Environ Sci Pollut Res (2018) 25:2570–2579
https://doi.org/10.1007/s11356-017-0627-5

RESEARCH ARTICLE

Effects of biochar on phytotoxicity and translocation of polybrominated diphenyl ethers in Ni/Fe bimetallic nanoparticle-treated soil

Juan Wu[1,2] · Yunqiang Yi[1,3] · Zhanqiang Fang[1,3] · Eric Pokeung Tsang[4]

Received: 6 June 2017 / Accepted: 26 October 2017 / Published online: 11 November 2017

Abstract In this study, soil culture experiments were conducted to explore the effects of biochar-supported Ni/Fe nanoparticles on the accumulation and translocation of polybrominated diphenyl ethers (PBDEs) in soil-plant system and its phytotoxicity to *Brassica chinensis*. Compared with those in BDE209 contaminated soils (S_1) and Ni/Fe nanoparticle-treated soil (S_3), the plant biomass, root, and shoot lengths in biochar-supported Ni/Fe nanoparticle-treated soil (S_4) were increased by 23 mg, 1.35 cm, and 2.08 cm and 27.2 mg, 1.75 cm, and 2.52 cm, respectively, suggesting that the phytotoxicity in S_4 treatment was significantly decreased. Moreover, in all treatments, the contents of BDE209, the total PBDEs, Ni, and Fe in sample plant tissues of S_4 were the lowest. In addition, the superoxide dismutase, peroxidase, and catalase activities in S_4 treatment were found to decrease by 33.8, 47.2, and 24.1%, respectively, compared to those in S_3. Results also showed that biochar addition not only reduced the uptake of PBDEs and heavy metals but also effectively improve soil fertility and reduce the leachability of Ni and Fe caused by Ni/Fe. Finally, the translocation factors (TFs) of PBDEs in four treatments followed the orders as $S_1 > S_3 > S_4 > S_2$, indicating that biochar has an inhibition effects on PBDE translocation in the plants. In summary, all of the results suggested that the phytotoxicity, translocation of PBDEs, and the negative effects caused by neat Ni/Fe nanoparticles in *B. chinensis* were decreased as a result of the effects of the biochar.

Keywords Polybrominated diphenyl ethers · Biochar · Ni/Fe particles · Phytotoxicity · Uptake · Translocation

Responsible editor: Philippe Garrigues

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11356-017-0627-5) contains supplementary material, which is available to authorized users.

✉ Zhanqiang Fang
zhqfang@scnu.edu.cn

1 School of Chemistry and Environment, South China Normal University, Guangzhou, Guangdong 510006, China

2 Institute of Environmental Sciences (CML), Leiden University, 2300 RA Leiden, The Netherlands

3 Guangdong Technology Research Center for Ecological Management and Remediation of Urban Water System, Guangzhou 510006, China

4 Department of Science and Environmental Studies, The Education University of Hong Kong, Hong Kong 00852, China

Introduction

Due to their high hydrophobic and lipophilicity, polybrominated diphenyl ethers (PBDEs), brominated flame retardants used in a variety of industrial and consumer products (Cincinelli et al., 2012; LaGuardia et al., 2006), are strongly bound to soil and sediment particles, making the soil and sediment seriously contaminated (Chen et al., 2009; Luo et al., 2009), and posing a serious risk on human and environmental health (Hale et al., 2006; Hites, 2004; McDonald, 2002). As a consequence, the modified nanozero-valent iron has been intensively used for the degradation of PBDEs due to its large specific surface area and strong reducing potential (Fang et al., 2011; Qiu et al., 2011; Yu et al., 2012; Zhuang et al., 2011). However, several previous studies have demonstrated that nanoparticles were certified to have potential toxic effects on plants due to their novel physicochemical and structural (El-Temsah and Joner, 2012; Wang et al., 2016). For example, Wang et al.(2016) showed that higher concentrations of nZVI in soil induced rice chlorosis due to inhibited active iron transportation. Moreover, although the behaviors of PBDEs, such as uptake, bioaccumulation, translocation, and metabolism in the soil-plant system have been investigated by numerous studies (Huang et al., 2010, 2011; Vrkoslavová et al., 2010; Wang et al., 2011a), the effects of iron-based materials on the uptake of PBDEs by plants in the treated contaminated soil remain unclear. Furthermore, a series of process about translocation and accumulation of the residual contaminants and products have been taken place by the application of nZVI in soil (El-Temsah and Joner, 2013; Gardea-Torresdey et al., 2014). Our prior work successfully demonstrated that biochar-supported Ni/Fe nanoparticles (BC@Ni/Fe) performed significant removal of the decabromodiphenyl ether (BDE209) in soil with a removal efficiency of 87.7% (Wu et al., 2016a). However, the lack of understanding is particularly disconcerting in terms of the possible negative effects of the soil residual Ni/Fe nanoparticles and PBDEs on plants.

Biochar is a carbon rich by-product produced from the pyrolysis of organic matter under zero oxygen concentrations at relatively low temperatures (< 700 °C), which is widely used as a cost-effective soil amendment in environmental remediation due to its high sorption ability (Bolan et al., 2014; Mohan et al., 2014; Meyer et al., 2011). Many studies have shown that amendment with biochar in soil could enhance the removal of different heavy metals and organic contaminants, thus reducing their bioavailability, phytotoxicity, and uptake of contaminants on plants (Bolan et al., 2014; Mohamed, et al., 2017). For instance, Denyes et al. (2012) described that biochar additions significantly decreased the uptake of PCBs into plant tissue by 89% and the bioavailability of PCBs to earthworms by 88%. Mohamed et al. (2017) also showed that biochar not only reduced heavy metal (Pb, Ni, and Co) bioavailability and uptake but also improved soil fertility and increased plant growth rate by up to 145%. Nevertheless, there is limited information on the effect of biochar on the phytotoxicity, uptake, and translocation of PBDEs in the nZVI-based material-remedied soil.

Therefore, the objective of this study was to investigate the effects of the addition of biochar on the phytotoxicity, uptake, translocation, and accumulation of PBDEs by using *Brassica chinensis* as the model plants from the nZVI-based material-remedied soil. The influence of biochar on soil properties, such as pH and organic matter, was also studied.

