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RESEARCH ARTICLE

Simultaneous enhanced removal of Cu, PCBs, and PBDEs by corn from e-waste-contaminated soil using the biodegradable chelant EDDS

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Abstract We evaluated the influence of the biodegradable chelant ethylenediamine disuccinic acid (EDDS) on plant uptake of polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and Cu by corn from electronic waste (e-waste)-contaminated soil. The highest concentration and highest total uptake of Cu in corn were observed in the treatment with 5 mM EDDS, which resulted in a 4-fold increase of the Cu translocation factor (C_{shoot}/C_{root}) compared to the control. The concentrations of PCBs and PBDEs in shoots and roots increased with increasing application rates of EDDS, and 1.58- and 1.32-fold average increases in the concentrations of PCBs and PBDEs, respectively, were observed in shoots in the EDDS treatments. A significant positive correlation was observed between shoot Cu and shoot PCBs and PBDEs. We speculate that PCBs and PBDEs were activated by the EDDS-triggered dissolved organic carbon (DOC) and then indiscriminately taken up by roots and translocated to shoots following damage to the roots mainly by the increased extractable Cu resulting from the EDDS application.

Keywords Biodegradable chelant · DOC · Bioavailability · POPs · Copper

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Introduction

As a hotly debated global issue, the primitive state of electronic waste (e-waste) recycling is a serious concern due to the release of abundant toxicants during the recycling process. Previous studies have shown that trace metals and persistent organic pollutants (POPs), such as polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs), were detected in various environment matrices adjacent to e-waste recycling sites, posing a potential risk to local residents and ecosystems (Gioia et al. 2011; Leung et al. 2011; Luo et al. 2011; Zhang et al. 2010). In China, three areas with intensive e-waste recycling, Taizhou, Qingyuan, and Guiyu, are of particular concern due to the extremely high levels of POPs and trace metals found in the nearby biota, and even in human blood (Li et al. 2008; Lin et al. 2006, 2008; Wong et al. 2007). The strong hydrophobicity, lipophilicity, and persistence of these POPs has lead to high bioaccumulation in the lipids of organisms, which is biomagnified through the food web, and finally is negatively impacting top-level carnivores (Armitage and Gobas 2007; Helm et al. 2008). With the banning of crude e-waste recycling activities by national and provincial laws, the exploration of effective techniques for cleaning up previously contaminated sites has become urgent (Hicks et al. 2005; Ni and Zeng 2009).

Although the pollution caused by e-waste recycling has been investigated extensively, efficient decontamination of

polluted soils is challenging due to the complexity of the contaminants. Heavy metal-contaminated soil can be treated using physical and chemical methods. Regarding chemical methods, various chelating agents, such as citric acid, nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), and S,S-ethylenediamine disuccinic acid (EDDS) (Hauser et al. 2005), have been used to increase the solubility of metals in soil. When a chelant is applied to planted soils, the translocation of metals from roots to shoots is greatly improved. Chelant-enhanced phytoremediation has been demonstrated to be a promising technique for the removal of metals from soils (Luo et al. 2005). For the treatment of POPs, biodegradation is common. It is known that plant roots can host a number of microbes and secrete root exudates, providing nutrition and sustaining the survival of these rhizospheric microbes, which can then accelerate the degradation, assimilation, metabolism, and detoxification of the organic pollutants by the plants (Chaudhry et al. 2005). Rhizospheric remediation of organic pollution has proved to be more efficient and environmental friendly compared to biodegradation alone. From this perspective, it is hypothesized that the removal of mixed contaminants (metals and POPs) from e-waste-contaminated soils through phytoremediation may be possible, and combined techniques incorporating physical, chemical, and biological methods have been developed to remediate contaminated soils (Mulligan et al. 2001; Semer and Reddy 1996).

