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Distribution and Chiral Signatures of Polychlorinated Biphenyls (PCBs) in Soils and Vegetables around an e-Waste Recycling Site

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ABSTRACT: The distribution and composition of polychlorinated biphenyls (PCBs) within soil−plant systems around a notorious e-waste recycling site were investigated. The average total PCB concentrations in rhizospheric soils (RSs) and nonrhizospheric soils (NRSs) were 2160 and 1270 pg g^{-1} dry weight (DW), respectively. PCBs were more enriched in RS than NRS for most vegetable species. PCB accumulation in plant tissues varied greatly among plant cultivars, ranging from 4020 to 14 500 pg g^{-1} DW in shoots and from 471 to 24 400 pg g^{-1} DW in roots. The compositions of PCBs in soil and plants showed that hexa- and hepta-chlorinated PCBs were preferentially accumulated in soils, while tri- and tetra-PCBs were abundant in plant tissues. These results indicated that low-chlorinated PCBs might be prone to accumulation and transfer within plants, which was confirmed by the relationship between the root concentration factor and octanol−water coefficient. The first eluting enantiomers of PCB 84 and PCB 95 were preferentially transferred between the soil and plants, while the stereoselectivity of PCB 136 varied among plant species. A significant difference in enantiomeric fractionation of PCB 84 between the soil and roots indicated that enantiomeric enhancement of PCB 84 occurred during its translocation from soil to root, whereas no such difference was observed in these chiral PCBs during their translocation from the root to the shoot.

KEYWORDS: *chiral signatures, polychlorinated biphenyls (PCBs), e-waste recycling site, soil−plant systems*

1. INTRODUCTION

The plant uptake of persistent organic pollutants (POPs) from environmental matrices has attracted research interest because plants are the primary point of entry for pollutants into the food chain.[1,2] In particular, the root−soil boundary region, generally referred to as the rhizosphere, represents the most important biotic−abiotic mass-transfer interface and plays an important role in the dissipation of pollutants in soil and plant uptake of soil pollutants.[3] Plants can enhance the removal of organic pollutants through adsorption or uptake by roots or through biodegradation or rhizoremediation.[4] In addition, the bioavailability of organic pollutants can be significantly increased through microbial metabolism and plant growth.[5] Differing results on the fate of POPs in the rhizosphere have been obtained, which may be related to plant species,[6] sampling procedures of the rhizospheric soil,[7] and aging of soil contaminants.[7] For example, lower levels of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) were observed in the rhizosphere compared to the bulk soil,[8,9] while different results were also observed for PAHs, polybrominated diphenyl ethers (PBDEs), and novel brominated flame retardants (NBFRs), all of which were observed in higher levels in the rhizosphere.[7,9,10] The potential plant uptake of POPs from various environmental matrices has been confirmed by pot experiments and field investigations.[11] More importantly, root physiological status has been shown to be an important factor in plant uptake of PBDEs and PCBs, with more PBDEs and PCBs penetrating roots and being translocated to shoots in a defective root system damaged by copper addition.[12,13] Hence, the distribution of POPs in soil and the corresponding plant uptake of POPs from contaminated sites is an important topic for investigation, especially in the presence of other pollutants such as heavy metals and organic pollutants in the current study area.

PCBs are a group of synthetic organic chemicals that are present in electronic waste recycling (e-waste); e-waste has been identified as an important source of PCBs.[14] High concentrations of PCBs and other contaminants have been detected in various environmental matrices around e-waste recycling sites.[7,10,11,14−17] For example, the PCB concentrations in farm lands around e-waste recycling sites and e-waste contaminated soil were in the range of 4.9−12 and 24−3552 ng/g dw, respectively.[18] Furthermore, abandoned e-waste recycling sites continue to act as a significant source of PCBs even 10 years after their abandonment.[17] Obviously, serious environmental pollution caused by previous e-waste recycling is still present.

Seventy-eight of the 209 PCB congeners display axial chirality and exist as rotational isomers or atropisomers. Of the 78 chiral PCB congeners, 19 form stable atropisomers under ambient conditions.[19,20] In general, the enantiomers of chiral PCBs are produced in equal proportions, although metabolic processes in plants and animals can preferentially target one

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stereoisomer. This enantiomeric fractionation is often used to track enantiomeric enhancement or biotransformation of chiral PCBs in different environmental matrices.[21−23] Although many studies have focused on plant uptake of PCBs, few have investigated the chiral signatures of PCBs in the soil−plant system. Among such studies, stereoselectivity of 2,2′,3,3′,6-pentachlorobiphenyl (PCB 84), 2,2′,3,5′,6-pentachlorobiphenyl (PCB 95),[24,25] and 2,2′,3,3′,6,6′-hexachlorobiphenyl (PCB 136)[24] in plants has been investigated more frequently than that of other chiral PCBs. Additionally, recent research showed that the stereoselectivity of chiral PCBs in plants is weakened after exposure to copper, which can be attributed to a potential reduction in biotransformation of chiral PCBs during their translocation within plant tissues. Whether this result can be extrapolated to in situ contaminated sites is of significant concern and has created great uncertainty. The present study was conducted at an e-waste contaminated site to investigate the distribution of PCBs in rhizospheric soils, nonrhizospheric soils, and plant tissues. The stereoselectivity of chiral PCB 84, 95, and 136 in soils and plant tissues was also examined to elucidate the potential sources of PCBs in plants. Our results clarify the plant uptake and translocation processes of PCBs and provide valuable information for food safety protection.