Materials and methods

Materials and chemicals

A standard solution of decabromodiphenyl ether was purchased from Cambridge Isotope Laboratories (CIL, Andover, USA) and used to establish the standard curve. Decabromodiphenyl ether (BDE209 > 98%), ferrous sulfate ($FeSO_4 \cdot 7H_2O$, > 99%), sodium borohydride ($NaBH_4$ > 98%), nickel chloride ($NiCl_2 \cdot 6H_2O$, > 99%), polyvinylpyrrolidone (PVP, K-30), and ethanol (EtOH, 99.7%) were purchased from Tianjin Damao Company. Acetonitrile and methanol (HPLC grade) were obtained from Tianjin Kermel Chemical Reagents Company. All chemicals were used as received without further purification.

The preparation and characterization of BC@Ni/Fe particles, Ni/Fe nanoparticles, and biochar were as demonstrated in our previous report (Wu et al., 2016a). The BET specific surface area of Ni/Fe, BC, and BC@Ni/Fe was 30.81, 352.59, and 82.18 m^2/g, respectively. Also, the average particle size of Ni/Fe is 28.4 nm (Wu et al., 2016a, b).

Soil collection and preparation

The test soil (type of loam) was collected from the 0–20-cm depth zone at the Higher Education Mega Center, southern China (23° 03′ 12.59″ N, 11,323′ 25.81″ E), then air dried, homogenized, and stored at 4 °C after ground to pass through a 60 mesh. The soil sample characterizations are shown in Supplementary material, Table S1. Soil was artificially contaminated with a slight modification of the method previously reported by Wu et al. (2016a). The final concentration of BDE209 in the contaminated soil was 8.7 ± 0.9 mg/kg, and the recovery was 87.92 ± 7.5%.

The BC@Ni/Fe particles, Ni/Fe nanoparticles, and biochar (0.03 g/g) were added into 50 g of BDE209 contaminated soil, respectively. The mixture was homogenized and placed on a shaker (300 rpm, 25 °C). After reaction of 3 days, the soil samples were dried and stored for use. Control groups were also prepared.

Growth and harvest of plants

Soil culture experiments were conducted according to the methods of Wang et al. (2016) with a minor modification to test phytotoxicity. The soil was divided into the following five treatments: S_0 (BDE209-free soil), S_1 (BDE209-contaminated soil), S_2 (biochar-treated soil), S_3 (Ni/Fe nanoparticle-treated soil), and S_4 (BC@Ni/Fe-treated soil). The *B. chinensis* seeds were obtained from the Chinese Academy of Agricultural Sciences. The seeds were sterilized (0.5% *w*/*v* NaClO, 15 min), washed three times with tap water, and then thoroughly rinsed with deionized water.

The five kinds of soil were further used to conduct soil culture experiments in a set of 120-mm Petri dishes. All seed germination tests were conducted using the same plant species and seed densities. Each of Petri dishes were filled with 50 g of prepared soil and appropriate amount of distilled water. The dishes were placed in a biochemical incubator for balance at 25 °C for 48 h. Then, 20 seeds were placed inside each Petri dish and the seeded dishes were incubated in the biochemical incubator which was maintained at 25 °C during the day and 20 °C at night with a 16/8-h photoperiod and light intensity of 144 μmol m^{-2} s^{-1}. During plant growth, DI water was added daily to maintain moisture content at 75% of its water holding capacity and seed germination was recorded. Triplicate pots of each treatment were carried out.

All treatments were harvested after 20 days and subsequently washed with tap water and DI water. The clean plant samples were then separated into roots and shoots and the length of shoots and roots was measured at once with a ruler (0.1-mm increments).The dry biomass was determined after the samples were kept in a drying oven at 70 °C for 48 h. For determining the concentration of Ni and Fe, the samples were dried at 105 °C for 48 h and then digested with 2 ml of nitric acid until less than 1 ml of the liquid. The concentration and constant volume of the solution were then measured via AAS.

The antioxidation ability analysis of *B. chinensis* seedlings

Plants treated for 20 days were harvested for enzyme assays. The antioxidation ability of the *B. chinensis* seedlings was evaluated by analyzing the superoxide dismutase (SOD), peroxidase (POD), and catalase (CAT) activities. The ρ-nitroblue tetrazolium chloride (NBT) method was used to conduct the SOD activity analysis. The POD activity was detected via guaiacol assay. The CAT activity was determined following the literature (Wang et al., 2016).

Test of soil properties

To estimate the effect of different amendments on the soil characteristics after remediation, soil pH, available iron, organic matter, available phosphorus, and hydrolysable nitrogen were determined. Details of the analysis methods were described in Section S1.

Extraction and analysis of PBDEs

The dried samples were pulverized and spiked with surrogate standards of ^{13}C-PCB208 and ^{13}C-PCB141 prior to extraction. Then, the samples were extracted with a mixture of hexane/acetone (1/1, *v*/*v*) by Soxhlet extraction for PBDE analysis. Finally, the extract was cleaned up, concentrated, and analyzed in a gas chromatograph (GC, Agilent 6890)/mass spectrometer (MS, Agilent 5975) with negative chemical ionization (NCI) in the selected ion monitoring (SIM) mode and equipped with a DB5-MS (20-m × 0.25-mm i.d., 0.1-μm film thickness) capillary column. The detailed analysis methods have demonstrated in previous report (Fang et al., 2011).

Statistical analysis

All statistical analyses were performed with the SPSS 19.0 for windows. One-way ANOVA tests were used to determine the significant differences among different treatments. Statistical significance was set at $p < 0.05$. Means and standard deviation were calculated for triplicates. The level of significance is indicated by a letter.

Results and discussion

Phytotoxicity test

Notable differences in *B. chinensis* morphology were observed in the five treatments. Compared with those in the control group (S_0), plants in the treatments S_1 and S_3 were withered and yellow and had fewer, shorter, and thinner roots (Fig. 1A). As shown in Table 1, the biomasses in the five treatments decreased in the following order: $S_2 > S_0 > S_4 > S_1 > S_3$. The dry biomass of plants cultivated in S_1 and S_3 treatments was decreased by 39.9 and 43.5 mg compared with that in S_0 (blank treatment), respectively. It has been clear that BDE209 and Ni/Fe nanoparticles were both found to be toxic to plants (Wu et al., 2016b). Moreover, the dry weight of plants in S_4 increased by 23 and 27.2 mg compared with those in S_1 and S_3, respectively. The above results suggested that the growth of *B. chinensis* in treatment S_4 was significantly improved.

As shown in Fig. 1B, the growth of plants was significantly inhibited in S_1 treatment, accompanying with the length of roots and shoots were 63.8 and 65.4% shorter than that of S_0, respectively. Compared with those in S_1, the root lengths of *B. chinensis* in S_2 and S_4 increased by 8.88 and 1.35 cm, while the shoot lengths increased by 3.99 and 2.08 cm, respectively. However, the root lengths and shoot lengths in S_3 treatment decreased by 30.3 and 26.8%, respectively, compared to those in S_1.