EDDS, a low-molecular-weight organic acid, exhibits low toxicity to plants, which suggests its potential to maintain the fertility and function of the original soils (Grcman et al. 2003; Kos and Lestan 2003; Luo et al. 2006a). Soil metals can be solubilized by EDDS due to its high chemical affinity with metals, and its ready biodegradability has resulted in its replacing EDTA in industrial products and soil remediation (Luo et al. 2007). When EDDS is applied to soil, the dissolved organic carbon (DOC) increases markedly, which likely influences the bioavailability of POPs. Therefore, hypothetically, when metals and POPs co-exist in the soil, the application of EDDS could simultaneously stimulate the translocation of both types of pollutants upward into shoots; however, this requires further study. If this hypothesis is correct, a new technology is anticipated. The aims of the present study were (1) to investigate the potential influence of the biodegradable chelant EDDS on the fate of metals and recalcitrant PCBs and PBDEs in e-waste-contaminated soils and (2) to determine the mechanism underlying plant uptake and translocation of pollutants.

Materials and methods

Experimental design

Longtang, located in the north of Guangdong Province, is one of the three largest e-waste dumping and recycling sites in China. Approximately 700,000 t of e-waste is processed using environmentally unsound techniques (Chen et al. 2014). Contaminated soil was collected from an e-waste recycling site in Longtang Town (N 23° 34′, E 113° 0′), whereas paddy soil was collected from a rural site (60 km away) which located in an agricultural base and has no e-waste recycling or industrial activities. After being air-dried, homogenized, and passed through a 2-mm sieve, e-waste-contaminated soil and paddy soil were mixed at a 1:20 ratio; the characteristics of the mixed soil are shown in Table 1. Soils were packed into ceramic pots (2 kg per pot, 16 pots in total). After being sterilized with 5 % sodium hypochlorite solution for 5 min, washed in tap water for 10 min, soaked in deionized water (DIW) for 12 h, seeds of corn (*Zea mays* L. cv. Nongda 108) were planted in the pots. The detailed information on cultivation process have been provided previously (Luo et al. 2015).

The corn was thinned to five plants per pot after 10 days. After another 25 days, 1, 3, and 5 mmol kg^{-1} soil Na_3 EDDS salt were applied to four pots each, and the remaining four pots were irrigated with the same volume of DIW as the control. Therefore, four treatments performed in quadruplicate were included in this experiment: control (corn without EDDS), 1 mM EDDS, 3 mM EDDS, and 5 mM EDDS.

The potential atmospheric deposition of PCBs and PBDEs were measured by passive air samplers (PAS) using polyurethane foam disks (PUF, 14 cm diameter, 1.2 cm thickness, 0.035 g m^{-3}). Two samplers were hung over the ceiling of greenhouse while another two were placed 400 m away from the greenhouse. Active air sampler was also used to calibrate the sampling rate by PAS deployment. Details of the setup have been described somewhere else (Luo et al. 2015).

Sampling

Plant and soil sampling were conducted at the end of cultivation (42 days). Corn was harvested 7 days after the application of EDDS. After being washed with tap water, rinsed with DIW, and lyophilized, corn shoots and roots were separated and measured biomass. Then, roots and shoots were ground to fine powder and stored in −20 °C freezer before extraction. At the end of cultivation, the PUFs were collected and wrapped in solvent-rinsed aluminum foil envelopes. Approximately 200 g of soil were collected, lyophilized, and ground. Soil and PUFs were respectively placed in polyethylene zip bags and stored in the freezer until extraction.

Chemical analysis

Trace metals and DOC analysis

Plant and soil samples were digested in a mixture of HNO_3 and $HClO_4$ (1:4, by volume), and total K and Cu were determined by inductively coupled plasma atomic emission

Table 1 Physicochemical properties of the tested soil

Texture		mg kg^{-1}			Cu mg kg^{-1}	PCBs ng g^{-1}	PBDEs ng g^{-1}
SOM %	pH	N	P	K			
1.36±0.1	7.43	108±36	42±9	673±22	640±81	2.6	14.8

The values are means ± SD (n=3)

spectroscopy (ICP-AES) (Luo et al. 2005, 2015). The detailed analytical method and quality assurance/quality control could be found at our previous study (Luo et al. 2015). The soil pH was measured using 0.01 mmol $CaCl_2$ at a 1:5 ratio (w/v) with a pH meter. The soil organic matter, total N, and P were measured using the procedures described by Avery (Avery and Bascomb 1982).

