatment, instrumental analysis, and quality control

Relevant information is described in detail in Supplementary Material and is given briefly here. All samples were rinsed with distilling water and the eluates were discarded before they were freeze-dried. Peanut and corn samples (0.1–4 g for each) were prepared for analyzing HOCs including PCBs, PBDEs, deca-bromodiphenyl ethane (DBDPE), and hexabromocyclododecane (HBCDs), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), hexabromobenzene (HBB), and dechlorane plus (DPs). The plant samples, spiked with surrogate standards for PCBs, PBDEs, and HBCDs to monitor their recoveries, were Soxhlet-extracted for 48 h with a mixture of hexane and acetone (v/v = 1:1). The extracts were concentrated to 2 mL and were treated with 2-mL concentrated sulfuric acid twice. The supernatants were purified and fractioned with a solid-phase extraction cartridge.

PCBs and other halogenated compounds except for HBCDs were analyzed by using an Agilent Technologies 7890 gas chromatograph coupled to an Agilent 5975C mass spectrometer, with an electron impaction source and electron capture negative ionization modes, respectively. HBCDs (α-, β-, and γ-stereoisomers) were analyzed by ultra-high performance liquid chromatography tandem mass spectrometer.

Field PUF disk blanks were routinely processed in each sampling session. A laboratory blank was run with each batch of field samples, and the concentrations were blank-corrected accordingly. The average recoveries of plant samples were $88 \pm 17\%$, $88 \pm 16\%$, and $93 \pm 14\%$ for PCB30, 65, and 204, $113 \pm 38\%$, $82 \pm 16\%$, and $86 \pm 33\%$ for BDE77 and 181, and ^{13}C-BDE209, and $77 \pm 20\%$, $56 \pm 20\%$, and $76 \pm 21\%$ for ^{13}C-α-, β-, and γ-HBCDs, respectively.

3. Results

3.1. Overall concentrations in plant tissues, air, and soils

The HOCs were found in various tissues in the peanut and corn plants and their concentrations are summarized in Table 2 and in more detail in Table S1. The total concentrations of PBDEs varied from 3.82 to 86.9 ng/g, with a geometric mean (GM) of 22.3 ng/g in peanut, and PCB concentrations ranged from 2.55 to 22.3 ng/g, with a GM of 11.9 ng/g. The highest concentration of individual pollutants was observed for BDE209 (GM = 11.4 ng/g), its concentrations were a little higher than DBDPE (GM = 6.07 ng/g) and DPs (GM = 6.22 ng/g). In corns, the total concentrations of PBDEs and

Table 1
Plant growth stages and samples collected at each stage.

Sampling day	No.	Peanut		Corn	
		Growth stage	Samples collected	Growth stage	Samples collected
April 1	D0	Sowing		Sowing	
April 7	D6-1	Emergence (VE)[a]	Radicle and cotyledon	Emergence (VE)	Radicle and hypocotyl
April 7	D6-2		*(Not available)*	First Leaf (V1)	Root and leaf
April 16	D15	Third tetrafoliolate (V3)	Root, stem, leaf, and cotyledon	Second Leaf (V2)	Root, stem, and leaf
May 9	D38	Beginning bloom (R1)	Root, stem, and leaf	Sixth Leaf (V6)	Root, stem, and leaf
May 24	D53	Beginning pod (R3)	Root, stem, leaf, and husk	Silking (R1)	Root, stem, leaf, husk, and tassel
June 8	D68	Beginning kernel (R5)	Root, stem, and husk	Blister (R2)	Root, stem, leaf, husk, tassel, and kernel
June 23	D83	Full kernel (R6)	Root, stem, leaf, husk, and kernel	Dough (R4)	Root, stem, leaf, husk, tassel, and kernel
July 7	D97		*(Not collected)*	Maturity (R6)	Root, stem, leaf, husk, tassel, and kernel
July 15	D105	Over-mature pod (R9)	Root, stem, leaf, husk, and kernel		*(Not available)*

[a] In the brackets, V means vegetative stages and R means reproductive stages.

Table 2
Concentrations (ranges and geometric means, ng/g dry weight) of HOCs in the main tissues of peanut and corn in all the growth stages.