As shown in Fig. 1 and Table 1, the high content of BDE209 in S_1 has obvious toxic effect on the growth of *B. chinensis* seedlings. The toxic effects on the plants cultivated in S_3 was the most significant because nanomaterials, heavy metal ions, and PBDE residual in the treated soil all had an inhibit effects on the plant growth. Just as reported in the literatures, the growth of plant would be significantly inhibited after being polluted by heavy metals and organic pollutants (Ahammed et al., 2012; Su et al., 2016). According to our results, the plants cultivated in S_2 and S_4 exhibited visually better growth than that in S_1 and S_3 because the presence of biochar could further remediate BDE209-contaminated soil and promote seedling growth and increase the biomass by mending soil structure, improving soil fertility and reducing the excessive leaching of mental ions (Jin et al., 2014). In particular, root elongations were significantly

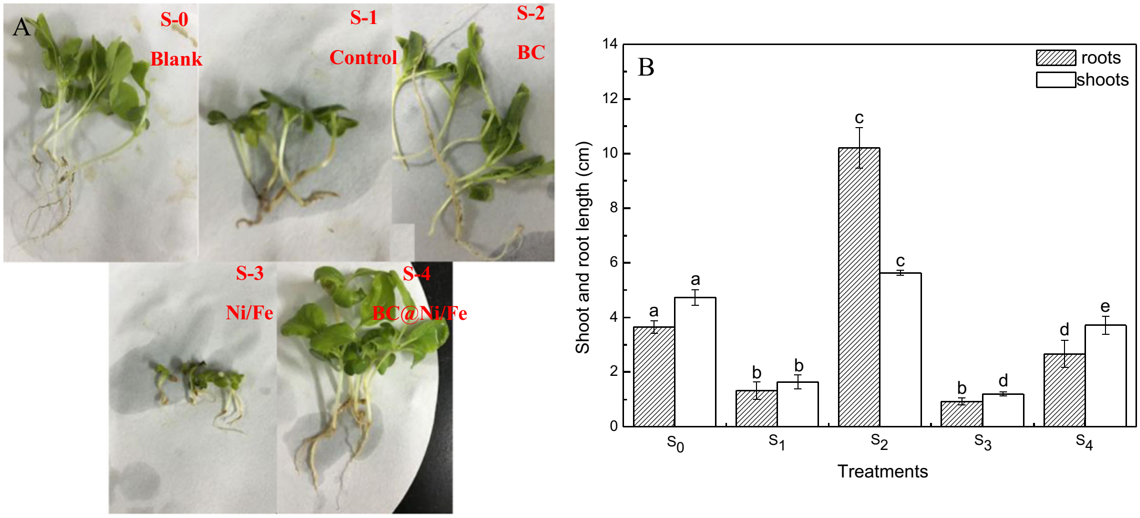


Fig. 1 **A** The physiognomy and **B** the length of roots and stems in each treatment. Within the same plant tissue, the different letters represent significant differences between the treatments and the same letters are not significantly different ($p < 0.05$)

inhibited (except for S_2) and more sensitive to the toxicity than shoot elongations in our experiments. Therefore, root is a more sensitive indicator to the toxic effect of soil pollution.

Antioxidative-enzyme activity in *B. chinensis* shoots

Effective antioxidant-enzyme systems can eliminate ROS build-up in plants and protect living organisms against oxidative stress (Lin et al. 2009). This study evaluated oxidative stress by quantitatively determining the activity of the enzyme system in terms of the SOD, POD, and CAT activities. Compared with those in the control treatment, the activity of SOD, POD, and CAT in shoots of plants grown in treatment S_2 increased by 29.1, 32.5, and 15.6%, respectively. This suggested that BDE209 induced the increasing SOD, POD, and CAT activity to remove excess radicals. According to the experiment results (Fig. 2), the SOD, POD, and CAT activity in S_3 increased by 20.4, 54.5, and 23.4% compared with those in S_2 treatment. The significant increase in the enzyme activity may be attributed to the excess O^{2-} caused by co-pollution (BDE209 and Ni/Fe nanoparticles). However, compared with those in S_3, the SOD, POD, and CAT activities in S_4 treatment were found to decreased by 33.8, 47.2, and 24.1%, respectively, indicating that the oxidative stress to plants was reduced in treatment S_4. These results all inferred that the phytotoxicity of the BDE209-contaminated soil was decreased as a result of the effects of the BC@Ni/Fe particles.

Table 1 Dry biomass of the seedlings grown in each treatment

Treatment	Dry weight (mg)	
	Shoots	Roots
S_0	49.8 ± 1.7a	6.6 ± 1.4a
S_1	16.0 ± 1.2b	1.1 ± 0.6b
S_2	104.7 ± 4.5c	12.4 ± 0.9c
S_3	11.9 ± 0.2b	1.0 ± 0.1b
S_4	37.2 ± 2.6d	2.9 ± 0.6d

The values followed by different letters are significantly different ($p < 0.05$)

Uptake and translocation of PBDEs in plants

Uptake and accumulation of BDE209 and total PBDEs in plants

The contents of BDE209 and total PBDEs in roots and shoot of each treatment are shown in Fig. 3. It is clear to see that the uptake of BDE209 and PBDEs in plant tissues was greater in roots than those in shoots. For instance, the concentration of BDE209 in shoots of treatments S_1, S_2, S_3, and S_4 decreased by 157, 168, 232, and 138 ng/g, respectively, compared with the roots of the corresponding treatment, indicating that the plant roots were more likely to take up and accumulate BDE209. The main function of roots is to absorb water and other molecules from the soil. Thus, BDE209 can be adsorbed to the outer surface of the roots, which contribute to the higher concentrations of BDE209 detected in roots. It is worth noting that the concentration of BDE209 in the shoots of plants cultivated in biochar-containing treatments (S_2 and S_4) was only 12 and 25 ng/g, which was 6.7 and 15.3% of the corresponding plant roots. The results can be speculated that biochar may have certain inhibitory effect on the upward translocation of BDE209 in plants, but the detailed mechanism of action remains to be studied.