2. MATERIALS AND METHODS

2.1. Chemicals. Thirty-five PCB congeners (indicator PCBs: PCB 28, 52, 101, 138, 153, and 180; dioxin-like PCBs: PCB 77, 105, 114, 118, 156, and 189; chiral PCBs: PCB 84, 95, and 136; and other PCBs: PCB 8, 37, 44, 49, 60, 66, 70, 74, 82, 87, 99, 126, 128, 158, 166, 169, 170, 179, 183, and 187) were purchased from Wellington Laboratories (Guelph, ON, Canada). Silica gel and Florisil were purchased from Sigma-Aldrich (St. Louis, MO). Alumina was purchased from MP Biomedicals (Santa Ana, CA). HPLC-grade solvents were purchased from Fisher Scientific (Pittsburgh, PA).

2.2. Sampling Site Description. Guiyu, located in eastern Guangdong Province [23° 3′N, 116° 03′E], South China, was selected for the present study. Numerous home-based e-waste processing workshops have been established in Guiyu since the early 1980s, resulting in its predominance among e-waste recycling areas in China. The agrotype in this area is red earth and organic carbon in the soil is in the range of 1.32−1.51% (Table S6). In this region, the average annual rainfall and temperature are 1721 mm and 21.5 °C, respectively.[26]

Plant and soil samples were collected from local vegetable gardens located approximately 1 km from an e-waste storage site. Briefly, 14 rhizospheric soil (RS) samples from various vegetable varieties and their corresponding nonrhizospheric soils (NRSs) were collected. Plants were gently pulled from the soil, and the soil was lightly crushed and shaken to obtain the soil located within 2 mm of the plant root surface, which was defined as RS. Bulk soil located 10−20 cm away from the corresponding plant and without significant root influence was collected as NRS. The 14 sampled vegetables included cabbage lettuce (*Lactuca sativa* L. var. *capitata* L.), Chinese cabbage (*Brassica pekinensis*), celery (*Apium graveolens*), Chinese kale (*Brassica alboglabra* L. H. Bailey), flowering cabbage (*Brassica campestris* L.), shallot (*Allium fistulosum*), cabbage (*Brassica oleracea* var. *capitata*), radish (*Raphanus sativus* L.), taro roots (*Colocasia esculenta* (L.) Schoot), crown daisy (*Chrysanthemum coronarium* L.), pak choi (*Brassica campestris* L.), snow pea (*Pisum sativum*), sweet potato (*Ipomoea batatas* (L.) Lam.), and lettuce (*Lactuca sativa*). Prior to sampling, all vegetables were grown for at least 2 months. A single vegetable type was sampled three times from the same garden, which meant that 3 whole plants were harvested for each vegetable type. Rhizospheric soil and bulk soil were also collected for each individual plant. All samples were wrapped in aluminum foil, placed in polythene zip-bags, and transported immediately to the laboratory. The plants were washed with tap water and deionized water to remove potential soil residue. All samples were stored at −20 °C until analysis.

2.3. Chemical Analysis. Soil and plant samples were freeze-dried and ground into a fine powder. Subsequently, approximately 0.5 g of plant samples and 5 g of soil samples, spiked with surrogate standards (PCB 30, PCB 198, and PCB 209), were Soxhlet extracted with dichloromethane (DCM) for 48 h and with hexane/acetone (3:1, v/v) for 72 h, respectively. The fractionated extracts were concentrated to ∼0.5 mL after solvent exchange to hexane. Plant extracts (prewashed with sulfuric acid) and soils were purified using a multilayer column containing, from the bottom to top, neutral alumina (3% deactivated), neutral silica gel (3% deactivated), 50% (w/w) sulfuric acid−silica gel, and anhydrous Na_2SO_4, with 20 mL hexane/DCM (1:1, v/v) as an eluent. After evaporation to approximately 50 μL, ^{13}C-PCB 141 was added as an internal standard prior to instrumental analysis.

PCBs were analyzed using an Agilent-5975 GC-MSD system with a Varian CP-Sil8 CB capillary column (50 m length, 0.25 mm i.d., 0.25 μm film thickness). The oven temperature was set to 150 °C for the initial 3 min, increased to 290 °C at a rate of 4 °C min^{-1}, and then held for 10 min. The injector and detector temperatures were set to 250 and 230 °C, respectively. A mixed standard including 33 congeners was used for the quantification of PCBs. Detailed information about the PCB congeners has been reported previously.[14] The capillary column used to separate the enantiomers was ChiraSil-DEX CB (25 m, 0.25 mm i.d., 0.25 μm film thickness) from Varian.

2.4. Determination of Enantiomer Fraction. Chiral signatures were described based on the enantiomer fraction (EF), defined as the peak area of the first eluting enantiomer divided by the sum of the peak areas of both enantiomers on an enantioselective chromatographic column. The first eluting enantiomer is the (−) enantiomer of PCB 84 and PCB 136, while the (+) and (−) enantiomers have not been identified for PCB 95.