For the extractable Cu and DOC measurements, exhaustive descriptions have been presented by our previous study (Luo et al. 2015). Briefly, soil and DIW (at a ratio of 1:5, soil/water) were added in a 50-mL polypropylene centrifuge tube; after shaking sufficiently and centrifuged, the supernatant was filtered through a 0.45-μm paper filter (Whatman, Maidstone, UK). The total DOC concentration was measured using a total organic carbon (TOC) analyzer (TOC-5000A, Shimadzu, Japan). The remaining supernatant was acidified with HNO_3, and the extractable Cu was analyzed using ICP-AES (Luo et al. 2005).

PCBs and PBDE analysis

Briefly, PUFs or 5-g soil samples were spiked with the surrogate standards (TCMX, PCB30, PCB198, and PCB209) and extracted with dichloromethane (DCM) for 48 h. Plant samples (5 g) homogenized with 5-g anhydrous sodium sulfate and spiked with the surrogate standards were extracted with hexane/acetone (3:1, v/v) for 72 h. The purify procedure of PUFs, soil and plant samples have been well elaborated previously (Luo et al. 2015). Finally, ^{13}C-PCB141 was added as the internal standard before instrumental analysis.

Samples were analyzed by gas chromatography-electron impact mass spectrometry (GC-EI-MS) (Agilent GC7890 coupled with 5975C MSD) using a Varian capillary column (50 m×0.25 mm inner diameter (i.d.)×0.25 μm film thickness) for 32 PCB congeners. Seven BDE congeners (BDE28, 47, 99, 100, 153, 154, and 183) and BDE209 were analyzed with gas chromatography-electron capture negative ion mass spectrometry (GC-ECNI-MS) applied with a DB5-MS capillary column (30 m×0.25 mm (i.d.)×0.25 μm film thickness) and a DB5-MS capillary column (15 m×0.25 mm (i.d.)×0.25 μm film thickness), respectively. Analytical details have been described previously (Luo et al. 2015; Wang et al. 2011).

Potential sample contamination and the repeatability of analysis was assessed by running a procedural blank, a spiked blank comprising all chemicals, and a duplicate sample among each batch of 10 samples. No target compound was detected in the blanks. The recoveries of the surrogate standards (2, 4, 5, 6-tetrachloro-m-xylene (TCMX), PCB30, PCB198, and PCB209) were 60.7±13.1, 62.1±17.8, 84.1±12.2, and 80.8 ±13.4 %, respectively. All results reported were corrected according to the surrogate recoveries.

Statistical analyses

A one-way ANOVA test (LSD) was used to analyze the statistical significance of differences and variance analysis (P<0.05) of pollutant accumulation in plants among the different treatments. The statistical analysis, such as correlation (Pearson) and significant differences, were performed using the statistical package SPSS 17.0 (SPSS, Inc.).

Results

Characteristics of the soil

Physicochemical properties of the soils are presented in Table 1. The concentrations of Cu, PCBs, and PBDEs were 640 mg kg^{-1}, 2.6, and 14.8 ng g^{-1}, respectively. The effects of EDDS on Cu and DOC are shown in Table 2. Both extractable Cu and DOC (triggered by the addition of EDDS) in soil increased with the increased application rate of EDDS. The lowest values appeared in the control group (with no EDDS addition): 1 mg kg^{-1} for extractable Cu and 19 mg L^{-1} for DOC. Generally, 7 days after the application of EDDS, average 20-, 23-, and 29-fold (extractable Cu), and 2.42-, 2.89-,

Table 2 Effects of EDDS on extractable copper and dissolved organic carbon

	Extractable Cu (mg kg^{-1}) 7 days	DOC (mg L^{-1}) 7 days
Control	1±0.4 a	19±2 a
1 mM EDDS	20±6 b	46±3 b
3 mM EDDS	23±2 b	55±1 bc
5 mM EDDS	29±6 c	61±2 c

The values are means ± SD (n=3). The *small letters* (a, b, c, d) stand for statistical significance at the 0.05 level with the LSD test

and 3.21-fold (DOC) increases were observed for 1 mM EDDS, 3 mM EDDS, and 5 mM EDDS, respectively.