It is also clear that the contents of BDE209 and PBDEs in both above and below ground parts were lower for plants grown in the soil with the presence of biochar (S_2 and S_4 treatments). It can be concluded that the addition of biochar

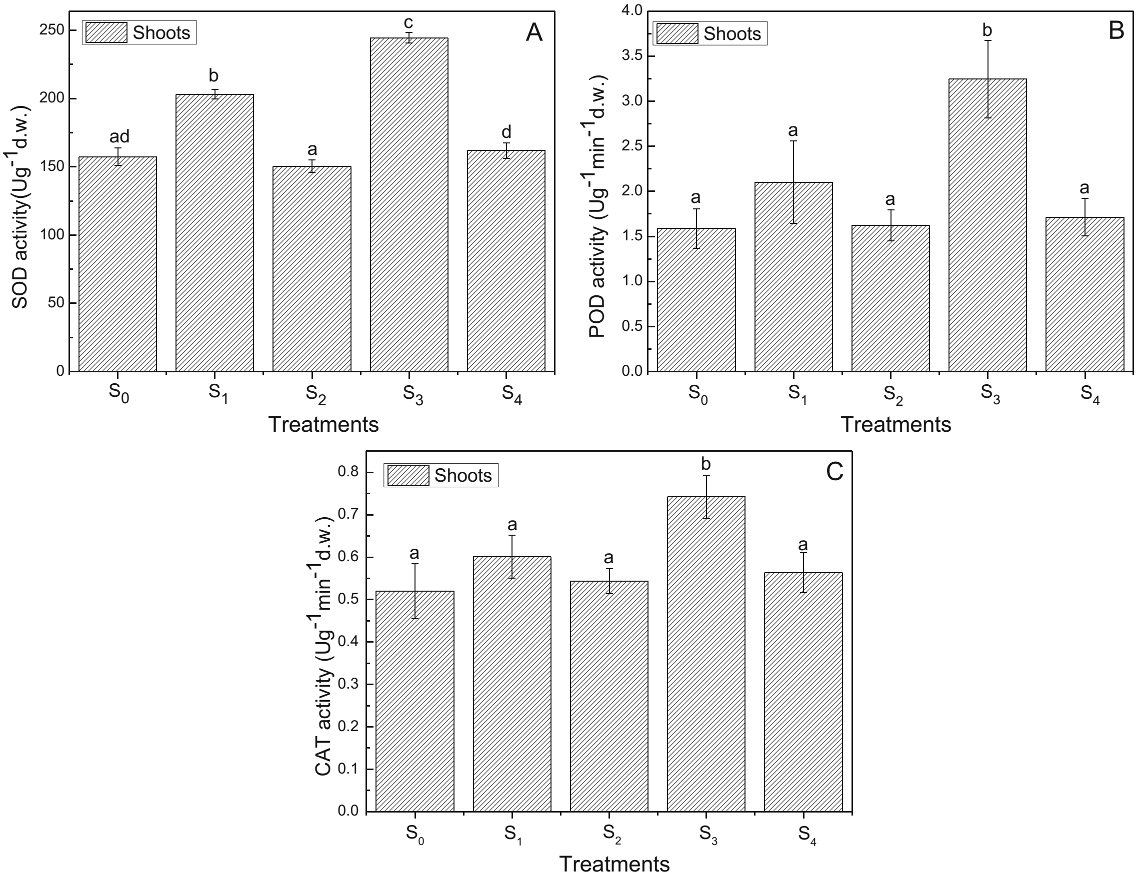
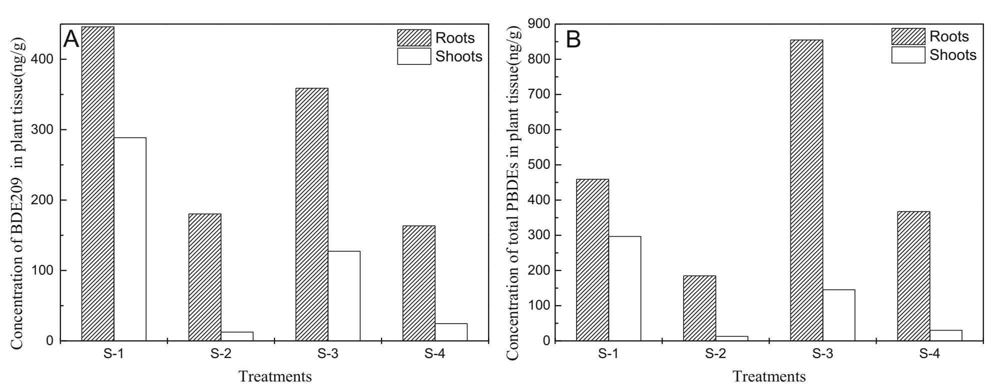


Fig. 2 **A** SOD activities, **B** POD activities, and **C** CAT activities in shoots of *B. chinensis*. The different letters represent significant differences between the treatments ($p < 0.05$)

reduced the bioavailability of PBDEs to plants. For example, the concentration of total PBDEs in the plant tissues of S_1 and S_3 decreased from 755.8 and 999.9 ng/g to only 197.8 and 397.5 ng/g for the treatments S_2 and S_4, which was amended with biochar. The results indicated that biochar can effectively prevent the uptake and accumulation of PBDEs in plants, thereby slowing down the toxic effects on plants. Adding biochar into the contaminated soil resulted in a sharp decrease in the accumulation of PBDEs, which is explained primarily by the strong physical adsorption and binding of PBDEs to the adsorbents, as demonstrated in our previous work and other studies (Vasilyeva et al., 2010; Wang et al., 2013; Wu et al., 2016a;). From Fig. 3, we can also notice that the accumulation of BDE209 and total PBDEs in treatment S_3 was highest. It may be due to the BDE209 removal efficiency in S_3 which was lower than that in S_4, resulting in higher residual content of BDE209 in the soil of S_3 and thus causing an increased concentration in the plants. The literatures also report that the amount of PBDEs uptaken by plants is positively correlated with the concentration of PBDEs in the soil (Vrkoslavová et al., 2010; Inui et al., 2008). As a result, the plants in S_3 showed a maximal phytotoxicity.

Fig. 3 Accumulation concentration of **A** BDE209 and **B** total PBDEs in plant roots and shoots



In summary, the above results indicated that using BC@Ni/Fe to remediate BDE209-contaminated soil could reduce the uptake and accumulation of PBDEs in plants, thereby reducing the phytotoxicity of the remediated soil and facilitating soil reproduction.