2.5. Quality Assurance and Quality Control. A procedural blank, a spiked blank containing all investigated chemicals, and a duplicated sample containing duplicated extracts of a test sample were included in each batch of 10 samples to assess potential sample contamination and the repeatability of the analysis. No target compounds were detected in laboratory blanks. The surrogate recoveries of PCB 30, 198, and 209 were 75 ± 13, 86 ± 5, and 92 ± 15% in soil and 55 ± 12, 75 ± 9, and 83 ± 12% in plants, respectively. The results of this study were not corrected based on surrogate recovery. The levels of tri-PCBs in plants reported here might be underestimates based on the low recovery of the associated surrogate standard, PCB 30. The method detection limits for all PCBs were approximately 5 pg/g for soils and 10 pg/g for plants.[14,17]

2.6. Data Analysis. The concentrations reported herein were calculated based on the dry weight (DW, g) of soil or plant samples. The root concentration factor (RCF) was calculated as the ratio of the concentration in the roots to the concentration in the rhizospheric soil. The C_{RS}/C_{NRS} ratio was determined as the ratio of the concentration in the rhizospheric soil to that in the nonrhizospheric soil. Statistical calculations, such as those to determine significant differences and correlations (Pearson), were performed using SPSS ver. 17.0. The statistical significance of differences and variances (p value <0.05) in PCB accumulation in soils and plants were determined with one-way ANOVA or Dunnett's test using Minitab 19.0.

3. RESULTS

3.1. Distribution of PCBs in Soils and Plants. The concentration of ∑PCBs in NRS and RS ranged from 0.65 to 2.70 and 1.2 to 4.2 ng g^{-1}, with mean concentrations of 1.3 and 2.2 ng g^{-1}, respectively. The highest ∑PCB levels in NRS were associated with cabbage lettuce and were significantly higher than those in flowering cabbage, shallot, cabbage, radish, crown daisy, pak choi, snow peas, sweet potato leaves, and lettuce. The highest ∑PCB in RS was observed in taro roots, and was

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significantly higher than those in Chinese cabbage, celery, Chinese kale, flowering cabbage, shallot, sweet potato leaves, and lettuce (see Figure 1 and Table S1). As shown in Tables S2 and S3, the total chiral PCB concentrations (sum of PCB 84, PCB 95, and PCB 136) ranged from 0.025 to 0.25 ng g^{-1} in RS and from 0.006 to 0.13 ng g^{-1} in NRS. Specifically, PCB 84 was the predominant chiral PCB congener. The concentration of PCB 84 ranged from 0.005 to 0.16 ng g^{-1} in RS and from 0.006 to 0.058 ng g^{-1} in NRS, with mean values of 0.063 and 0.024 ng g^{-1}, respectively. Chiral PCB 136 was present in relatively low levels, ranging from 0.002 to 0.023 ng g^{-1} (mean, 0.012 ng g^{-1}) and from 0.0005 to 0.033 ng g^{-1} (mean, 0.005 ng g^{-1}) in RS and NRS, respectively.

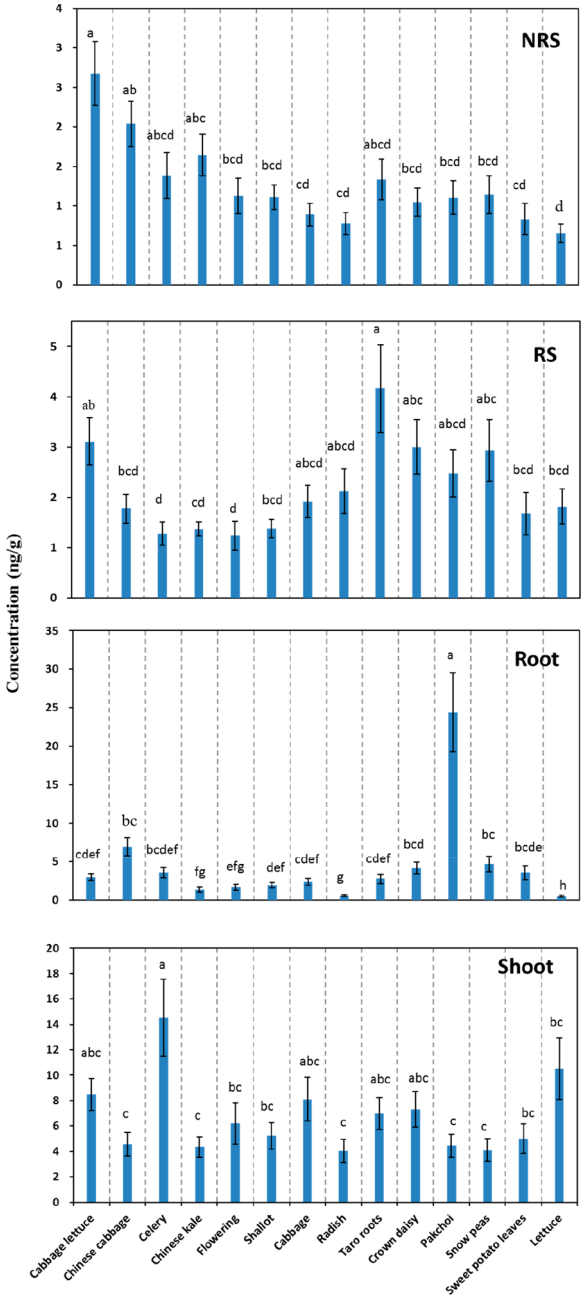

Figure 1. Concentrations of PCBs in soil and vegetable tissues (ng/g DW). RS and NRS represent rhizospheric soil and nonrhizospheric soil, respectively (n = 3). The letters represent the ANOVA results of the comparison of the concentrations among the samples; concentrations sharing the same letter are not statistically different at $p < 0.05$. The error bars represent the standard deviations of the concentrations.