Biomass of corn

The dry mass yields of corn are presented in Fig. S1. During the entire cultivation period, corn in the control showed normal development without any visual symptoms of toxicity. The application of EDDS showed prohibiting effects on plant growth with a greater effect on roots than shoots. In comparison with the control, the average decreases of shoots and roots in the EDDS treatments were 20.7 and 55.7 %, respectively. The lowest biomasses of shoots and roots appeared in the 3 mM EDDS treatment, reaching 4.25 and 0.38 g pot^{-1}, respectively, 24.5 and 75 % decreases compared to the controls. For the roots, the order of decrease was 3 mM EDDS > 1 mM EDDS > 5 mM EDDS. However, for the shoot dry biomass, there were no significant differences among the three EDDS treatments ($P>0.05$).

Uptake of Cu by corn

The concentration and total uptake of Cu in corn are shown in Fig. 1. The concentration of Cu in shoots increased with increasing amounts of EDDS, and the highest shoot Cu concentration was found in the treatment of 5 mM EDDS with a value of 75.9 mg kg^{-1}, 1.28-, 1.63-, and 4.19-fold increases compared to the 3 mM EDDS, 1 mM EDDS, and control treatments, respectively. A similar tendency was observed in the total uptake of Cu in shoots, with the 5 mM EDDS treatment being highest followed by the 3 mM EDDS treatment. For roots, the addition of 1 mM EDDS resulted in the highest concentration of Cu which was 1.23-, 1.14-, and 1.03-fold of the control, 3 mM EDDS, and 5 mM EDDS treatments, respectively. The highest value for the total uptake of Cu in the roots was observed in the control, reaching 0.81 mg pot^{-1}, followed by the treatment with 5 mM EDDS. The lowest value appeared in the 3 mM EDDS treatment (Fig. 1).

Levels and compositions of PCBs in corn tissues

The distribution and concentration of PCB homologues in corn tissues are presented in Fig. 2 and Table 3. The application of EDDS to the soil enhanced the concentrations of PCBs in shoots and roots compared to the control. Generally, the concentrations of PCBs in roots increased with increasing levels of EDDS, and more PCB congeners were concentrated in roots from the 3 and 5 mM EDDS treatments than from the 1 mM EDDS and control treatments. Among the congeners, PCB28, PCB44, PCB49, and PCB52 were dominant, showing the highest concentrations in root tissues. The higher chlorinated PCB homologues, such as hexa-PCBs (PCB128, 138, 153, 156, 158, 166, and 169) and hepta-PCBs (PCB170, 179, 183, 180, 187, and 189), also appeared in the roots at concentrations of 0.02–3.34 ng g^{-1}. A similar trend was observed in the shoots, in which the lower chlorinated PCBs (PCB28, 37, 44, 49, 52, 60, and 66) were the dominant congeners, and the highest concentration was observed for PCB49. However, in contrast to the roots, six PCB homologues (PCB44, 52, 60, 87, 101, and 105) in shoots showed greater accumulations in the control than in the treatments with EDDS, possibly due to the larger surface area of the leaves receiving more PCBs from the atmosphere. The levels of hexa- and hepta-chlorinated biphenyls in shoots were below the detection limits.

The total uptake of PCBs is presented in Table 3. PCB accumulation was significantly higher in the shoots treated