Distribution and translocation of PBDEs in plants

In this study, the uptake of PBDEs by *B. chinensis* seedlings in the four treatments was analyzed by using GC-MS after planting for 20 days. As shown in Fig. 4, a total of 13 PBDE homologs were detected in this study. The congener profiles of PBDEs differed slightly among four soil groups. For treatments S_1 and S_2, the congeners in the plant tissues comprised of deca- and nona-BDE206 and 207. Previous studies have shown that the removal of BDE209 by biochar was only through adsorption and complexation, which would not lead to further de-bromination (Wu et al., 2016a). As a result, we hypothesized that the nona-congeners in the plant tissues of S_1 and S_2 were derived from the metabolism of the *B. chinensis*, agreeing with reports that BDE209 could be metabolized inside plants in the process of uptake and inclined to lose one bromine atom to form nona-BDE (Wang et al., 2011a, b; Huang et al., 2010; Chow et al., 2015). In addition to BDE209, BDE207, and BDE206, the lower bromine products of octa- through penta-BDE congeners in plants were detected in samples S_3 and S_4, including BDE205, 183, 181, 154, 153, 138, 100, 99, 49, and 47. As demonstrated in our previous work (Wu et al., 2016b), low brominated diphenyl ether in plant tissues can be derived from the plant metabolism, high brominated diphenyl was de-brominated by Ni/Fe nanoparticles in plants and uptake directly from soil. It is worthwhile to notice that the distribution of PBDEs was significantly different in S_3 and S_4. For example, BDE209, 207, 206, 205, 183, 138, 153, 154, and 99 were detected in both treatment groups. However, hepta-bromide BDE-181 was only detected in the plants of S_4, while BDE-100 (penta-BDE) and lower brominated products, BDE47 and BDE49, were detected only in the plants of S_3 treatment. The result showed that BC@Ni/Fe composites can effectively adsorb and immobilize the low brominated products produced from degradation in soil, so that the plants are less likely to uptake the higher toxic by-products and reduce the toxic effect. In addition, hepta-BDE was not detected in the plant roots of S_3 treatment, but a small amount of hepta-BDE (BDE-183, 2%) was detected in the aboveground part of the plant. Also, the content of BDE205 in the aboveground part of S_3 treatment was slightly higher than that in the plant roots. These results indicated the translocation and further metabolism of PBDEs were happened in the root-aboveground system. Although some literatures reported that accumulation of PBDEs in shoots may result from a combination of uptake through the root-to-shoot pathway and foliar uptake from the air (Huang et al., 2010, 2011; Wang et al., 2011a). However, in this study, the constant presence of water in the soil surface prevents the PBDEs from evaporating off the soils, so the foliar uptake had no appreciable contribution for the plant accumulation of PBDEs. Therefore, the PBDEs in the aboveground parts of the plants in this study are considered to be derived from the root-to-shoot pathway and the metabolism inside plants.

TFs of PBDEs were also calculated and plotted in Fig. 4B for the further analysis of acropetal translocation in different treatments. TFs are calculated as the ratio of the concentration of PBDEs in the aboveground part of the plant to that in the root, expressing the ability of pants to transfer PBDEs from roots to shoots. The results further indicated that PBDEs can transfer from the roots to the aboveground parts. The TFs of total PBDEs and BDE209 for the S_1, S_2, S_3, and S_4 treatments followed the orders as $S_1 > S_3 > S_4 > S_2$, suggesting notable differences in the translocation capability of plants in the four treatments. The TFs of S_1 and S_3 treatments in this study showed the different trends as the concentrations, that is, the

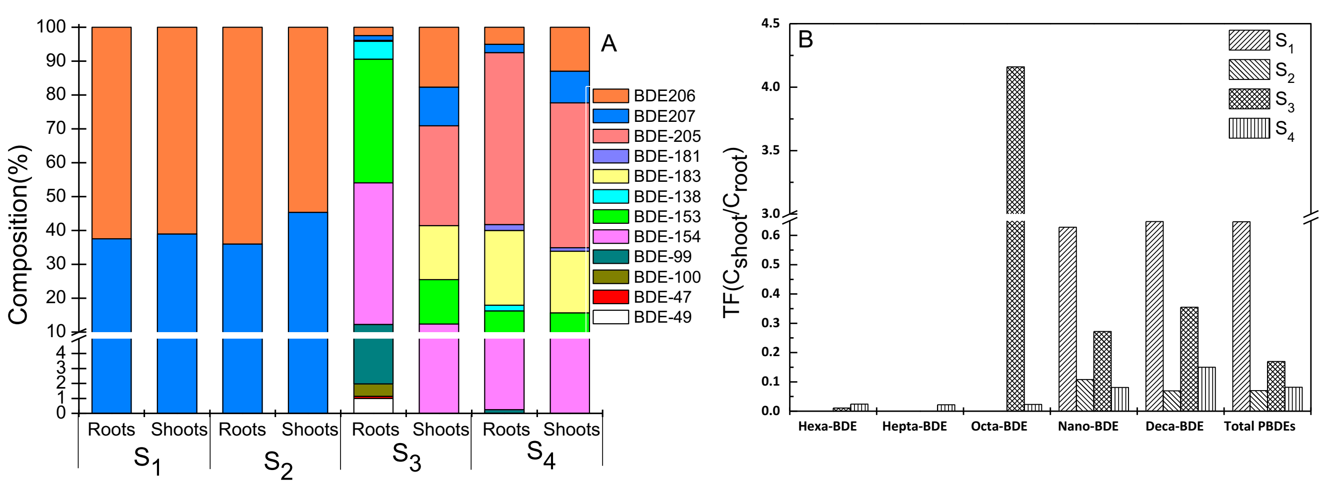


Fig. 4 **A** Composition profiles of PBDEs in the roots and shoots of plant. **B** Relationship between the translocation factor (TF) and the concentration of PBDEs in plants

TFs of deca-BDE and nano-BDE in S_1 increased by 45.2 and 56.7% compared to those in S_3, respectively. This is due to the higher accumulation of BDE209 in the plant roots in S_1 than that in S_3. In addition, compared with those in S_3, the total PBDEs, deca-, nano-, and octa-BDE in S_4 were decreased by 51.8, 57.7, 70.3, and 99.4%, respectively, indicating that the remediation of BDE209 by BC@Ni/Fe can have an inhibition effects on translocation of PBDEs in the plants. In addition, the order of TFs in S_4 treatment were as follows: deca- > nano- > octa- > hexa- > hepta-BDE. The TFs of the higher brominated diphenyl ethers were slightly higher than those of the corresponding lower brominated diphenyl ethers. The results indicated that higher brominated diphenyl ethers are more likely to translocate upward. However, the results of the different studies were different. For example, as reported by Wang et al. (2011a), the TF values were in the order: BDE28 > BDE15 > BDE47 after maize being exposed in PBDEs for 150 h. This may be due to the notable differences in the translocation capability of PBDEs in different plants (Wang et al., 2011a; Deng et al., 2016). Furthermore, as Huang et al. (2010) reported, accumulation of BDE209 in roots might be affected not only by root uptake from the soil but also by root-to-shoot translocation. The more PBDEs transferred upward, the fewer PBDEs accumulated at the roots. And the acropetal translocation of PBDEs in plants was more complicated than their root uptake of PBDEs. Thus, the combined contribution of both root-to-shoot translocation and metabolism of PBDEs inside plants would make much uncertainty of TFs and make more detailed explanation of TFs of PBDEs in root-aboveground system difficult.