PCB levels in vegetable tissues were generally higher than those in soils. The ∑PCB concentrations ranged from 0.47 to 24 ng g^{-1} (mean, 4.4 ng g^{-1}) and from 4.0 to 15 ng g^{-1} (mean, 6.7 ng g^{-1}) in root and shoot samples, respectively. The ∑PCB concentration in roots of pak choi was significantly higher than those of other plant species. The highest ∑PCB concentration, found in the shoots of celery, was significantly higher than those of Chinese cabbage, Chinese kale, flowering cabbage, shallot, radish, pak choi, snow peas, sweet potato leaves, and lettuce (Figure 1, Tables S4 and S5). The total concentration of chiral PCBs in vegetable tissues varied greatly among plant cultivars, ranging from 0.055 to 1.7 ng g^{-1} in roots and 0.22 to 1.7 ng g^{-1} in shoots. The highest and lowest total chiral PCB concentrations in vegetable (sum of shoot and root) tissues were 2.4 and 0.33 ng g^{-1}, as observed in taro root and radish, respectively. Although all plants were grown at least for 2 months, we were not able to rule out the uncertainty of differences on plant uptake of PCBs caused by different growth period.

3.2. Composition of PCBs in Soils and Plants. Similar PCB compositions in soils and plants were observed among plant species (Figure 2). In general, high-chlorinated PCBs were more abundant in soils, while the opposite trend was observed in plant tissues, where low-chlorinated PCBs were dominant. Specifically, the average percentages of high-chlorinated PCBs in RS and NRS, including hexa- and hepta-PCBs, were 57 and 60%, respectively; the corresponding percentages for these PCB congeners in root and shoot samples were 27 and 32%, respectively. By contrast, the sums of tri- and tetra-PCBs in roots and shoots were significantly higher than those in RS and NRS (53% for roots and 51% for shoots vs 28% for RS and 29% for NRS).

3.3. Chiral Signatures of PCBs in Soils and Plants. Overall, the first eluting enantiomers of PCB 84 and PCB 95, and the second eluting enantiomer of PCB 136 were preferentially enriched in soil (Figure 3). The EF values (mean ± standard deviation) of PCB 84, PCB 95, and PCB 136 were 0.539 ± 0.052, 0.535 ± 0.072, and 0.471 ± 0.0139 in RS and 0.543 ± 0.051, 0.528 ± 0.049, and 0.474 ± 0.025 in NRS, respectively. The stereoselectivities of PCB 84, PCB 95, and PCB 136 in plant tissues were consistent with those in soil. Specifically, the EF values of PCB 84, PCB 95, and PCB 136 were 0.604 ± 0.059, 0.542 ± 0.086, and 0.474 ± 0.176 in shoots and 0.597 ± 0.070, 0.522 ± 0.043, and 0.486 ± 0.061 in roots, respectively. In general, the EF values of PCB 84, PCB 95, and PCB 136 in soils were more similar to the values of racemic mixtures than to those in plant tissues, especially for PCB 95 and PCB 136 (Table 1).

4. DISCUSSION

4.1. Rhizospheric Effect. Generally, the levels of PCB congeners were higher in RS than in NRS, implying that PCB distributions differed between RS and NRS. Previous studies have demonstrated that several factors can affect the dissipation of organic chemicals in the rhizosphere, with root exudates and root microbes being the major drivers.[10,27] Root exudates generally represent a convenient source of carbon and energy, and are likely to favor fast-growing microbes in the rhizosphere with high metabolic abilities.[28] Additionally, the

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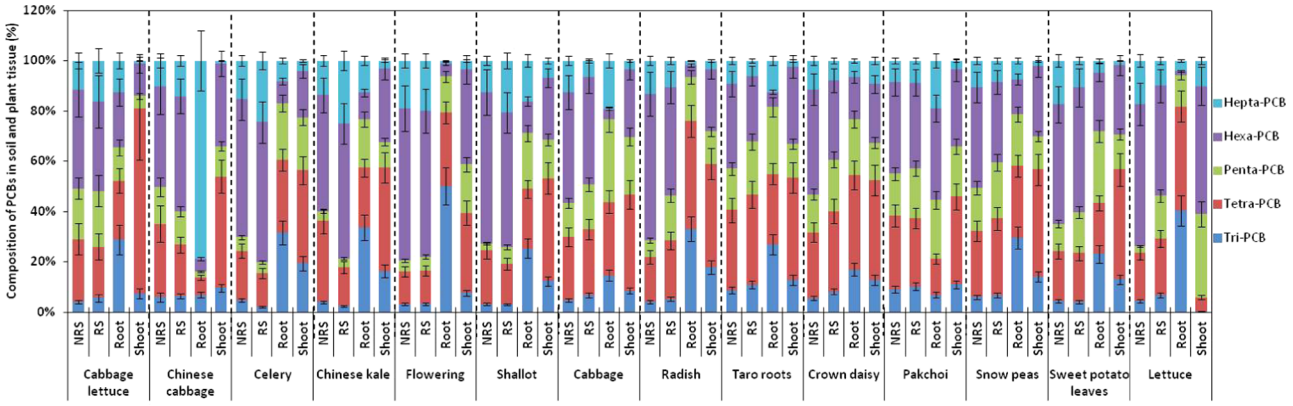