Congener	Root	Stem	Leaf	Husk	Kernel
			Peanut		
ΣPCBs [a]	16.0−43.3 (24.4)	2.95−12.7 (6.80)	16.2−31.6 (24.1)	2.85−5.22 (3.89)	0.23−0.31 (0.40)
L-PBDEs [b]	4.11−17.2 (8.84)	1.51−15.4 (7.09)	1.56−8.46 (6.59)	1.98−3.38 (5.45)	1.66−1.75 (4.66)
BDE209	7.31−56.9 (22.1)	4.33−131 (22.9)	1.97−113 (11.2)	2.13−103 (15.9)	0.83−0.88 (0.85)
ΣPBDEs	19.4−62.3 (34.5)	10.7−134 (38.5)	3.53−118 (23.9)	4.11−106 (25.5)	2.49−2.63 (5.52)
DBDPE	1.47−67.4 (18.3)	0.23−56.1 (6.60)	0.85−20.0 (3.40)	6.95−40.2 (13.7)	0.01−0.18 (0.04)
BTBPE	2.63−4.34 (3.50)	1.76−2.83 (2.21)	1.57−3.54 (2.41)	1.23−2.79 (2.09)	1.44−1.55 (1.49)
ΣDPs	6.70−19.6 (13.2)	3.67−13.8 (5.72)	3.69−11.8 (5.95)	4.88−5.45 (5.11)	4.48−4.64 (4.56)
ΣHBCDs	0.05−0.47 (0.14)	0.05−0.64 (0.20)	0.12−1.43 (0.40)	0.14−0.37 (0.18)	0.24−0.26 (0.25)
HBB	0.15−0.71 (0.31)	0.11−0.90 (0.23)	0.11−0.53 (0.25)	0.05−0.12 (0.08)	0.03−0.04 (0.03)
			Corn		
ΣPCBs	4.41−66.4 (17.8)	0.86−52.1 (5.55)	9.46−60.2 (19.1)	1.84−10.3 (3.92)	0.25−2.03 (1.21)
L-PBDEs	0.69−63.9 (7.68)	0.11−26.3 (2.83)	0.62−25.1 (3.24)	nd-1.28 (1.61)	nd-1.28 (1.23)
BDE209	11.3−70.8 (35.8)	nd-10.2 (1.51)	nd-8.29 (5.24)	0.11−6.38 (1.38)	nd-1.03 (0.38)
ΣPBDEs	12.0−114 (45.9)	0.47−26.6 (5.30)	4.83−25.1 (10.7)	1.25−7.66 (4.04)	nd-1.54 (2.11)
DBDPE	6.51−80.0 (24.1)	0.42−91.8 (4.17)	4.16−31.9 (12.4)	1.72−11.6 (4.80)	nd-2.97 (1.84)
BTBPE	0.83−7.72 (2.30)	0.21−10.9 (0.81)	0.72−9.90 (2.06)	0.38−1.15 (0.62)	0.29−0.96 (0.47)
ΣDPs	0.96−10.6 (4.00)	0.04-2.50 (0.30)	0.27−4.96 (1.08)	0.09−1.38 (0.20)	nd [c]
ΣHBCDs	0.12−0.65 (0.28)	0.04−0.26 (0.09)	0.13−0.40 (0.19)	0.02−0.50 (0.07)	0.04−0.34 (0.12)

[a] Sum of 23 selected PCB congeners (CB18, 20, 28, 44, 52, 66, 74, 87, 95, 99, 101, 105, 110, 115, 118, 132, 138, 149, 153, 164, 180, 187, and 209).

[b] Sum of 15 PBDE congeners (BDE28, 47, 66, 85, 99, 100, 153, 154, 183, 196, 197, 203, 206, 207, 208).

[c] Not detectable.

PCBs ranged from 7.63 to 50.7 ng/g and 6.68−46.4 ng/g (with GMs of 16.6 and 13.6 ng/g), respectively. The concentrations of BDE209 (GM = 9.68 ng/g) were comparable to those of DBDPE (GM = 12.0 ng/g). The concentrations of other HOCs were substantially lower. Overall, the concentrations of HOCs in corns were not significantly different from those in peanuts ($p > 0.07$), except for DPs and BTBPE with higher concentrations in peanuts ($p < 0.020$).

Concentrations of HOCs in the soils and air were summarized in Table S2. BDE209, DBDPE, and DPs were also the primary pollutants in soils. The soil concentrations did not vary significantly during the growth stages of the two species compared to those in the plants (mentioned below) for most HOCs (Fig. S3). Significant differences in the rhizosphere soil concentrations of the HOCs between the two species were only observed for DBDPE (higher in corn, $p = 0.022$) and PCBs (higher in peanut, $p = 0.006$). In the air, PCBs, PBDEs, and DBDPE were the primary HOCs, with mean concentrations of 1029 ± 184, 84.2 ± 23.1, and 27.1 ± 6.95 pg/m^3, respectively. The air concentrations of HOC showed different temporal trends during the period of plant growth (Fig. S3).