Uptake and accumulation of Fe and Ni in plants

Numerous studies have reported that excessive accumulation of Fe and Ni in the organism will cause some toxic effects (Auffan et al., 2008). Therefore, it is necessary to investigate the uptake and transport of Fe and Ni among five treatments and evaluate the detrimental effects of Fe and Ni on plants in the application of BC@Ni/Fe. As shown in Fig. 5, the application of the materials had significant effects on the concentration of Fe and Ni in plant tissues. Compared to those in S_0, the contents of Fe in roots and shoots of plants in S_3 were 2.4 times (3895 mg/kg) and 3.7 times (1221 mg/kg) higher than those of S_0, respectively, which might be attributed to the highest activity of bimetallic in S_3. In addition, the contents of Fe in plant roots and aboveground parts in S_4 were reduced by 35.9 and 53.6% compared with those of S_3. This indicated that biochar could effectively inhibit the excessive absorption of Fe, thereby reducing the toxic effects on plants. Meanwhile, the accumulation of Ni in plants showed the same trend as the result of Fe. The total amount of Ni uptake by plants in plants in the S_4 treatment was 7.4 mg/kg, decreasing by 39.8% compared with that of S_3 (12.3 mg/kg). This once again showed that biochar could inhibit over-accumulation of metal elements by plant to reduce its toxic effects. The results can be explained primarily by the capability of biochar to immobilize metals such as Ni and Fe in the soil by sorption and complexation due to their large surface area, the rich pore structure and the rich surface functional groups (carboxyl, carbonyl, and hydroxyl) (Song et al., 2014; Zhou et al., 2014). In addition, the accumulation of Fe and Ni in the roots and shoots of the three treatment groups was found to be similar, that is, the content of Ni and Fe in root of plants was higher than that in aboveground parts.

Effects of the materials on soil properties

As shown in Table 2, the pH of the pure soil was 5.83 which is moderate acidic, with no significant difference in pH for soil + BDE209 (S_1) compared to the pure soil ($p > 0.05$). However, the pH of S_3 treatment was 6.39, which was due to the fact that the Ni/Fe nanoparticles that participate in the reaction may consume the H ions of the system. Compared to those in S_0, the soil pH of S_2 and S_4 increased by 0.83 and 1.11, respectively, demonstrating that the addition of biochar can improve soil pH. Soil pH is the main factor that controls the potential release of the immobilized heavy metals or metalloids and surface precipitation. The increased soil pH after biochar addition will result in the precipitants of metal oxy/hydroxides that are formed due to increased hydrolysis of heavy metals (Jiang et al., 2012), which will reduce heavy metal bioavailability.

The content of available Fe in S_3 was obviously higher than the control group S_1 (about three times), which was mainly due to excessive iron ions released during the remediation process by Ni/Fe nanoparticles. Compared to that of S_3, the available iron of S_4 was decreased by 61.2%, indicating that BC@Ni/Fe could effectively reduce the release of iron ions and resolve the problem of the excessive release of iron caused by Ni/Fe nanoparticles.

In this paper, soil organic matter content in S_3 had a slight decrease compared to that in S_0 (5.5 mg/kg), which may be due to the reaction of Ni/Fe nanoparticles with macromolecular compounds such as amino acids, proteins, and organic acids. Noteworthily, the soil organic matter increased from 65.49 to 140.88 and 88.56 mg/kg after the biochar and BC@Ni/Fe remediation, respectively. The results proved that the presence of biochar can significantly increase the content of soil organic matter, mainly because biochar is rich in biomass. The application of biochar is beneficial to the accumulation and formation of soil organic matter and has important significance in improving the soil fertility and stabilizing the soil organic carbon pool (Kimetu and Lehmann, 2010).

Moreover, the changes of available phosphorus and available nitrogen in different treatments were also compared. The available phosphorus of S_3 was lower than that of S_1 and S_0,

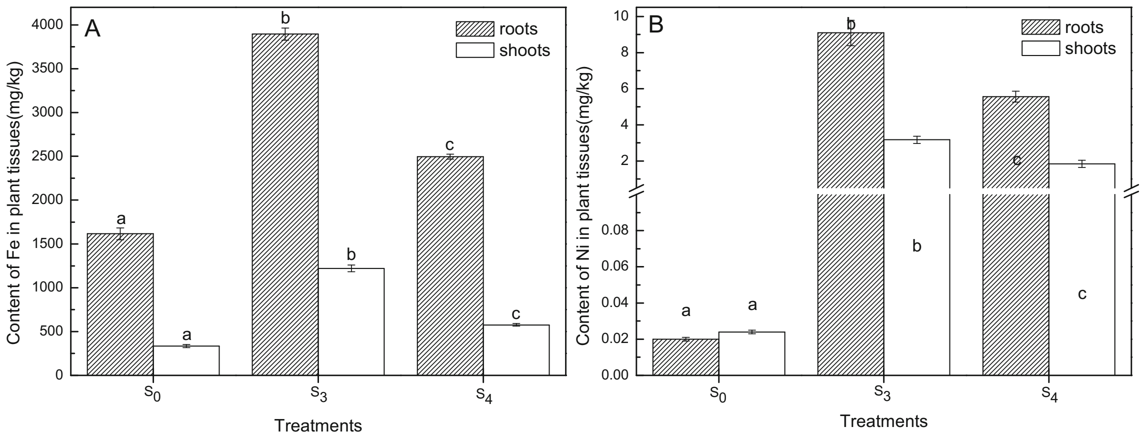


Fig. 5 Uptake and accumulation of **A** Fe and **B** Ni of Chinese cabbage. Within the same plant tissue, the different letters represent significant differences between the treatments and the same letters are not significantly different ($p < 0.05$)

indicating that Ni/Fe nanoparticles could destroy soil available phosphorus and reduce soil fertility, which was not conducive to plant growth. The contents of available phosphorus in soil were increased from 9.81 to 17.33 and 11.9 mg/kg after the remediation of biochar and BC@Ni/Fe, respectively. The results showed that the addition of biochar could significantly increase the content of available phosphorus in soil, probably because the biochar contains large amounts of phosphorus and its availability is high (Glaser et al., 2005). Furthermore, the determination results of available nitrogen in the soil showed a similar trend to that of available phosphorus. Compared with those of S_1, the available nitrogen of S_3 decreased by 3.05 mg/100 g, while those of S_2 and S_4 treatments increased by 58.12 mg/100 g and 18.7 mg/100 g, respectively.

