Immobilization of pentachlorophenol in soil using carbonaceous material amendments

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Carbonaceous material amendment was a potential *in situ* remediation method for pentachlorophenol contaminated soil.

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ABSTRACT

In this study, three pentachlorophenol (PCP) laboratory-spiked and one field-contaminated soil were amended with 2.0% char, humic acid (HA) and peat, respectively. The amended soils were aged for either 7 or 250 days. After amendment, CaCl_2 extractability of PCP was significantly decreased. Desorption kinetics indicated that the proposed amendment could lead to a strong binding and slow desorption of PCP in soils. Amendment with char reduced the bioaccumulation factor (BAF) of PCP most significantly for earthworms (*Eisenia fetida*) in all soils studied. The results of both physicochemical and biological tests suggested that amendment reduced PCP bioavailability quickly and enduringly, implying that carbonaceous material amendment, especially char amendment, was a potentially attractive *in situ* remediation method for sequestration of PCP in contaminated soil.

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1. Introduction

Soil and sediment are regarded as ultimate sink of large number of organic contaminants in terrestrial and aquatic ecosystem (Davies et al., 1999; Skrbic and Durisic-Mladenovic, 2007). Soil remediation technologies emphasize the transformation and detoxification of contaminants. Compared with conventional expensive, invasive, and sometimes ineffective techniques, such as excavation and dredging, *in situ* treatment strategies are more effective at reducing risk and decreasing expenditures on management. Among various *in situ* treatments, bioremediation is thought to enable permanent elimination of pollutants at low cost. However, its effectiveness is limited by the appropriate soil conditions for microbial activity, recalcitrance of pollutants to biodegradation, and formation of metabolites which may be more toxic than the parent contaminant (Boopathy, 2000). Moreover, natural organic matters in soil and sediment serve as dominant environmental “compartments” for sorption and accumulation of organic pollutants. The degradation of organic pollutants in soil is affected mainly by soil organic matter (SOM) and clay mineral contents and compositions, which limits the bioavailability of

organic pollutants to microbes (Hatzinger and Alexander, 1995; Boopathy, 2000).

Based on the above observations, an *in situ* remediation method to reduce bioavailability of organic pollutants by repartitioning of organic contaminants to carbonaceous sorbents that were mixed with soil to enhance the natural process of contaminant stabilization was proposed by Weber et al. (2006). They developed engineered sorbents from natural organic materials, such as peat, soybean stalk and pine needle under superheated temperature/pressure conditions, for sorption of polycyclic aromatic hydrocarbons (PAHs) in contaminated soils. Both natural and engineered natural materials significantly decreased the extractability and bioavailability of PAHs from contaminated soil (Tang and Weber, 2006; Weber et al., 2006; Tang et al., 2007). Addition of active carbon to sediments affected desorption of polychlorinated biphenyls (PCBs) and PAHs (Zimmerman et al., 2004). The bioavailability and bioaccumulation of PCBs were reduced remarkably by activated carbon amendment in both laboratory (Millward et al., 2005) and field (Cho et al., 2007) tests. These works demonstrated clearly the effectiveness of amendments for immobilization of hydrophobic organic contaminants in soil/sediment. However, it should be pointed out that the carbonaceous materials were only used to immobilize non-polar hydrophobic organic contaminants in the above noted studies. The effectiveness for stabilization of polar or ionizable organic contaminants such as pentachlorophenol (PCP) has not been addressed.

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Cation surfactant bound bentonite has been proposed for potential application in remediation of contaminated water and soil based on its powerful sorption of polar and ionizable organic contaminants (Chen et al., 2005). However, synthetic surfactants may become an environmental problem because of their biological toxicity (Conte et al., 2005).

The use of PCP and its salt since the 1930s as a biocide and a wood preserving reagent has led to serious soil contamination (Boyd et al., 1989). The objective of this work was to determine the effect of three common organic amendments, char, humic acid (HA), and peat, on the immobilization of PCP in contaminated soils. Serial comparisons were made before and after amendments, including (1) fractionation distribution pattern of PCP in soils; (2) desorption kinetics and (3) bioaccumulation to earthworm (*Eisenia fetida*). Additionally, the immobilization of PCP in the amended soil as affected by the incubation time was also assessed.