Figure 2. Composition (in averaged %) of PCBs in soil and vegetable tissues. RS and NRS represent rhizospheric soil and nonrhizospheric soil, respectively (n = 3). The error bars represent the standard deviations.

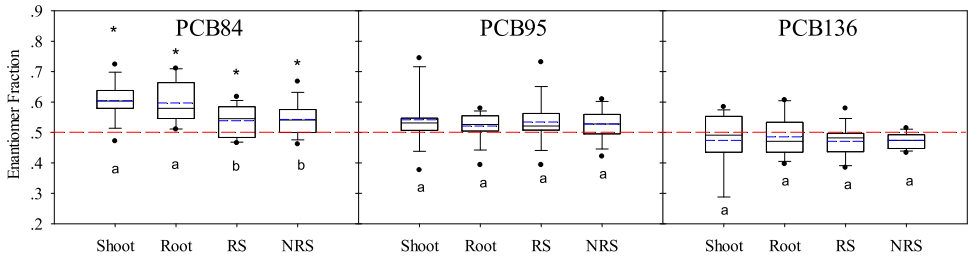

Figure 3. Chiral signatures of PCBs in soil and vegetable tissues. The boxes represent the 25th and 75th percentiles, the whiskers represent the 10th and 90th percentiles, the dots represent the maximum and minimum, and the black horizontal solid line and blue dashed line inside each box represent the median and mean value, respectively. RS and NRS represent rhizospheric soil and nonrhizospheric soil, respectively (n = 14). The letters represent the ANOVA results of the comparison of the enantiomer fractions among the samples; enantiomer fractions sharing the same letter are not statistically different at $p < 0.05$. The asterisk represents that the enantiomer fractions were significantly different than 0.5 (Dunnett's test).

mobilization of the soil organic matter can be promoted by root exudates, such as low-molecular weight organic acids, which in turn enhance the bioavailability of absorbed organic compounds.[29] Such complex interactions among root exudates, root microbes, and xenobiotic pollutants indicate that the dissipation of xenobiotic pollutants in soil is comprehensively regulated, leading to conflicting observations on the occurrence of these chemicals in the rhizosphere. For instance, PCB concentrations were lower in rhizospheric soil than in bulk soil, which can be attributed to degradation and dissipation processes in the rhizosphere.[8] PAHs have been observed to decrease logarithmically in samples collected closer to the surface of the ryegrass root.[9] On the other hand, evidence of rhizospheric enrichment of phenanthrene and pyrene,[6] PBDEs,[10] and NBFRs[10] have also been reported, which are consistent with the results of the present study. Such observations have cast doubt on the generalizability of the rhizosphere dissipation effect to other xenobiotic compounds. Moreover, the ratio of PCB concentration in RS to that in NRS varied greatly among plant species. The highest ratio of 3.1 was observed in taro, while the lowest ratio (0.8) was observed in Chinese kale (see Table S3). Compared to PCB concentrations in NRS, significantly higher RS concentrations were observed in cabbage, radish, taro roots, crown daisy, pak choi, snow peas, sweet potato leaves, and lettuce while indistinguishable differences were observed in other plant cultivars (Table S3). Possible explanations for this difference include differences among plant cultivars as well as soil properties and chemical characteristics. The variation could also be caused by the potential difference in plant growth status.

4.2. Translocation of PCBs within the Soil–Plant System. Normally, root and foliar uptake are the two primary routes by which PCBs enter plant tissues, these processes can be evaluated using $\log K_{ow}$ and $\log K_{oa}$, respectively.[30,31] In the soil-root-shoot pathway, previous studies have demonstrated that only compounds of moderate hydrophobicity could be taken up by roots and transferred to shoots.[30,32,33] PCBs with high $\log K_{ow}$ values were constrained to the surface of root tissues, and had difficulty passing through the xylem of plants;[34,35] however, PCBs, and in particular tetra-PCBs, were confirmed to be transported upward to shoots through the xylem of pumpkin (*Cucurbita pepo* ssp. *pepo* cv. Howden).[36] In the present study, a significant negative (p = 0.022) relationship between $\log$ RCF and $\log K_{ow}$ of PCB congeners was observed (Figure S1). However, the low R^2 value of this association, indicating that it explains a small percentage of variability in the data, cannot be ignored. The highest and lowest log RCF values were observed for PCB 8 and PCB 169, respectively. We also found the predominance of high-chlorinated PCBs (hexa- and hepta-) in soil and low-chlorinated PCBs (tri- and tetra-) in root and shoot tissues. These findings suggest that the potential capacity for PCB translocation in plants is mainly controlled by the physicochemical properties of PCBs. In other words, low-chlorinated PCBs were preferentially taken up by roots and translocated to shoots. Meanwhile, the negative correlation between $\log$ RCF and $\log K_{ow}$ may be caused by increased absorption of hydrophobic compounds. Interestingly, it has been reported that chemicals with higher $\log K_{ow}$ were preferentially accumulated in roots.[37] Such difference can be