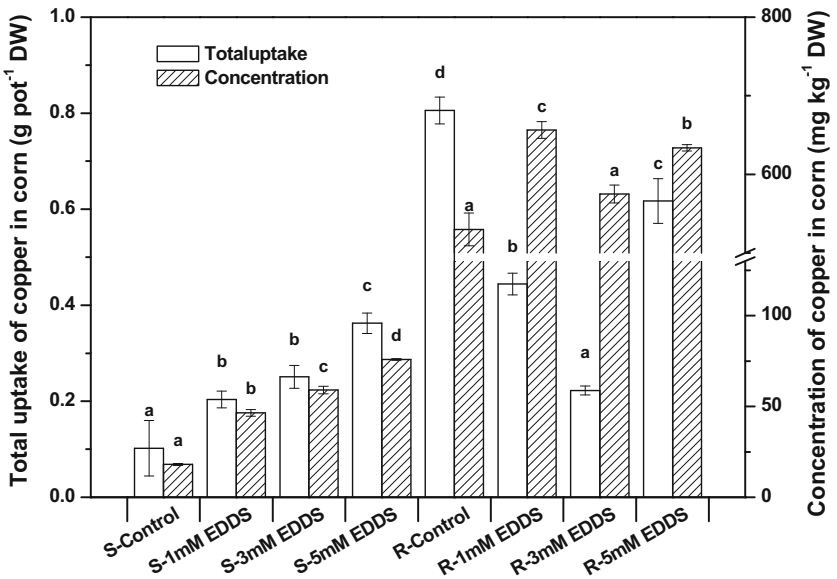

Fig. 1 The concentration and total uptake of copper in corn. (*S-Control* shoot of control, *S-1mM EDDS* shoot of treatment with 1 mM EDDS, *S-3mM EDDS* shoot of treatment with 3 mM EDDS, *S-5mM EDDS* shoot of treatment with 5 mM EDDS, *R-Control* root of control, *R-1mM EDDS* root of treatment with 1 mM EDDS, *R-3mM EDDS* root of treatment with 3 mM EDDS, *R-5mM EDDS* root of treatment with 5 mM EDDS. The *lowercase letters* (*a*, *b*, *c*, *d*) stand for statistical significance at the 0.05 level with the LSD test)

with EDDS, on average 58.7 % higher than the control. No significant difference was observed among the three EDDS treatments. However, the lowest root uptake was observed in the 3 mM EDDS treatment, consistent with the low root biomass (Fig. S1).

The PCB compositions of soil, air, and corn tissues are also analyzed (Fig. S2). Tri- and tetra-PCBs were the dominant homologue groups in all samples. The higher chlorinated biphenyls, such as penta- and hexa-PCBs, were more concentrated in roots than shoots. As expected, the composition of PCBs in roots was similar to that of the soil, while the PCB compositions in shoots and in the air tended to be analogous.

Levels and compositions of PBDEs in corn tissues

Concentrations and total uptakes of PBDEs in corn tissues are presented in Table 4. BDE28, 47, and 209 were the dominant congeners in shoots, the concentrations of which in shoots were higher in the EDDS treatments than that in the control. Similarly, the application of EDDS increased the concentrations of PBDEs in roots; the highest concentrations of all congeners were observed in the treatment with 5 mM EDDS. The highest total uptakes of PBDEs in shoots and roots were observed in the 3 mM EDDS and control treatments, reaching 2.03 and 21.58 ng pot^{-1}, respectively (Table 4). Deca-BDE was the dominant congener in shoots; this differed from the roots and soil, which tended to be analogous. Among the PBDE congeners, penta-BDE and hexa-BDE were dominant in roots (Fig. S3).

Discussion

Corn growth and Cu uptake influenced by EDDS

Upon solubilization of soil Cu by EDDS, plant roots could experience severe physiological damage (Luo et al. 2005), possibly leading to a breakdown of the root exclusion mechanism and finally to the indiscriminate uptake of solutes by plants. Moreover, EDDS is slightly toxic to plant roots (Fässler et al. 2010). Upon EDDS application, plants may have suffered from the co-toxicity of Cu^{2+}, EDDS, and the Cu-EDDS complex; the phytotoxicity has been demonstrated to be in the order Cu^{2+} > EDDS > Cu-EDDS (Niu et al. 2012). In the present study, the growth of both shoots and roots was significantly affected by the application of EDDS. Within 7 days after the application of 1, 3, and 5 mM EDDS, root dry matter yields decreased to 44, 25, and 64 % of the control plants, respectively. This can be attributed to the increased extractable Cu, as the solubilized Cu could induce toxic effects on the plant tissues, the roots in particular (Table 2). The lowest biomass being in the 3 mM EDDS treatment is attributable to the higher activity of free Cu^{2+} compared to the 5 mM EDDS treatment, in which more Cu^{2+} would be bound in the form of Cu-EDDS chelate complexes.