2. Materials and methods

2.1. Chemicals

Dichloromethane (DCM), methanol, *n*-butanol (BuOH), and *n*-hexane (Mallinckrodt, USA) were of HPLC grade. Anhydrous potassium carbonate, anhydrous sodium sulphate, dehydrate calcium chloride (Beijing Chemical Reagents Company, China) were of analytical grade. Anhydrous sodium sulphate was heated at 400 °C for 4 h in muffle furnace before use to remove organic compounds. Sodium azide (Dongyang Tianyu Chemical Ltd., Zhejiang, China) was of analytical grade.

Reference standards of PCP (AccuStandard Inc., New Haven, USA), internal standard 2,4,6-tribromophenol (TBP, AccuStandard Inc., New Haven, USA) were made in *n*-hexane, stored in sealed volumetric flasks and preserved at 4 °C. All containers were weighed and volatile solvents were compensated before use. Working solutions were prepared by diluting stock solutions and derivatized.

2.2. Carbonaceous materials

Char, HA, and peat were used as carbonaceous materials in this study. Char was prepared by atmospheric pyrolysis according to the method of Braidat et al. (2003). Willow-wood shavings were placed in a 15-cm watch-glass-covered crucible and heated at 400 °C for 2 h. The samples were then rinsed with ultrapure water. Peat used in this study was commercially available (Klasmann-Deilmann GmbH, Germany). HA was isolated from peat according to the International Humic Substances Society (IHSS) procedure as described in our previous work (Wen et al., 2007). Briefly, to each of six 250 ml glass centrifuge bottles, 20 g of the peat soil was added, and each bottle was filled with 200 ml of distilled water. The pH of the soil suspensions was then adjusted to 1–2 with 1 M HCl. After shaking for 1 h, the suspensions were centrifuged (at 6555 rpm, 30 min) and the supernatants decanted. The solids were then neutralized by 1 M NaOH to pH 7, and 200 ml of 0.1 M NaOH was added to resuspend the solid under a N₂ stream. The suspensions were immediately sealed, shaken overnight, and centrifuged. The supernatants were decanted, acidified with 6 M HCl to pH 1, and allowed to sit for 24 h before HA and fulvic acid (FA) fractions were separated by centrifugation. The precipitated HA fraction was then redissolved in a minimum amount of 0.1 M KOH under N₂, to which KCl was added to give approximately 0.3 M for K⁺. The HA solution was again centrifuged to remove the suspended solids. This dissolution-precipitation procedure was repeated three times. The HA solution was then acidified and transferred to a dialysis bag having a molecular cutoff of 12,000–14,000 Da, it was dialyzed with distilled water until the test of Cl[−] in water with AgNO₃ turned negative. The dialysis step also removed the residual FA in HA. The solid HA was obtained by freeze-drying.

The char, HA and peat obtained were pulverized in a mortar to pass through a 0.25 mm sieve, and stored in a glass vial at room temperature. The pH values are 7.53, 2.87 and 4.28 for char, HA and peat, respectively. The ash contents of all carbonaceous materials were lower than 10%. The OC fractions were 45.3, 51.3 and 72.9% for char, HA and peat, respectively.