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Table 1. Enantiomer Fraction of Chiral PCBs in Soil and Vegetables[a]

	PCB 84				PCB 95				PCB 136			
	shoot	root	RS	NRS	shoot	root	RS	NRS	shoot	root	RS	NRS
cabbage lettuce	0.586 ± 0.012^{h}	0.595 ± 0.022^{d}	0.472 ± 0.021^{h}	0.461 ± 0.018^{g}	0.507 ± 0.025^{f}	0.492 ± 0.015^{e}	0.561 ± 0.015^{b}	0.496 ± 0.022^{f}	0.432 ± 0.013^{h}	0.447 ± 0.019^{ef}	0.489 ± 0.019^{de}	0.448 ± 0.023^{d}
Chinese cabbage	0.601 ± 0.024^{fg}	0.513 ± 0.010^{i}	0.594 ± 0.023^{b}	0.538 ± 0.019^{de}	0.536 ± 0.019^{de}	0.563 ± 0.024^{b}	0.571 ± 0.029^{b}	0.520 ± 0.014^{e}	0.469 ± 0.023^{f}	0.437 ± 0.025^{fg}	0.484 ± 0.021^{e}	0.514 ± 0.012^{a}
celery	0.560 ± 0.016^{i}	0.617 ± 0.026^{c}	0.465 ± 0.032^{h}	0.529 ± 0.016^{e}	0.501 ± 0.015^{f}	0.539 ± 0.025^{c}	0.522 ± 0.025^{d}	0.421 ± 0.017^{h}	0.515 ± 0.018^{d}	0.469 ± 0.029^{d}	0.501 ± 0.023^{c}	0.445 ± 0.019^{de}
Chinese kale	0.723 ± 0.041^{a}	0.552 ± 0.017^{g}	0.582 ± 0.023^{bc}	0.528 ± 0.021^{e}	0.376 ± 0.017^{g}	0.505 ± 0.019^{d}	0.393 ± 0.018^{g}	0.539 ± 0.021^{d}	0.490 ± 0.023^{e}	0.452 ± 0.031^{e}	0.445 ± 0.018^{g}	0.489 ± 0.023^{b}
flowering	0.618 ± 0.031^{e}	0.652 ± 0.021^{b}	0.538 ± 0.016^{e}	0.547 ± 0.023^{d}	0.569 ± 0.024^{c}	0.521 ± 0.013^{g}	0.568 ± 0.026^{b}	0.561 ± 0.023^{c}	0.565 ± 0.019^{b}	0.542 ± 0.025^{b}	0.468 ± 0.024^{f}	0.466 ± 0.021^{c}
shallot	0.588 ± 0.027^{gh}	0.574 ± 0.018^{ef}	0.573 ± 0.021^{c}	0.501 ± 0.016^{f}	0.540 ± 0.027^{d}	0.516 ± 0.012^{d}	0.501 ± 0.025^{ef}	0.559 ± 0.019^{c}	0.522 ± 0.024^{d}	0.414 ± 0.016^{h}	0.513 ± 0.017^{b}	0.464 ± 0.025^{c}
cabbage	0.634 ± 0.034^{d}	0.700 ± 0.018^{a}	0.617 ± 0.019^{a}	0.667 ± 0.018^{a}	0.507 ± 0.016^{f}	0.507 ± 0.014^{d}	0.517 ± 0.016^{d}	0.494 ± 0.025^{f}	0.400 ± 0.025^{i}	0.505 ± 0.026^{c}	0.398 ± 0.023^{i}	0.433 ± 0.026^{e}
radish	0.557 ± 0.031^{i}	0.710 ± 0.021^{a}	0.593 ± 0.015^{b}	0.586 ± 0.024^{b}	0.508 ± 0.019^{f}	0.393 ± 0.023^{f}	0.540 ± 0.019^{c}	0.471 ± 0.018^{g}	0.493 ± 0.019^{e}	0.396 ± 0.031^{i}	0.496 ± 0.021^{cd}	0.481 ± 0.016^{b}
taro roots	0.610 ± 0.025^{ef}	0.709 ± 0.025^{a}	0.553 ± 0.028^{d}	0.597 ± 0.021^{b}	0.508 ± 0.025^{f}	0.554 ± 0.025^{b}	0.546 ± 0.030^{c}	0.521 ± 0.025^{e}	0.176 ± 0.013^{j}	0.531 ± 0.035^{b}	0.496 ± 0.029^{cd}	0.483 ± 0.017^{b}
crown daisy	0.606 ± 0.041^{ef}	0.510 ± 0.010^{i}	0.490 ± 0.025^{f}	0.491 ± 0.025^{f}	0.527 ± 0.024^{e}	0.558 ± 0.020^{b}	0.521 ± 0.018^{d}	0.595 ± 0.016^{b}	0.449 ± 0.018^{g}	0.606 ± 0.028^{a}	0.579 ± 0.028^{a}	0.489 ± 0.018^{b}
pak choi	0.651 ± 0.021^{c}	0.528 ± 0.018^{h}	0.487 ± 0.023^{fg}	0.547 ± 0.015^{d}	0.688 ± 0.028^{b}	0.539 ± 0.017^{c}	0.510 ± 0.017^{de}	0.518 ± 0.013^{e}	0.436 ± 0.025^{h}	0.603 ± 0.028^{a}	0.481 ± 0.026^{e}	0.446 ± 0.025^{d}
snow peas	0.471 ± 0.013^{j}	0.585 ± 0.021^{de}	0.474 ± 0.025^{gh}	0.497 ± 0.025^{f}	0.744 ± 0.021^{a}	0.532 ± 0.018^{c}	0.513 ± 0.021^{de}	0.535 ± 0.019^{d}	0.584 ± 0.028^{a}	0.495 ± 0.026^{c}	0.384 ± 0.016^{j}	0.467 ± 0.017^{c}
sweet potato leaves	0.673 ± 0.024^{b}	0.552 ± 0.023^{g}	0.572 ± 0.026^{c}	0.544 ± 0.017^{d}	0.536 ± 0.027^{de}	0.504 ± 0.017^{de}	0.489 ± 0.017^{f}	0.609 ± 0.015^{a}	0.552 ± 0.029^{c}	0.430 ± 0.037^{g}	0.421 ± 0.030^{h}	0.508 ± 0.017^{a}
lettuce	0.586 ± 0.025^{h}	0.561 ± 0.025^{fg}	0.532 ± 0.017^{e}	0.572 ± 0.021^{c}	0.537 ± 0.025^{de}	0.579 ± 0.019^{a}	0.731 ± 0.023^{a}	0.556 ± 0.023^{c}	0.556 ± 0.026^{bc}	0.473 ± 0.021^{d}	0.442 ± 0.025^{g}	0.504 ± 0.025^{a}