A number of studies have shown that in chelate-buffered nutrient solutions and chemically enhanced phytoremediation of heavy metals from contaminated soil, the uptake of metals by plants is strongly dependent on the concentration of the metal-chelate complex and the breakdown of the root exclusion mechanisms (Beninger et al. 2004; Hattori et al. 2006; Luo et al. 2006b). In the present study, the application of 1 mM kg^{-1} EDDS enhanced the accumulation of Cu in root

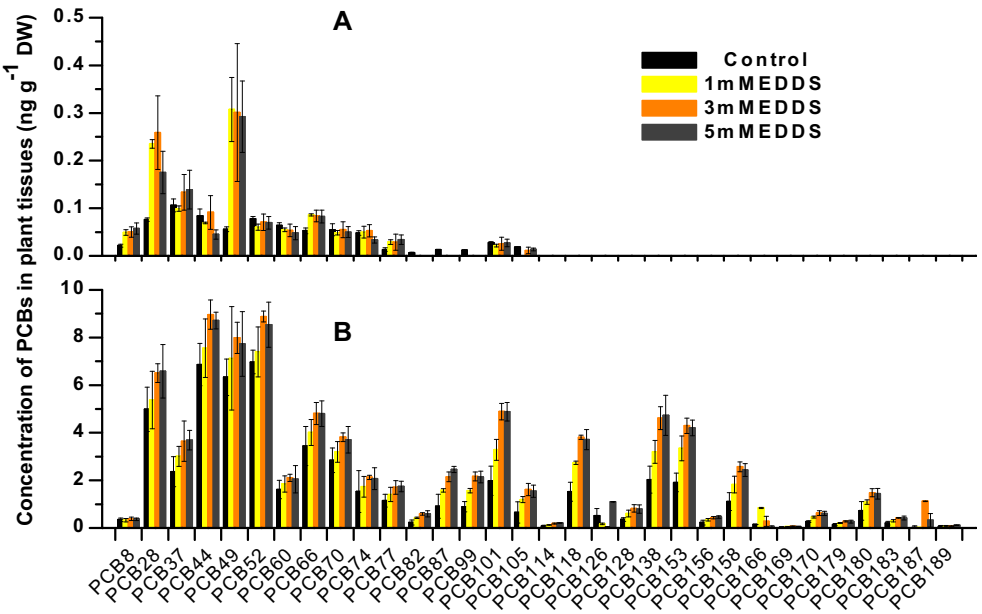

Fig. 2 Distribution of PCB homologues in plant tissue (ng g^{-1} DW). (*A* shoots, *B* roots, *Control* without EDDS, *1mM EDDS* treatment with 1 mM EDDS, *3mM EDDS* treatment with 3 mM EDDS, *5mM EDDS* treatment with 5 mM EDDS)

Table 3 Concentrations and total uptake of PCBs in plant tissues

	Shoot		Root	
	Concentration (ng g^{-1} DW)	Total uptake (ng pot^{-1})	Concentration (ng g^{-1} DW)	Total uptake (ng pot^{-1})
Control	0.79±0.05 a	4.43±0.25 a	52±2 a	80±8 c
1 mM EDDS	1.21±0.09 b	5.30±0.42 b	66±1 b	45±6 b
3 mM EDDS	1.33±0.04 b	5.68±0.20 b	83±3 c	32±3 a
5 mM EDDS	1.22±0.07 b	5.80±0.38 b	82±2 c	80±5 c

Control without EDDS, *1 mM EDDS* treatment with 1 mM EDDS, *3 mM EDDS* treatment with 3 mM EDDS, *5 mM EDDS* treatment with 5 mM EDDS; the *small letters* (*a*, *b*, *c*, *d*) stand for statistical significance at the 0.05 level with the LSD test

with a 0.071 translocation factor (TF, C_{shoot}/C_{root}), while a higher efficiency of phytoextraction was achieved in the 3 mM EDDS (TF=0.10) and 5 mM EDDS (TF=0.12) treatments compared to the control (TF=0.03). It is assumed that metal-chelate complexes enter the roots through breaks in the root endodermis and the Casparian strip and are then rapidly transported to the shoots (Bell et al. 1991; Romheld and Marschner 1981). Thus, in the present study, Cu-EDDS concentrations in the external soil solution and xylem sap would rapidly equilibrate, and translocation from the roots to the shoots under the transpiration stream would lead to higher concentrations of Cu in the shoots with increasing EDDS application ratios.