3.2. Concentrations in plants during growth stages

3.2.1. Peanut
Fig. 1 displays the time dependent HOC concentrations in plants along the whole cultivation cycle. PCBs were nearly not detected in the original seeds. On day 6 at the stage of emergence, PCB concentrations reached 7.76 ng/g in the radicles and 1.68 ng/g in the first pair of leaves. Tissue PCB concentrations (24.2 ng/g in primary roots and 16.2 ng/g in leaves) at the stage of seedling day 15 also increased substantially. PCBs were also found in the cotyledon (13.5 ng/g) and stems (7.41 ng/g) at the seedling stage, but the concentrations were slightly lower than those in the leaves and roots. On day 38 (the early reproductive stage), PCBs concentrations in roots (43.3 ng/g) and stem (12.7 ng/g) increased, whereas leaf PCBs concentration was comparable to the previous. Overall, PCB concentrations in the tissues varied less during the period of following reproductive stages (from days 53−105). This trend differed from a previous observation of a reduction in concentrations of polycyclic aromatic hydrocarbons in rice tissues at heading stage due to the formation of seeds (Wang et al., 2015b).

L-PBDEs were present in the initial peanut seeds (with a total of 6.72 ng/g). L-PBDE concentration in radicles (14.4 ng/g) on the day 6 increased two folds compared to seed concentration. L-PBDEs in root, leaf, and stem reached their maximum levels on day 15, and after that their concentrations were stable in roots and hulls and varied in stems and leaves. However, distinct variations of BDE209 concentrations over the period of peanut growth were observed. Its concentrations in tissues at the emergence stage were lower than that in the initial seeds, whereas there was a steady increase in the
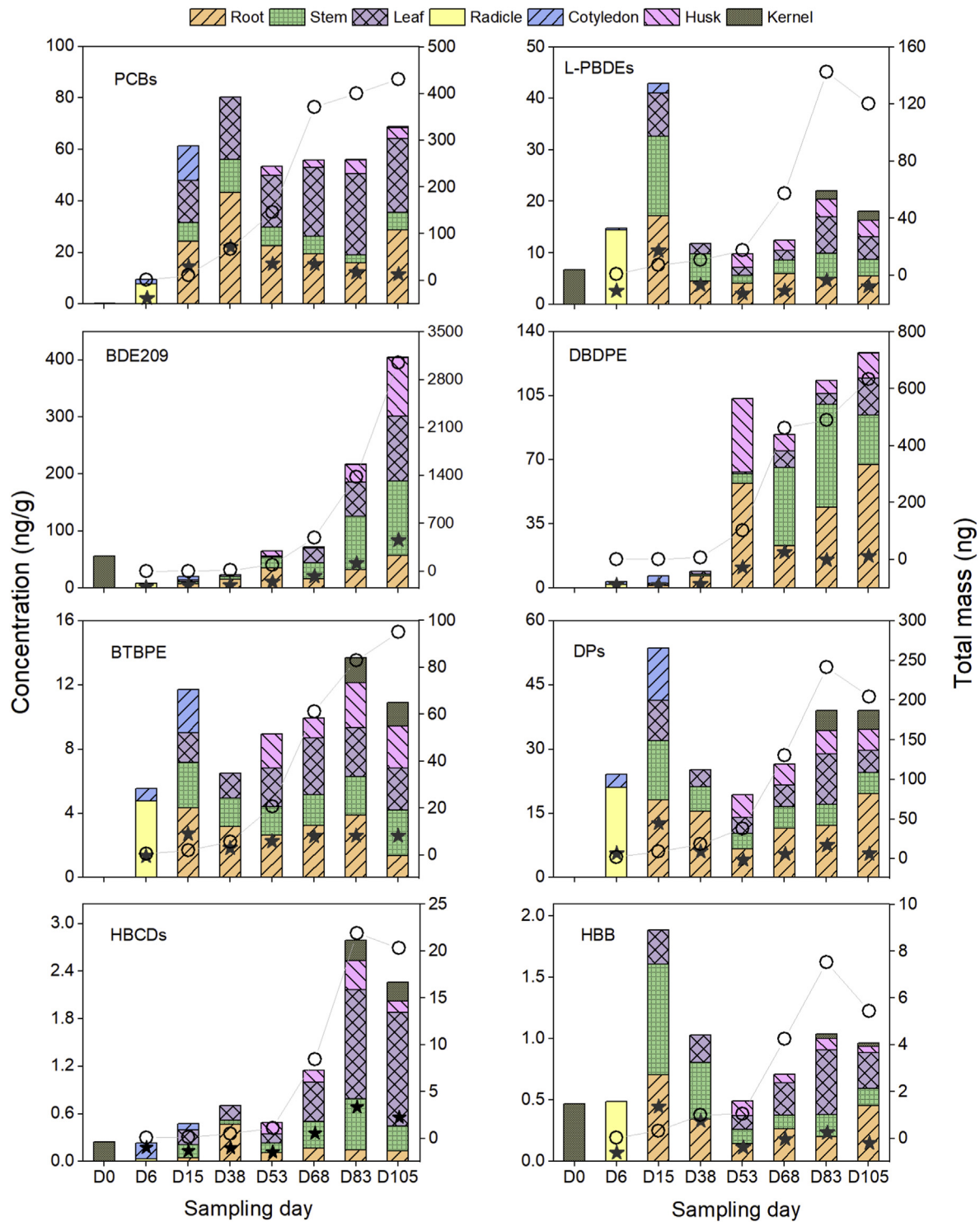
Fig. 1. Tissue-specific concentrations (ng/g dw, bars), overall whole-plant concentrations (ng/g dw, stars), and total mass (ng, circles) of major HOCs in peanut at different growth stages during plant life.

tissue concentrations during the period of plant growth.