[a]The letters represent the ANOVA results of the comparison of the enantiomer fractions among the plant species; enantiomer fractions sharing the same letter are not statistically different at $p < 0.05$. The sample size was 3 for each plant species.

potentially explained by the reduced bioavailability of weathered POPs in the field, in particular for the high-chlorinated PCBs, which were supposed to absorb in the soil organic matter. However, to some extent, the low-chlorinated PCBs may be desorbed from the soil organic matter in the presence of root exudates and rhizospheric microbes, given their low $\log K_{ow}$ values. In general, a similar PCB profile among most plant cultivars indicated that there is no significant difference in PCB translocation among plant cultivars. However, we are not able to rule out the uncertainties between specific plant cultivars, root exudates, and the corresponding rhizosphere effects on the PCB distribution and translocation within the soil−plant system, given that Chinese cabbage, pak choi, and lettuce had high proportions of low-chlorinated PCBs in soils than in plant tissues. In addition, the differences in PCB accumulation among plant cultivars may be a result of the differences in growth forms of plant cultivars. For example, the highest PCBs accumulation in taro root was probably related to the longer growth period of taro root than other plant cultivars.

Theoretically, shoot PCBs might be derived from PCBs translocated from the roots or deposited from the air, which complicates the analysis of the relationship between shoot concentration factor and $\log K_{ow}$. Significant positive correlations ($p = 0.002$) were found between PCBs in shoots and in soils, indicating that shoot PCBs and soil PCBs likely share the source, this finding corresponds well with published data from a field trial.[14] As noted above, low-chlorinated PCB congeners were predominant in plant shoots in the current study. Overall, PCBs were preferentially sorbed onto soil organic carbon after entering the soil system.[38] Consequently, the desorption−absorption equilibration of PCBs in soil results in differing bioavailability among soil PCB congeners, which also varies among plant cultivars and their corresponding root exudates.[39] Although the mobility and bioavailability of low-chlorinated PCBs in soil are higher than those of high-chlorinated PCBs, they are also prone to escaping from the soil reservoir, evaporating into the air, and then being deposited onto the plant leaf surface, resulting in an increased PCB concentration in the shoots. As expected, low-chlorinated PCBs make up a larger portion of the total PCBs in plant shoots compared to high-chlorinated PCBs. However, given that the PCBs profile between roots and shoots were highly similar, the contribution to shoot PCBs from roots may be higher than that from soils.

4.3. Stereoselectivity of PCBs within the Soil−Plant System. Stereoselectivity of chiral PCBs is a useful tool for studying the biotransformation of chiral PCBs and tracing their sources in different environmental matrices. In this study, the chiral signatures of three chiral PCBs, including PCB 84, PCB 95, and PCB 136, in soils and plant tissues were used to characterize biochemical processes within the soil−plant system.