In summary, the remediation of BC@Ni/Fe has beneficial effects on the soil physical and chemical properties, effectively improves the soil fertility, and is conducive to the growth of plants.

Conclusion

This study suggested that the remediation of BDE209-contaminated soil by BC@Ni/Fe has the potential to reduce the uptake and translocation of PBDEs from soil into *B. chinensis*, especially for lower brominated PBDEs. Soil culture experiments showed that the morphological growth of plants cultivated in S_1 and S_3 were significantly inhibited, suggesting that BDE209 and Ni/Fe nanoparticles were both found to be toxic to the plants. Moreover, the phytotoxicity in S_4 treatment was significantly decreased compared with that in S_1 and S_3 treatments, accompanied plant biomass, root, and shoot length were significantly increased, while the contents of BDE209 and the total PBDEs were significantly decreased. In addition, the content of Ni and Fe accumulated in plants was the least in S_4. Furthermore, the concentrations of BDE209, Ni, and Fe accumulated in plant tissues were greater in the roots than those in the shoots, which indicated that roots were more sensitive to the toxicity than shoots. Results also showed that higher brominated PBDEs were more readily to translocate upward than the lower brominated PBDEs. Meanwhile, BC@Ni/Fe can effectively improve the soil physical and chemical properties and increase soil fertility, which is conducive to the plant growth. For example, the enhanced soil pH and soil organic matter may contribute to a decrease in the available concentration of heavy metals by reducing metal bioavailability. Further studies should be conducted to determine the long-term effects of biochar on phytotoxicity and translocation of polybrominated diphenyl ethers at the field scale.

Table 2 The influence of the materials on soil properties

Samples	S_0	S_1	S_2	S_3	S_4
pH	5.83 ± 0.02a	5.85 ± 0.05a	6.66 ± 0.03b	6.39 ± 0.02c	6.94 ± 0.02d
Available iron (mg/kg)	118.66 ± 0.18a	102.8 ± 1.93b	93.58 ± 5.32c	350.55 ± 3.1d	135.99 ± 0.13e
Organic matter (g/kg)	65.49 ± 0.97a	68.46 ± 0.26b	140.88 ± 0.02c	59.99 ± 0.31d	88.56 ± 0.90e
Available phosphorus (mg/kg)	9.72 ± 0.77a	9.81 ± 0.38a	17.33 ± 0.38b	8.09 ± 0.26c	11.90 ± 0.15d
Hydrolysable nitrogen (mg/100 g)	15.07 ± 0.74a	15.95 ± 0.25a	74.07 ± 1.03b	12.90 ± 0.51c	34.65 ± 1.03d

In the same index, the different letters represent significant differences between the treatments and the same letter are not significantly different ($p < 0.05$)

Funding This work was supported by the National Natural Science Foundation of China (Grant number: 41471259), Joint Foundation of NSFC-Guangdong Province (Grant number: U1401235), and the Guangzhou External Science and Technology Cooperation Project (Grant number: 2016201604030002). This work was also supported by the Guangdong Technology Research Center for Ecological Management and Remediation of Water System.

References

Ahammed GJ, Wang MM, Zhou YH, Xia XJ, Mao WH, Shi K, Yu JQ (2012) The growth, photosynthesis and antioxidant defense responses of five vegetable crops to phenanthrene stress. Ecotox Environ Safe 80:132–139

Auffan ML, Achouak W, Rose JR (2008) Relation between the redox state of iron-based nanoparticles and their cytotoxicity toward *Escherichia coli*. Environ. Sci. Technol. 42(17):6730–6735

Bolan N, Kunhikrishnan A, Thangarajan R, Kumpiene J, Park J, Makino T, Kirkham MB, Scheckel K (2014) Remediation of heavy metal(-loid)s contaminated soils-to mobilize or to immobilize? J Hazard Mater 266:141–166

Chen DH, Bi XH, Zhao JP, Chen LG, Tan JH, Mai BX, Sheng GY, JM F, Wong MH (2009) Pollution characterization and diurnal variation of PBDEs in the atmosphere of an e-waste dismantling region. Environ Pollut 157:1051–1057

Chow KL, Man YB, Tamd NFY, Liang Y, Wong HM (2015) Uptake and transport mechanisms of decabromodiphenyl ether (BDE-209) by rice (*Oryza sativa*). Chemosphere 119:1262–1267

Cincinelli A, Martellini T, Misuri L, Lanciotti E, Sweetman A, Laschi S, Palchetti I (2012) PBDEs in Italian sewage sludge and environmental risk of using sewage sludge for land application. Environ Pollut 161:229–234

Deng DY, Liu J, Xu MY, Zheng GL, Guo J, 2016. Uptake, translocation and metabolism of decabromodiphenyl ether (BDE-209) in seven aquatic plants. Chemosphere152, 360–368

Denyes MJ, Langlois VS, Rutter A, Zee BA (2012) The use of biochar to reduce soil PCB bioavailability to *Cucurbita pepo* and *Eisenia fetida*. Sci Total Environ 437:76–82

El-Temsah YS, Joner EJ (2012) Impact of Fe and Ag nanoparticles on seed germination and differences in bioavailability during exposure in aqueous suspension and soil. Environ Toxicol 27:42–49

El-Temsah YS, Joner EJ (2013) Effects of nano-sized zero-valent iron (nZVI) on DDT degradation in soil and its toxicity to collembola and ostracods. Chemosphere 92:131–137

Fang ZQ, Qiu XH, Chen JH, Qiu XQ (2011) Debromination of polybrominated diphenyl ethers by Ni/Fe bimetallic nanoparticles: influencing factors, kinetics, and mechanism. J Hazard Mater 185: 958–969

Gardea-Torresdey JL, Rico CM, White JC (2014) Trophic transfer, transformation, and impact of engineered nanomaterials in terrestrial environments. Environ. Sci. Technol. 48:2526–2540