2.3. Soils

Three uncontaminated Chinese cultivated soils were collected from Jiangxi Province, South China (S1), Hebei Province, North China (S2), Beijing, North China (S3) in the year 2003. The soils were air-dried, ground, and passed through a 2-mm sieve to remove stones, plant roots, and other large particles. Soil pH was measured in both distilled water and 0.01 mol/L CaCl₂ solution, respectively, using a soil/solution ratio of 1:5 (w:v). Organic matter content was determined by the Walkley–Black procedure (Nelson and Sommers, 1982). The uncontaminated soils were sterilized and spiked with PCP, stored for 4 years. Details of soil spiking and aging were described previously (Hu et al., 2005). Total concentrations of PCP in soils were determined. Char, HA and peat were mixed with soils separately at a carbonaceous material to soil ratio of 2.0% (w:w). The amended soils were thoroughly mixed on a rotary shaker for 24 h, and transferred into glass jars. The jars were sealed with screw caps fitted with Teflon liners and stored in the dark at 20 ± 1 °C for either 7 days or 250 days prior to sequential extraction, desorption and earthworm uptake experiments. Soils without carbonaceous material amendment were used as control. Soil S2 without PCP spiking was used as blank. No detectable PCP was found in blank and earthworm incubated in blank. The field-contaminated soil was collected from Hubei Province (F) at the end of 2006, amended with carbonaceous materials and stored in parallel with the spiked soils. The characteristics of the soils and initial concentrations of PCP in the soils are shown in Table 1.

2.4. Sequential extraction

PCP in soils with and without amendments was subjected to a sequential extraction. The extractions were carried out in triplicate. Extraction details are described below.

2.4.1. Step 1. 0.01 mol/L CaCl₂ extraction

Ten milliliter of 0.01 mol/L CaCl₂/1.5 mmol/L NaN₃ aqueous solution was added to 1.0 g (dry weight) of soil in 50 ml glass centrifuge tubes. The tubes were shaken for 24 h on a tumble shaker at 100 rpm at 22 ± 1 °C (preliminary experiments showed apparent equilibrium was achieved within 24 h), and then centrifuged at 4000 rpm for 20 min. The supernatant was carefully transferred to another clean glass centrifuge tube. Then 5 ml was transferred to another clean centrifuge tube and adjust the pH to 4.0. The acidic solution was extracted twice with 10 ml hexane. The upper organic layers were collected and concentrated to 1 ml under a gentle stream of N₂, and then cleaned, derivatized and determined.

2.4.2. Step 2. Butanol extraction

The residue from step 1 was freeze dried and then 20 ml of butanol was added. The tubes were covered, and the soil–butanol slurry was mixed strongly to break down the soil mass, after that the tubes were shaken for 24 h on a tumble shaker at 100 rpm at 22 ± 1 °C (preliminary experiments showed apparent equilibrium was achieved within 24 h), then centrifuged at 4000 rpm for 30 min. The supernatant was carefully removed, concentrated to 1 ml, cleaned, derivatized, and determined.

2.4.3. Step 3. DCM extraction

The soil residue from step 2 was freeze dried, loosened using a clean stainless steel spatula, weighed, transferred to a filter paper package mixing with anhydrous sodium sulphate, and extracted with dichloromethane for 24 h using a Soxhlet apparatus. The extractants were concentrated to 1 ml, cleaned, derivatized and determined.

2.5. XAD-2 assisted desorption experiment

Desorption of PCP from soil S2 was conducted in triplicate by a modified XAD-2 shaken slurry desorption method of Northcott and Jones (2001).

Amberlite XAD-2 resin (Supelco, Bellefonte, PA), a macroporous, polystyrene, nonionic bead, with particle size of 20–60 mesh, surface area of 300 m²/g, wet density of 1.02 g/ml, and a pore diameter of 90 nm, is applied to assist the desorption of PCP from Hebei soil. The resin was prepared by soaking in methanol (MeOH) to remove entrapped air and trace of residual monomeric compound and preservative reagents. After 24 h the MeOH was decanted and exchanged with a freshly prepared solution of 0.01 mol/L CaCl₂ aqueous solution containing 100 mg/L NaN₃ which was

Table 1
Characteristics of soils studied.

Soils		OC (%)	pH		PCP concentration (μg/g)	Particle size (%)		
			Water	CaCl ₂		Sand	Silt	Clay
Lab-contaminated soils	S1	0.893	6.01 ± 0.04	5.65 ± 0.02	0.79 ± 0.01	19.5	35.2	45.3
	S2	2.63	7.62 ± 0.14	7.15 ± 0.06	1.21 ± 0.13	13.7	59.0	27.3
	S3	0.783	8.16 ± 0.03	7.73 ± 0.01	7.19 ± 0.60	37.6	51.6	10.8
Field-contaminated soil	F	2.12	7.79 ± 0.01	7.63 ± 0.07	2.44 ± 0.28	27.6	46.6	26.6

used to inhibit bacteria activity. The aqueous solution was changed 10 times to ensure complete removal of MeOH.