EDDS effect on soil DOC and POP uptake

In contrast to plant uptake of metals, hydrophobic compounds bind strongly to soil particles and are poorly taken up by plant tissues. Normally, there are two main pathways for plant uptake of xenobiotic compounds: First, chemicals are assimilated by roots via the vapor or water phases of soil; second, chemicals may diffuse into plant foliage via the cuticle or the stomata by dry or wet deposition (Barber et al. 2004). In the present study, all pots were placed in a greenhouse in which two passive air samplers were used to monitor the deposition of POPs from the atmosphere and the potential evaporation of POPs from soil. Chemical deposition from the atmosphere was measured at 64 pg m^{-3} for PCBs and 76 pg m^{-3} for PBDEs; this was similar to measurements taken 400 m from the greenhouse, indicating minimal evaporation of PCBs and PBDEs from soil to air during the cultivation period. Therefore, PCBs and PBDEs in plant tissues were probably taken up mainly through roots and translocated upwards to shoots. In this case, two factors, increased DOC and potential root damage, are believed to play a great role in the enhanced uptake of POPs. The DOC in soil solution was increased by the application of EDDS (Table 2), resulting in increased levels of bioavailable PCBs and PBDEs and their absorption into plant tissues. In the current study, the application of increasing levels of EDDS resulted in 1.53-, 1.68-, 1.54-fold and 1.26-, 1.59-, 1.57-fold increases in shoot and root PCB concentrations, respectively. Additionally, previous studies have demonstrated that organic acids secreted by plant roots can act as surfactants, mobilizing PCBs and enhancing their absorption into plant tissues (Campanella et al. 2002). Potential root damage associated with the increased soluble metal levels

Table 4 Concentrations and total uptake of PBDEs in plant tissues

	Shoot (ng g^{-1} DW)				Root (ng g^{-1} DW)			
	Control	1 mM EDDS	3 mM EDDS	5 mM EDDS	Control	1 mM EDDS	3 mM EDDS	5 mM EDDS
BDE28	0.073±0.012	0.087±0.015	0.094±0.019	0.075±0.023	0.550±0.088	1.515±0.231	1.811±0.298	1.598±0.335
BDE47	0.021±0.006	0.025±0.007	0.030±0.006	0.018±0.005	1.855±0.385	2.306±0.452	2.381±0.361	2.486±0.407
BDE100	0.004±0.001	0.008±0.003	0.004±0.001	0.007±0.002	1.035±0.230	2.197±0.417	2.568±0.396	2.361±0.389
BDE99	0.011±0.003	0.017±0.003	0.023±0.006	0.019±0.006	1.994±0.279	2.657±0.438	2.552±0.232	2.933±0.433
BDE154	0.004±0.001	0.003±0.001	0.005±0.001	0.007±0.001	3.116±0.415	3.498±0.359	3.480±0.338	3.667±0.376
BDE153	0.001±0	0.014±0.004	0.013±0.004	0.007±0.002	1.593±0.202	1.910±0.235	1.904±0.217	2.014±0.221
BDE183	0.007±0.003	0.041±0.009	0.035±0.008	0.036±0.010	1.981±0.319	2.089±0.403	2.008±0.336	2.176±0.354
BDE209	0.210±0.014	0.233±0.022	0.272±0.035	0.245±0.040	2.07±0.301	1.96±0.329	1.26±0.288	2.59±0.328
∑PBDEs	0.333±0.057	0.429±0.082	0.477±0.080	0.413±0.069	14.197±1.30	18.129±1.54	17.964±1.88	19.825±1.76
Total uptake (ng pot^{-1})	1.876±0.269	1.882±0.323	2.028±0.447	1.968±0.452	21.580±2.88	12.146±1.95	6.826±1.04	19.230±2.67

Control without EDDS, *1 mM EDDS* treatment with 1 mM EDDS, *3 mM EDDS* treatment with 3 mM EDDS, *5 mM EDDS* treatment with 5 mM EDDS