Glaser B (2005) Manioc peel and charcoal: a potential organic amendment for sustainable soil fertility in the tropics. Biol. Fertil Soil 41: 15–21

Hale RC, La Guardia MJ, Harvey E, Gaylor MO, Mainor TM (2006) Brominated flame retardant concentrations and trends in abiotic media. Chemosphere 64:181–186

Hites RA (2004) Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. Environ. Sci. Technol. 38:945–956

Huang HL, Zhang SZ, Christie P, Wang S, Xie M (2010) Behavior of decabromodiphenyl ether (BDE-209) in the soil-plant system: uptake, translocation, and metabolism in plants and dissipation in soil. Environ. Sci. Technol. 44:663–667

Huang HL, Zhang SZ, Christie P (2011) Plant uptake and dissipation of PBDEs in the soils of electronic waste recycling sites. Environ Pollut 159:238–243

Inui H, Wakai T, Gion K, Kim Y-S, Eun H (2008) Differential uptake for diox-inlike compounds by zucchini subspecies. Chemosphere 73: 1602–1607

Jiang TY, Jiang J, RK X, Li Z (2012) Adsorption of Pb(II) on variable charge soils amended with rice-straw derived biochar. Chemosphere 89:249–256

Jin J, Sun K, Wu FC, Gao, Wang ZY, Kang MJ, Bai YC, Zhao Y, Liu XT, Xing BS (2014) Single-solute and bi-solute sorption of phenanthrene and dibutylphthalate by plant- and manure-derived biochars. Sci Total Environ 473-474:308–316

Kimetu JM, Lehmann J (2010) Stability and stabilisation of biochar and green manure in soil with different organic carbon contents. Aust J Soil Res 48(7):577–585

LaGuardia MJ, Hale RC, Harvey E (2006) Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. Environ. Sci. Technol. 40:6247–6254

Lin C, Fugetsu B, Su Y, Watari F (2009) Studies on toxicity of multi-walled carbon nanotubes on Arabidopsis T87 suspension cells. J Hazard Mater 170:578–583

Luo Y, Luo XJ, Lin Z (2009) Polybrominated diphenyl ethers in road and farm-land soils from an e-waste recycling region in Southern China: concentrations, source profiles, and potential dispersion and deposition. Sci Total Environ 407:1105–1113

McDonald TA (2002) A perspective on the potential health risks of PBDEs. Chemosphere 46:745–755

Meyer S, Glaser B, Quicker P (2011) Technical, economical, and climate-related aspects of biochar production technologies: a literature review. Environ. Sci. Technol. 45(22):9473–9483

Mohamed BA, Ellis N, Kim CS, Bi XT (2017) The role of tailored biochar in increasing plant growth, and reducing bioavailability, phytotoxicity, and uptake of heavy metals in contaminated soil. Environ Pollut 230:329–338

Mohan D, Sarswat A, Ok YS, Pittman CU (2014) Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent—a critical review. Bioresour Technol 160:191–202

Qiu XH, Fang ZQ, Liang B, FL G, ZC X (2011) Degradation of decabromodiphenyl ether by nano zero-valent iron immobilized in mesoporous silica microspheres. J Hazard Mater 193:70–81

Song ZG, Lian F, ZH Y, Zhu LY, Xing BS, Qiu WW (2014) Synthesis and characterization of a novel MnOx-loaded biochar and its adsorption properties for Cu^{2+} in aqueous solution. Chem Eng J 242:36–42

Su HJ, Fang ZQ, Tsang PE, Fang JZ, Zhao DY (2016) Stabilisation of nanoscale zero-valent iron with biochar for enhanced transport and in-situ remediation of hexavalent chromium in soil. Environ Pollut 214:94–100

Vasilyeva GK, Strijakova ER, Nikolaeva SN, Lebedev AT, Shea PJ (2010) Dynamics of PCB removal and detoxification in historically contaminated soils amended with activated carbon. Environ Pollut 158:770–777

Vrkoslavová J, Demnerová K, Macková M, Zemanová T, Macek T, Hajšlová J, Pulkrabová J, Hrádková P, Stiborová H (2010) Absorption and translocation of polybrominated diphenyl ethers (PBDEs) by plants from contaminated sewage sludge. Chemosphere 81:381–386

Wang J, Fang ZQ, Cheng W, Yan XM, Tsang PE, Zhao DY (2016) Higher concentrations of nanoscale zero-valent iron (nZVI) in soil induced rice chlorosis due to inhibited active iron transportation. Environ Pollut 210:338–345

Wang S, Zhang SZ, Huang HL, Christie P (2011a) Behavior of decabromodiphenyl ether (BDE-209) in soil: effects of rhizosphere and mycorrhizal colonization of ryegrass roots. Environ Pollut 159: 749–753

Wang Y, Luo CL, Li J, Yin H, Li XD, Zhang G (2011b) Characterization of PBDEs in soils and vegetations near an e-waste recycling site in South China. Environ Pollut 159:2443–2448

Wang Y, Wang L, Fang GD, Herath HMSK, Wang YJ, Cang L, Xie ZB, Zhou DM (2013) Enhanced PCBs sorption on biochars as affected by environmental factors: humic acid and metal cations. Environ Pollut 172:86–93

Wu J, Yi YQ, Li YQ, Fang ZQ, Tsang PE (2016a) Excellently reactive Ni/Fe bimetallic catalyst supported by biochar for the remediation of decabromodiphenyl contaminated soil: reactivity, mechanism, pathways and reducing secondary risks. J Hazard Mater 320:341–349

Wu J, Xie YY, Fang ZQ, Cheng W, Tsang PE (2016b) Effects of Ni/Fe bimetallic nanoparticles on phytotoxicity and translocation of polybrominated diphenyl ethers in contaminated soil. Chemosphere 162:235–242

Yu K, Gu C, Boyd SA, Liu C, Sun C, Teppen BJ, Li H (2012) Rapid and extensive debromination of decabromodiphenyl ether by smectite clay-templated subnanoscale zero-valent iron. Environ. Sci. Technol. 46:8969–8975

Zhuang Y, Ahn SW, Seyfferth AL, Masue-Slowey Y, Fendorf S, Luthy RG (2011) Dehalogenation of polybrominated diphenyl ethers and polychlorinated biphenyl by bimetallic, impregnated, and nanoscale zerovalent iron. Environ Sci Technol 45:4896–4903

Zhou YM, Gao B, Zimmerman AR, Chen H, Zhang M, Cao XD (2014) Biochar-supported zerovalent iron for removal of various contaminants from aqueous solutions. Bioresour Technol 152:538–542