Generally, the concentrations of DBDPE and HBCDs in the main tissues at the vegetative stages were much lower than those at the reproductive stages (Table 2), which was also observed for BDE209. Relatively, the concentrations of DPs and BTBPE in many tissues displayed smaller variations, and no increasing trends existed. These HOCs were frequently detected in hulls, however many of

them were not found or present at low concentrations in kernel peanuts.

3.2.2. Corn

At the emergence stage (day 6-1), total PCB concentrations in hypocotyl and radicle of corn are similar (19.7 ng/g versus 18.9 ng/g), which were much higher than that in the original seeds (1.88 ng/
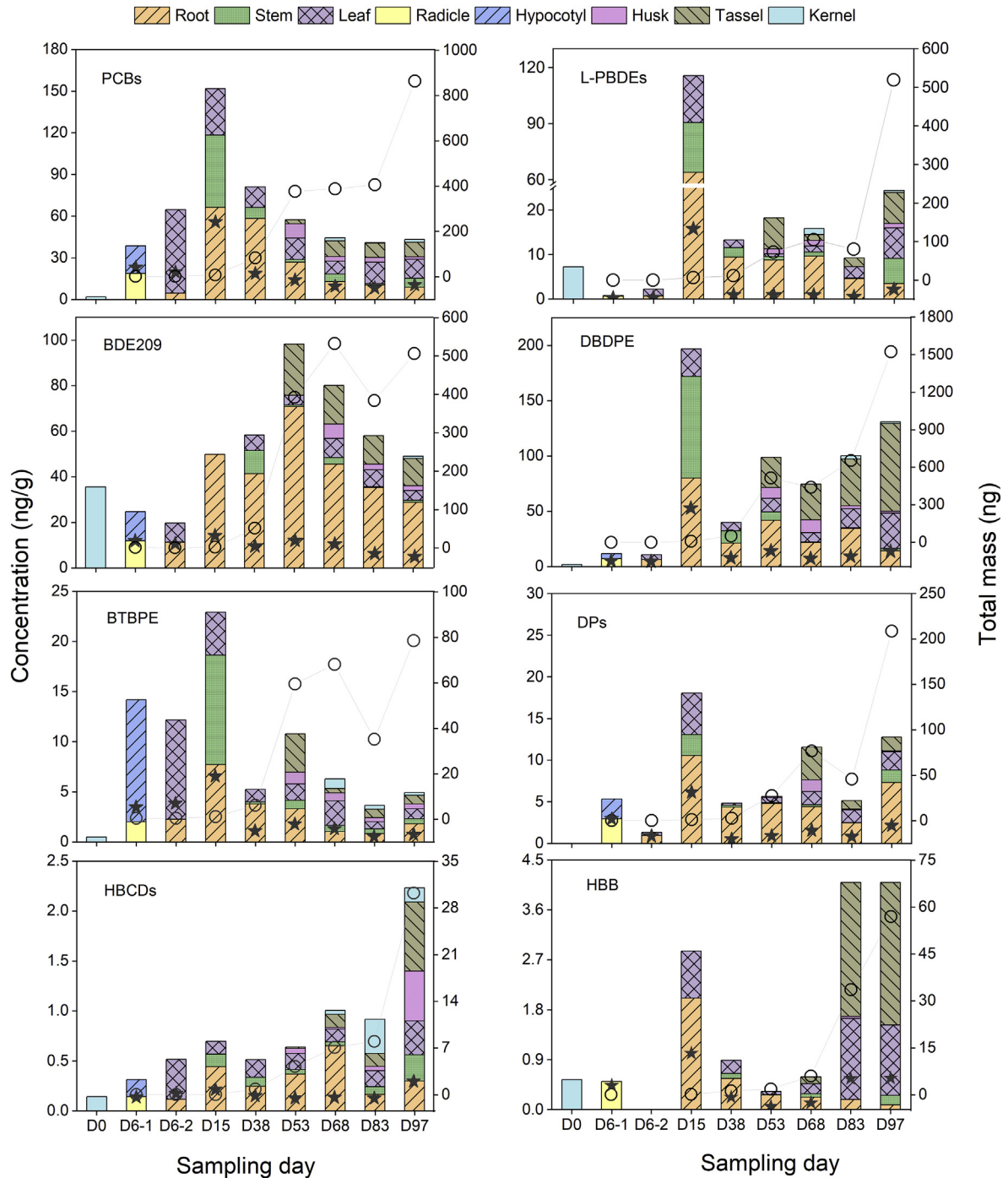
Fig. 2. Tissue-specific concentrations (ng/g dw, bars), overall whole-plant concentrations (ng/g dw, stars), and total mass (ng, circles) of major HOCs in corn at different growth stages during plant life.