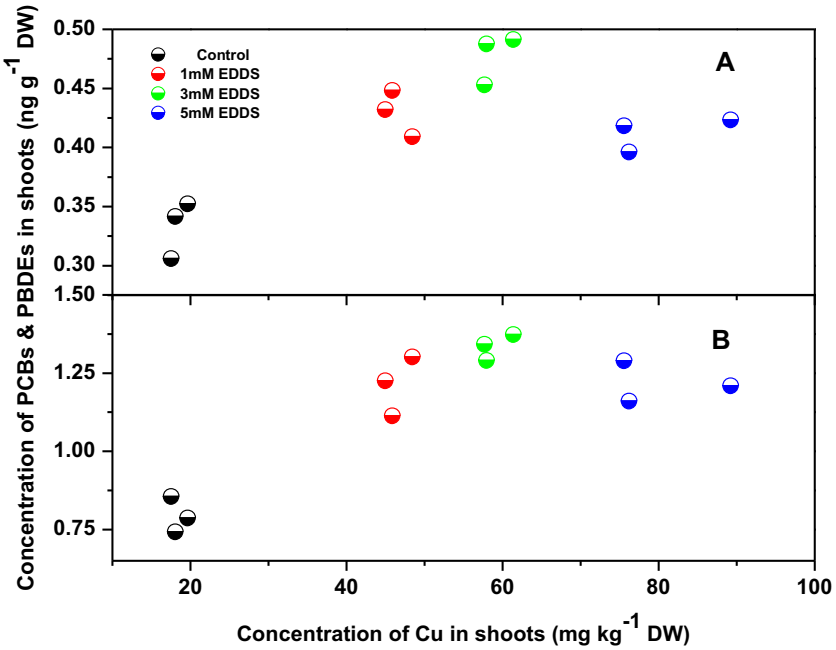

Fig. 3 Correlation between PCBs, PBDEs, and Cu in shoots. (*A* PBDEs, *B* PCBs, *Control* without EDDS, *1mM EDDS* treatment with 1 mM EDDS, *3mM EDDS* treatment with 3 mM EDDS, *5mM EDDS* treatment with 5 mM EDDS)

resulting from the application of EDDS could lead to a breakdown of root exclusion mechanisms and indiscriminate uptake of solutes, including PCBs and PBDEs. Although greater than 90 % of the PCBs and PBDEs were concentrated in root tissues (Fig. 2), some higher brominated biphenyl ethers, especially deca-BDE, were also detected in shoot tissue.

Co-linearity between Cu and PCBs or PBDE accumulations in corn

The correlation between Cu and PCBs or PBDEs was used to evaluate the relationships between Cu and PCBs or PBDEs in plant tissues. As shown in Fig. 3, PBDE and PCB concentrations in shoots increased with increasing Cu concentrations in shoots. In comparison to the control, in the EDDS treatments, shoot PCB and PBDE concentrations increased by averages of 1.58- and 1.32-fold, respectively. Significant positive correlations were also found between PBDEs and PCBs in shoots and Cu in shoots (R^2=0.625, P<0.05 for PBDEs; R^2=0.770, P<0.01 for PCBs). In the present study, the ion channels of corn roots were activated by Cu^{2+} due to the application of EDDS; thereafter, bioavailable PCBs and PBDEs were concentrated in roots and then translocated to shoots (Limmer and Burken 2014). In other words, solutes are taken up and transferred to shoots indiscriminately in cases in which the regulation of ion channel absorption is unconventional. Previously, because of their lipophilicity, POPs were considered to be difficult to be transported in plant tissues (Zhu et al. 2007). Some studies also demonstrated that POPs tended to be restricted to roots, with a positive correlation coefficient between root POP concentrations and root lipid concentrations (Huang et al. 2010; Zhu et al. 2007). However, in the present study, we demonstrated that POPs can be transferred from roots to shoots under certain environmental conditions, and it is therefore necessary to reevaluate the potential risk of POPs to the biosphere and determine potential mechanisms of phytoremediation under various soil conditions.

Conclusions

The inappropriate recycling and disposal of e-waste has become an important source of PCBs, PBDEs, and trace metals. This study has demonstrated that plant roots can be damaged by increased soluble copper levels triggered by the application of EDDS, which leads to the indiscriminate uptake of PCBs and PBDEs into roots and their subsequent transfer to shoots. The application of EDDS to soil can increase DOC levels, facilitating the bioavailability of PCBs and PBDEs in soil solution and resulting in increases in PCB and PBDE concentrations in plant roots according to the EDDS application rate. Higher brominated biphenyl ethers were also found in shoot tissue, indicating that solutes can be transferred to shoots when the regulation of ion channel absorption acts unconventionally (Limmer and Burken 2014). Future studies are required to examine the impact of EDDS on phytoremediation of soils containing other combinations of contaminants, and field experiments must be performed to evaluate the efficiency of phytoremediation under complex environmental conditions.

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