Soil samples of 0.25 g and 0.5 g wet XAD-2 resin were weighed directly into a glass centrifuge tubes (50 ml) equipped with Teflon lined screw cap. Forty milliliters of 0.01 mol/L CaCl_2 –100 mg/L NaN_3 solution was added. An aqueous solution of 0.01 mol/L CaCl_2 was used to prevent the dispersion of soil clay particles, while 100 mg/L NaN_3 was included to prevent microbial growth. The tubes were sealed, placed on a tumble shaker at 100 rpm at $22 \pm 1^\circ\text{C}$. Triplicate tubes were removed and analyzed. At each desorption time interval, 2.0 g of K_2CO_3 was added to promote phase separation. The tubes were resealed, vigorously shaken by hand to mix the contents. Then the tubes were stood vertically for 5 min to allow settling of the soil–resin–water slurry, and centrifuged at 4000 rpm for 20 min to separate the soil and resin. The resin was isolated, washed with 10 ml 0.01 mol/L CaCl_2 –100 mg/L NaN_3 solution to remove K_2CO_3 . Then it was transferred into another glass tube, mixed with 2 g anhydrous Na_2SO_4 . The PCP absorbed to XAD-2 resin was extracted by 5 ml of hexane for 3 times. The extractant was concentrated to 1.0 ml by rotary evaporation prior to analysis.

In order to make certain the XAD-2 resin extraction method, the sorption ability of XAD-2 resin under different pH condition (4.0, 6.0 and 8.0) was evaluated in our preliminary experiments. The results showed that XAD-2 could sorb 10 $\mu\text{g}/\text{ml}$ PCP from 40 ml 0.01 mol/L CaCl_2 solution under different pH effectively within 5 min, with the recovery higher than 95%. Mass balance was checked as the sum of PCP desorbed at each transfer time plus the residual PCP mass remaining in the soil. The recovery was $98 \pm 15\%$ of the initial soil concentration.

Two-compartment first-order kinetic model (Northcott and Jones, 2001) was used to describe the desorption of PCP from Hebei soil. It is assumed that desorption of PCP from soil has two discrete, independent compartments, labile and resistant for PCP binding. Simultaneous first-order desorption for this system is expressed mathematically as

$$\frac{q(t)}{q_0} = \Phi_1 \exp(-k_1 t) + (1 - \Phi_1) \exp(-k_2 t) \quad (1)$$

where $q(t)$ is the solid-phase PCP concentration at a given time t ; q_0 is the initial solid-phase PCP concentration; Φ_1 is the labile fraction of PCP; k_1 and k_2 are the apparent first-order rate constants for the labile and resistant fractions, respectively; t is the desorption time.

2.6. Earthworm uptake

Earthworms (*Eisenia fetida*) were served to assess the bioavailability of the sorbed PCP to biological uptake. They were purchased from the Agricultural University of China (Beijing, China), with an average 0.50 g fresh weight each and 3.5–4.5 cm in length.

The uptake of PCP by earthworm in both amended and unamended soil samples was determined. Fourteen adult earthworms were transferred to moist (20%) soil samples (350 g) in 500 ml glass beaker, which was covered with aluminum foil with 2 holes per square centimeter to prevent earthworm escape and allow air exchange. The beakers were kept in the dark at $22 \pm 2^\circ\text{C}$. Four replicates were tested for each soil sample. After 30 days of exposure, the earthworms were removed from the glass beaker, washed with deionized water, transferred to wet filter paper in glass beaker in the dark to allow purging of gut contents. After 24 h, they were rinsed with deionized water, wiped with filter paper, weighed, put into an aluminum foil and kept in -20°C refrigerator before measurement. The bioaccumulation factors (BAFs) were obtained based on the following equation:

$$\text{BAF} = C_{\text{worm}}/C_{\text{soil}} \quad (2)$$

where C_{worm} is the concentration of PCP in earthworms on a wet-weight base (mg/kg) and C_{soil} is the concentration of PCP in soil on a dry-weight base (mg/kg), which is considered constant, because the uptake of PCP by earthworms results in only a negligible reduction of their concentrations in soil.