Soil properties have been reported to influence the EF values of chiral PCBs, with nonracemic ratios of PCB 95 and PCB 149 found in soils with higher levels of carbonic, humic, and fulvic acids.[40] Soil properties, especially those of RSs, can be modified by a range of processes that occur during plant growth. Consequently, the stereoselectivity of chiral PCBs in soil might be affected by the relatively abundant microbial community and the enhanced metabolic processes found in RS, which could result in differing EF values between RS and NRS. However, no significant difference in EF values for PCB

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84, PCB 95, or PCB 136 was observed between RS and NRS. Previous research showed that the shift from a racemic mixture of soil chiral PCBs may be associated with more sustainable and active soil microflora.[40] In addition, EF values of soil chiral PCBs are reportedly related to their concentrations, with nonracemic EFs being increasingly probable in soils with relatively low PCB concentrations.[40] The soil PCB concentrations measured in the present study were lower than those reported in other studies, in which the PCB concentrations ranged from 24 to 12 000 ng/g,[18] and EFs were generally more nonracemic than in previous reports. This finding corresponds well with the results of a previous study.[40]

The enantiomer fraction of PCB 95 in plant tissue, with the first eluting enantiomer being preferentially enriched, was in accordance with previous reports on the stereoselectivity of PCB 95 in lotus,[41] poplar,[24,25] eucalyptus, and pine needles.[18] For PCB 84, differences in enantiomer stereoselectivity were observed among plant cultivars, with the second eluting enantiomer of PCB 84 preferentially enriched in eucalyptus leaves and pine needles, as reported in a previous study,[18] whereas the first eluting enantiomer was enriched in plant tissues during translocation in this study. Similarly, the stereoselectivity of PCB 136 varied among the species studied (see Table 1). The differential stereoselectivity of chiral PCBs by plants can be ascribed to differences among PCB congeners and plant cultivars. First, the stereoselectivity of chiral PCBs depends on the presence of unsubstituted vicinal meta and para positions, substrate size, binding position, and enzyme affinity.[42] In particular, the 2,5-dichloro substitution pattern of PCB 95 might be susceptible to metabolic attack.[43] PCB 84, which contains hydrogen atoms in the same two meta-para positions and has the same molecular mass as PCB 95, showed a similar deviation from racemic to PCB 95. For PCB 136, the higher molecular mass was assumed to result in smaller deviation from the racemic state. Second, differences in plant esterases and the corresponding genotypes of CYP 450 among plant cultivars might explain the difference in stereoselectivity. Previous studies have suggested that distinct chiral PCB metabolic rates might be observed due to the specificity of P450 enzymes in different animal species,[20] based on differences in the structures of the relevant P450 enzymes[44] as well as hepatic P450 enzyme and isoform compositions.[45,46]

Generally, POPs can be transported into plants from the soil and transferred among plant tissues through abiotic and biotic processes, including the symplastic and apoplastic pathways. Apoplastic water movement involves diffusion between cell walls without entry into cells, while symplastic movement occurs through the cytoplasm or vacuoles between interconnected cells via plasmodesmata.[47,48] Previous research showed that enantioselective translocation of certain weathered chlordane components through soil was followed by enantioselective processes within various plant tissues.[49] Dinitrotoluene and dinitrobenzene transport into plants via the symplastic pathway has been reported, while phenanthrene and pyrene can be transported via the apoplastic pathway.[50] However, the mechanisms by which specific chemicals, such as PCBs, move into the root system and then are transported to shoots through the apoplastic or symplastic pathways remain unclear. In this study, a significant difference was observed in the EF values of PCB 84 between soil and roots (p = 0.012), while such trends were not found for PCB 95 (p = 0.276) and PCB 136 (p = 0.470) between soil and roots. This finding indicates that the uptake of PCB 84 by plant roots, coupled with enantiomeric enhancement of PCB 84, leads to stereoselectivity of PCB 84 by roots associated with its uptake from soil to roots.

Regarding the biotransformation of chiral PCBs within plant tissues, some recent studies have reported that the first eluting enantiomer of PCB 95 can be removed by poplar following hydroponic exposure to PCB 95.[24,25] Enantioselective metabolism of PCB 95 was observed in the middle and lower xylem, with EF values of 0.307 and 0.449, respectively. On the other hand, PCB 136 remained nearly racemic in most parts of poplars with the same exposure time, suggesting that PCB 136 was more resistant to enantioselective biotransformation than PCB 95 in poplar.[24] Interestingly, no significant difference was observed in the EF values of PCB 84 (p = 0.782), PCB 95 (p = 0.231), or PCB 136 (p = 0.758) between roots and shoots in the present study. These results did not show evidence of tissue specific enantioselective biotransformation.

5. CONCLUSIONS

The migration of PCBs from e-waste recycling sites into the surrounding environment remains an issue due to previous unregulated recycling and disposal of e-waste. The concentrations of PCBs in rhizospheric soils were higher than those in bulk soils, suggesting the enrichment of soil PCBs by plant roots. Different occurrence patterns of PCBs between soils and plant tissues indicate that the plant uptake of PCBs is driven by the physiochemical properties of PCBs, which was confirmed by the relationship between log RCF and log K_{ow}. The enantioselectivity of chiral PCBs varies among plant cultivars and PCB congeners. The significant difference in the enantioselectivity of PCB 84 between soil and roots indicates that enantiomeric enhancement of PCB 84 occurs during its translocation from the soil to roots. Further study is necessary to characterize the metabolites of low-chlorinated PCBs in plant tissues.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jafc.0c00479.

Data on the total PCB concentration in soil and plant, individual PCB congeners in soil and plant, total organic carbon in soil, and the relationship between log RCF and log K_{ow} of PCBs (PDF)

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Notes

The authors declare no competing financial interest.

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