g) (Fig. 2). The concentration in leaves increased sharply (60.2 ng/g) at the early seedling (day 6-2) stage, but the root concentration was significantly lower. On the day 15, the highest concentration of PCBs in roots and elevated concentration in stems (52.1 ng/g) was found. However, PCB concentration in leaves decreased at this stage. PCB concentration on day 38, remained comparably high, but after that their concentrations decreased gradually (8.74 ng/g in the end). Nevertheless, the concentrations in leaves (9.46−15.6 ng/g) and tassels (3.00−11.2 ng/g) increased during this period of time. During these stages, the concentrations in the stems fluctuated

significantly, and the concentrations in kernel corns and husks were consistently low.

L-PBDEs was also present in the initial corn seeds (7.33 ng/g), higher than that in peanuts. However, the concentrations of both L-PBDEs and BDE209 decreased at the early seedling stage compared with that in seeds, differing from the observation for PCBs. The concentrations of L-PBDEs in all the tissues (root, stem, leaf) were highest on day 15, after which a decreasing trend for the root concentrations and an increasing trend for leaf concentrations were observed. Peak concentration of BDE209 in roots occurred on day

53, whereas the leaf concentrations were stable. DBDPE, BTBPE, and HBB showed similar temporal changes in roots to PCBs and L-PBDEs; while their leaf concentrations varied significantly. The temporal changes also indicated that their concentrations in roots are likely little influenced by rhizosphere soil concentrations during the growth period. Compared with those in peanut, the stem concentrations of HOCs in corn were lower. The concentrations in both husks and kernels were very low (<11.6 ng/g). Nevertheless, significant amounts were found in tassels with concentrations of nondetectable (nd)-79.3 ng/g.

Figs. 1 and 2 also shows the overall concentrations of HOCs in the whole peanut and corn plants at each stage. The concentrations of BDE209, DBDPE, and HBCD in the reproductive stages were remarkably higher than those in the vegetative stages in peanut. For other HOCs, the highest concentrations were found on day 15 (except for PCBs on day 38). In corns, the concentrations of HOCs in the whole plants also reached maximum in the middle vegetative stage. A generally decreasing temporal trend for many HOCs such as PCBs, PBDEs, and BTBPE was observed.

3.3. Tissue distribution

Fig. S4 shows the biomass (dry) of peanut increased exponentially until the beginning pod (R3) stage; however, in the following stages the biomass changed little compared with that in R3 stage except for kernels. In contrast, there was a continuous increase in the biomass of corn during the whole growth process. At the harvesting stage, the main tissues of root, stem, leaf, and kernel accounted for 5%, 21%, 28%, and 25% of the total biomass of peanut and 10%, 39%, 34%, and 10% of the total biomass of corn, respectively. The mass tissue-distributions of HOCs in the plants were displayed in Fig. S5. In peanut, 39%−78% (64% on average) of the PCBs in the whole plants were localized in leaves and the fractions increased through the growth stages. The fractions of PCBs in roots ranged from 8% to 28%, displaying a reducing fraction through the growth stages. Stem contributed only 12% on average of the whole-plant PCBs. The fractions of PBDEs in leaves (16%−53%, 34% on average) were less than those of PCBs. The increased fractions in leaves and decreased fractions in roots were also found for PBDEs at the later growth stages. PBDE fractions in stems (31%−46%) were significantly higher than PCBs. For DPs, BTBPE, and HBB, similar tissue-distributions were observed and their contributions in leaves, roots, and stems were comparable. For HBCDs, leaves (51%−71%) dominated the loadings in the plants during the whole growth period, and roots made a substantially small contribution (<10%). DBDPE displayed lower fractions (5%−38%) in leaves. Only for DPs and BTBPE, kernel made a noticeable contribution (14%−20%). Altogether, HOCs were more localized in the vegetative compartments rather than in the edible parts, and a similar result has also been observed in a previous study (Lechner and Knapp, 2011). In corn, the tissue-distributions were generally similar to those in peanut, except that the fractions in stems were significantly lower.

Fig. S6 depicts the vertical distributions of HOCs in segmented corn plants. The concentrations of most HOCs in leaves were higher in low layer than those in the middle and upper layers, in which concentrations were comparable, before the ripening stages. At the ripening stages, increased concentrations in the upper-layer were observed for several HOCs. However, there were no clear trends for the vertical distributions of most HOCs in stems.