2.7. Long-term effect

In order to test the long-term effect of carbonaceous material amendment, the fractionation and earthworm uptake tests in soil S2 were conducted after 250 days of aging. The procedures of fractionation and earthworm uptake tests were the same as those described in Sections 2.4 and 2.6.

2.8. PCP quantification

PCP in soils and earthworm was extracted by DCM using Soxhlet extraction. The soils were freeze dried prior to Soxhlet extraction. The frozen earthworms were ground with a mortar and pestle. Soil (0.2 g) or ground earthworm tissue (0.1 g) was mixed with ca. 10 g anhydrous Na_2SO_4 in paper extraction thimbles and then extracted with 80 ml dichloromethane for 24 h at 10 min cycle $^{-1}$. The extractant was then concentrated to 2 ml by rotary evaporator. To assure quality of the proposed analytical method, blank was analyzed in each analytical run. The blank values were determined by extracting an empty cellulose thimble by the same procedure as the real sample. No chromatographic peak of derivatized PCP was found in

chromatograms of the blank. All the samples were cleaned using a column (1 cm i.d. $\times$ 5 cm). The column was prepared by packing silica gel (60–80 mesh), which was activated at 120°C for 2 h, deactivated by a water to silica ratio 3:100 (w:w), and deposited in dichloromethane, covered by a 2 cm layer of anhydrous Na_2SO_4 , and then washed with 60 ml dichloromethane. The eluate was concentrated to 1 ml by rotary evaporator prior to derivatization.

Acetic anhydride was used for derivatization of PCP. In brief, 10 ml of 0.1 mol/L K_2CO_3 , 10 μl of the internal standard TBP (10 mg/L) were added sequentially. The solution was stirred for 10 min, and then 0.5 ml acetic anhydride was added. After stirring for 20 min, 9 ml hexane was added. The tube was stirred and set for 10 min before analysis.

Gas chromatography (Agilent 6890N) equipped with an ^{63}Ni electric capture detector (ECD) (Hewlett-Packard 6890, USA) and an HP-5 capillary column (30-m $\times$ 0.32-mm-id $\times$ 0.25- μm) (J&W, USA) was used to determine the quantity of PCP in samples. The injector temperature was set at 250°C ; the detector temperature was 300°C ; the initial column temperature was 59°C , programmed at 59°C for 1 min, then from 59 to 180°C at $30^\circ\text{C}/\text{min}$, and maintained at the temperature for 3 min, then from 180°C to 185°C at $10^\circ\text{C}/\text{min}$, and then from 185°C to 250°C at $30^\circ\text{C}/\text{min}$, with the final temperature maintained for 2 min. The total analytical time was 12.7 min. The recovery of the extraction–clean up–derivatization–determination process ranged from 83.2% to 92.0%.

2.9. Data analysis

Statistical analyses were conducted with the software SPSS 11.5 for Windows (SPSS Inc. Chicago, USA). Parameter sets for Eq. (1) were optimized by nonlinear regression at 95% confidence. The values of soil pH, total concentrations of PCP in soil and fractions, and in earthworms are reported as mean $\pm$ standard errors. Paired-samples t -test analysis was performed to establish significant differences between treatments with and without carbonaceous amendments.