3.4. Compositions in plants during growth stages

BDE209 was the dominant PBDE congeners nearly in all the tissues of the two species. Its average contributions in hull, root, and stem (all around 76%) were higher than those in leaf (69%) and

kernel (52%) in peanut. In corn, BDE209 was most abundant in root and tassel (both 81%), followed by leaf and husks (64%), stem (53%), and kernels (38%). Fig. S7 shows the composition profiles of the eight major PBDE congeners except for BDE209 at each growth stage. In peanut, BDE154 (54%) and 197 (30%) were the dominant congeners in original seeds. At the vegetative stage (days 6−15), PBDE congener profiles in tissues were similar, with BDE47 being the most congener (27%−28%), except for cotyledon in which BDE197 remained dominated (62%). During the reproductive period, similar PBDE compositions were observed among tissues at some stages or in the same tissue at different stages. In corns, PBDE compositions varied significantly with a few exceptions. In the original peanut seeds, only trace amount of PCB28 and 153 were detected (Fig. S7). PCB28 remained a major congener (29%) in cotyledon but contributed only 5% in radicles on day 6. PCB153 became the major congener in all the tissues (22%−60%) on day 15. While tissue differences existed, PCB compositions within each tissue through the reproductive stage (since day 38) were generally similar, dominated by PCB153 in most cases. In corns, PCB composition profiles were generally different. PCB153 remained the most abundant congener, followed by PCB28 and 52. This related to the fact that PCB153 is the main component of the technical formula and a recalcitrant molecule (Greenwood et al., 2011).

The compositions of DP isomers, expressed by f_{anti} (the fraction of anti-isomer) were shown in Fig. S8. The f_{anti} values in various compartments and the growth stages of peanut were constant, which were 0.51 in the original seeds and 0.37−0.50 during the growth. The values were obviously smaller than those in the corresponding rhizosphere soils (mean = 0.73) and air (0.56) as well as in the technical DP products (0.65−0.80) (Chen et al., 2013). In contrast, f_{anti} values among the tissues or the growth stages of corns (0.23−1.00, with a mean of 0.64) were mostly close to those in the technical products and generally followed an order of root > leaf > stem. In peanut, only γ-HBCD was found in the original seeds (Fig. S9). However, α-HBCD became generally dominant during the vegetative and early reproductive stages. This was distinct from those in the soils and the technical products with γ-HBCD being the dominant stereoisomer. At the reproductive stage (on day 53) α- and γ-HBCDs were both the primary diastereoisomer. From day 68 to the harvest, γ-HBCD became the predominant diastereoisomer in all the tissues contributing 58%−100% of total HBCDs. In corn, only γ-HBCD was found in original seeds and in radicle and hypocotyl. Through the following stages, γ-HBCD remained the most abundant diastereoisomer nearly in all the tissues (with contributions of 28%−100%). Interestingly, α-HBCD preferentially accumulated in tassels.

3.5. Bioaccumulation and translocation

Root bioaccumulation factor (RCF), reflecting the root bioaccumulation of HOCs from soil, was calculated (see Supplementary Material). The overall RCFs of peanut (median = 0.31) were significantly higher than those of corn (median = 0.21) ($p = 0.01$). The compound-specific RCFs through the growth (Fig. S10) showed that in most cases the RCFs were <1. The lower brominated PBDEs, HBB, and BTBPE in the vegetative stage of peanut were noticeably higher than the reproductive stage, while an inverse trend was observed for BDE209, DBDPE, and HBCDs. In corn, the RCFs were generally higher in the middle stages (with maximums on the day 15 for most HOCs) than the beginning and maturity stages. The assumptive stem/root transfer factors (TFs) of most HOCs in peanut (median = 0.35) were also significantly higher than those in corn (median = 0.11) ($p = 0.01$, Fig. S11). The TFs were higher at the early stages than the later reproductive stages in peanut, except for a few

highly halogenated compounds. In corn, the TF values varied significantly during the growth.

The plant/air partition coefficients (K_{PA}) over the growth period were given in Fig. S12. It indicated that the log K_{PA} values of seven PCB congeners in peanut increased slightly or changed less during most of the time, but this was not found in corn. In both plant species, highly chlorinated PCB congeners had higher log K_{PA} values. In peanut, L-PBDEs and HBB had higher log K_{PA} in the early growth stages, while other pollutants including BDE209, DBDPE and BTBPE had higher log K_{PA} in the later growth stages. In corn, lower halogenated compounds showed high variability of log K_{PA} during the plant growth. In both the species, noticeably higher log K_{PA} values in the early growth stages were found for some HOCs. Presumably, the relatively higher leaf concentrations could be attributed to translocation from roots in the early life stage.

4. Discussion

The air and soil concentrations of HOCs in the present study were one or two orders of magnitude lower than previous data measured at this site (Chen et al., 2014; Tian et al., 2012). The substantial reduction in their concentrations was due to e-waste recycling regulation by local government. However, the air concentrations of PBDEs and PCBs here were still high compared to those found in Chinese urban air (with means of 35−110 pg/m^3) (Liu et al., 2016; Ma et al., 2017; Qi et al., 2014).

The concentrations of most HOCs in the initial seeds of both peanut and corn were much lower relative to the cultivated plants. This is not surprising as the seeds were produced in remote rural areas and some of the chemicals have been banned for years. Nevertheless, the presence of HOCs in radicles and cotyledons suggests uptake of these pollutants from the environment initiated at the emergence stages. The results indicated different accumulation behaviors of HOCs in plants during the growth period. We observed rapid uptake at the early vegetative stages in both species for lower halogenated HOCs that mostly had low concentrations in the initial seeds. Their concentrations decreased or leveled off during the reproductive stages, which was likely a result of reduced plant uptake ability or dilution effect because of rapid plant growth. In a previous chamber study, Zhu et al. (2016) also observed rapid absorption followed by a slow absorption of HBCDs by new plant leaves from both soil and air, but a level-off was not found during the experiment duration (within several weeks). The rapid uptake kinetics of HOCs could mainly relate to diffusion and sorption onto the lipophilic root solids and leaf surface wax (Lechner and Knapp, 2011; Zhu et al., 2016). However, for highly halogenated compounds (e.g., BDE209, DBDPE, and HBCD) with significant concentrations in seeds, slow uptake at the (early) vegetative stages was observed. The presence in the initial seeds or the high molecular weight possibly hindered the efficient absorption in the beginning development stage. Robust plant uptake of these HOCs at the reproductive stages suggests a delayed uptake of these high molecular weight pollutants by the plants. It may require more time for large molecules to reach equilibrium (Huang et al., 2011; Moeckel et al., 2008), because they need to pass through an increasing number of biological barriers during the long-distance transport in plants (Blaine et al., 2014; Sun et al., 2019b).

The considerably lower concentrations in peanut and corn kernels for most HOCs indicated these compounds may not easily enter the peanut and corn kernels, probably attributed to barrier effect of hull and husks as well as weak translocation of these hydrophobic HOCs from other tissues. This is consistent with previous result that perfluorinated chemicals are predominantly dislocated to the vegetative compartments rather than the storage organs of grain (Fismes et al., 2002; Lechner and Knapp, 2011). The tissue-

distributions in this field trial demonstrated that leaves serve as a significant reservoir of HOCs absorbed by peanut and corn (Fig. S5) attributed to the large leaf mass proportions (15%–69% of the total plant) and the relatively large surface areas which enhanced uptake of HOCs from the air. Furthermore, the vertical distributions of HOCs in corn leaves suggest that uptake of pollutants in the vapor or particle phrases via evaporation or suspension from soil were a significant pathway. The translocation capacity of HOCs to corn stem was substantially restricted compared with peanut stem, in which considerable amount of HOCs were found. This difference may be a result of the plant morphology and/or plant physiology of the two species. For instance, the large plant size of corn substantially limited the long-distance transport of HOCs in the vascular tissues. Enhanced acropetal translocation of PBDEs in corn grown hydroponically has been reported previously (Zhao et al., 2012). Wang et al. (2015a) also found that more PBDEs will penetrate the roots and are acropetally translocated in the shoot in a defective root system (caused by high concentration of copper) in their pot experiment. These observations differed from the result obtained under field conditions in the present study.

Despite the significant levels of HOCs in the roots of both species, root is not a significant reservoir of most HOCs in late development stages especially in peanut because of the small root biomass (Fig. S4). There was a generally decreasing trend in the root fractions and an increasing trend in the leaf fractions of HOCs through the plant lifetime. The result indicated that plant uptake of HOCs was initiated from root absorption from soils and it was subsequently surpassed by leaf absorption from the air (in a few cases by stem absorption) since the late seedling stage or early reproductive stage. Leaf HOCs were predominantly from the air (via gaseous and/or particle-bound deposition) as evidenced by previous studies (Collins et al., 2006). Nevertheless, HOCs in stem can be derived from various sources (direct uptake from air or translocation from leaves and/or roots) (Bakker et al., 2001; Mikes et al., 2009; Zhang et al., 2015b). Similar variations of concentrations of PCBs, BTBPE, and DPs between peanut roots and stems indicated dominantly upward translocation from roots; while downward translocation from leaves was likely responsible for the occurrence of PBDEs and HBCDs in peanut stems. An explanation for the differences is not available. Interestingly, corn tassels contained a significant amount of HOCs relative to its biomass, which has not been reported previously to the best of our knowledge. Tassels have a rough surface, and the specific surface area led to the higher concentrations. This should be expected, since tassels have evolved to interact with the air. Nevertheless, the HOCs accumulated in tassels were not transferred effectively to the corn kernels.

The lowest proportions of BDE209 found in kernels of both species also indicated decreased uptake from the environment or translocation from other tissues of this highly brominated congener. The compositions of PBDEs and PCBs in initial seeds were distinct from those in tissues in the early growth stages of peanut. It is speculated that these pollutants in the seeds encountered substantial metabolism during germination and early seedling growth. The underlying mechanism is not known, although several possible metabolisms of xenobiotics in plants have suggested (Sun et al., 2019a). A previous hydroponic experiment demonstrated dehalogenation and halogen rearrangement of HOCs in corns (Wang et al., 2011). Seeds provide important nutrition for plant development, but these pollutants in early stage plants should be from the environment instead of seeds. The similar PBDE congener profiles in peanut implied inter-compartment translocation or no significant metabolism during the plant development. The similar PCB profiles in roots and stems in most stages indicated a main uptake route most likely occurring through the soil compartment. Alternatively, airborne particle deposition arising from soil suspension

could be another explanation. The varied compositions of PBDEs and PCBs in corn tissues were explained not only by diverse sources but also by metabolism of these compounds in plant.

On the contrary, the DP composition profiles demonstrated peanut rather than corn is likely prone to stereoisomer-selectively absorb and/or metabolize DPs. In the literature, most average plant f_{anti} values were in the range of 0.57−0.70 (Table S3), comparable to that in the corn of this study. Although the stereoisomeric compositions of HBCDs in peanut in the early development period were closer to those in the air, it was unlikely that they were mainly from air given the low air concentrations. Instead, this indicated a noticeably selective uptake of α-HBCD from soils or preferential biotransformation of γ-HBCD stereoisomers. A recent study preferential degradation reactions of γ-HBCD by corn microsomal cytochrome P450 enzymes (Huang et al., 2019). In the later period, the compositions were close to the soil where γ-HBCD became dominated. The dramatic change in HBCD stereoisomeric compositions was likely attributed to changes in plant physiological and biochemical functions involving in stereoisomer-specific uptake or metabolism of HBCDs in the growth stages. A clear shift of the HBCD stereoisomeric compositions was not observed in corn, where γ-HBCD was basically dominant in most compartments. Overall, the result in the present study as well as data in the literature (Table S3) indicated the frequent diastereomer-selective uptake, translocation, or biotransformation of HBCD in plant, implying these phyto-mediated processes in the environment may significantly alter the HBCD stereoisomeric compositions in soil.

The bioaccumulation and translocation potential of these HOCs within the plants (especially in corn) were low for most HOCs. Lower RCFs (<1) of HOCs have reported in numerous field studies, in contrast to the RCFs obtained from either spiked soil systems or hydroponics (Mikes et al., 2009; Whitfield Aslund et al., 2008; Wu et al., 2012; Zhang et al., 2015b; Zhu et al., 2017). Temporal variations of RCFs showed that typically lower halogenated compounds in the early growth stages and highly halogenated compounds in the later reproductive stages preferentially accumulate in the plants. Enrichment of HOCs in leaves was significant, suggesting the importance of atmospheric deposition pathway for the plant uptake under the field conditions.

This study has its limitations. Plant uptake in the field is more influenced by factors such as heterogeneity in soil texture, temporal variability of air pollution, and meteorological conditions than controlled experiments. This leads to difficulty in revealing the inherent uptake and translocation of HOCs under field conditions. Thus, the results in the present study could indicate a tendency of plant uptake and translocation of HOCs in the field rather than give precise evidence. This study fails to provide insights into the potential mechanisms, for example, for growth and development related uptake and inter-compartment translocation. This study also warrants more attempts of field research to enhance the understanding of the accumulation of HOCs in plants.

5. Conclusion

Plant uptake of HOCs was motivated even at the emergence stage of plants. HOCs showed varied accumulation potential in the plants during the growth and development, which was dependent on their physicochemical properties or presence at the original seeds. These HOCs accumulate predominantly in leaves because of the large biomass as well as the importance of atmospheric deposition pathway. Although noticeable inter-compartment translocation in peanut was observed, the transfer factors in the two plant species were generally low, especially into the kernels. Stereoisomer-selective uptake and/or biotransformation of some HOCs by the plants were found, but the underlying mechanism was not clear. Despite the limitations, this study provides significant information on the uptake and translocation of HOCs into plant in the field throughout the whole life cycle.

Declaration of interests

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.

CRediT authorship contribution statement

Yun Fan: Investigation, Writing - original draft, Formal analysis, Methodology. **She-Jun Chen:** Conceptualization, Writing - review & editing, Supervision. **Qi-Qi Li:** Investigation. **Yuan Zeng:** Investigation. **Xiao Yan:** Resources. **Bi-Xian Mai:** Project administration.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.114400.

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