3. Results and discussion

3.1. Effect of carbonaceous material amendment on soils pH

PCP is a hydrophobic weak organic acid ($\text{pK}_a = 4.75$); therefore, it exists as either a protonated or a deprotonated species. When soil pH is below 2 more than 99% of total PCP is present as protonated species, whereas more than 95% of total PCP is present as deprotonated form when the pH is above 6 (Diaz-Flores et al., 2006). Stapleton et al. (Stapleton et al., 1994) found that sorption of PCP was affected by pH condition. Between pH 4 and 8.5, the sorption decreases by three times and the solubility increases 3 orders of magnitude as the dominant aqueous species change. Thus, effect of amendment on pH of the soils was conducted. Soil pH values determined in water are shown in Fig. 1. Amendment with HA resulted in 1.1, 1.2, 1.3 and 1.0 pH unit decrease for S1, S2, S3 and F soils, respectively ($p < 0.05$), while amendment with peat led to significant soil pH decrease only for S3 and F soils ($p < 0.05$).

Fig. 1. pH of soils amended with carbonaceous materials. Error bars represent one standard deviation. Bars with same letter or letters imply no significant difference ($p < 0.05$).

According to Stapleton's finding (Stapleton et al., 1994), PCP's protonated form is strongly hydrophobic with a low aqueous solubility. Therefore, it could be postulated that decrease of soil pH might result in partial conversion of PCP^- into PCP^0 , thereby increasing sorption of PCP in soils. Char amendment significantly increased pH of soil S1 ($p < 0.05$), but did not change pH of S2, S3 and F soils. Similar tendency was observed for soil pH measured in 0.01 mol/L $CaCl_2$ solution (data not shown).

3.2. Fractionation of PCP in the soils amended by carbonaceous materials

In order to evaluate the validity of the fractionation and determination performance, soils were subjected to the fractionation and subsequent determination of PCP before carbonaceous amendment. The relative standard deviation of PCP concentrations for six replicated determinations in $CaCl_2$, *n*-butanol and DCM fractionations was in the range of 2.8–14.7%. The sum of PCP in the three fractions was comparable with the total PCP contents obtained by Soxhlet extraction of soils, thereby showing the validity of the fractionation and determination performance (data not shown).

The fraction distribution of PCP differed significantly among various soils (Fig. 2). The extracted PCP by 0.01 mol/l $CaCl_2$ aqueous solution for unamended S1, S2, S3 and F soils was 21.9, 23.5, 52.8, and 18.4% of total PCP contents in soils, respectively. After carbonaceous material amendment $CaCl_2$ extractable PCP was significantly decreased for all soils studied ($p < 0.05$, Fig. 2). Lee et al. (1990) suggested that hydrophobic sorption of protonated PCP predominates at $pH < 7$, which could be predicted by solution pH and soil organic carbon content. At $pH > 7$, sorption of deprotonated PCP form (PCP^-) and the formation and sorption of neutral ion pairs [e.g., metal cation (M^+) + (PCP^-) = $MPCP^0$] was considered. After HA amendment, pH value of all the soils was lower than 7.0. In this case, SOM and added HA play important roles in retention of PCP.

Peat is an inexpensive and easily available adsorbent. It is used extensively with very good results as plant growth media (Herrera et al., 2008). Tanjore and Viraraghavan (1997) applied peat for removal of PCP from acidic aqueous media. In this study, $CaCl_2$ extractable PCP was reduced to 8.30, 16.2, 39.2 and 11.5% of total PCP for S1, S2, S3 and F soils amended with HA, respectively. However, no significant change of DCM extractable PCP was found after peat amendment (Fig. 2).

Char is one of the high surface area carbonaceous materials. It has high sorption capacity not only for HOCs (Cornelissen et al., 2005), but also for anion (Daifullah et al., 2007). Mukherjee et al. (2007) used char to sorb phenolic compounds from water over a wide pH range. Among carbonaceous material amendments studied, the most significant changes of PCP distribution patterns were found by char amendment. After char addition, $CaCl_2$ extractable PCP decreased to 10.1, 15.0, 37.0 and 2.14% of total, while the DCM extractable PCP increased significantly ($p < 0.05$) to 29.6, 27.1, 22.2 and 45.0% of total PCP in S1, S2, S3 and F soils, respectively (Fig. 2).

It is assumed that extraction with 0.01 mol/l $CaCl_2$ removes polar PCP and soluble neutral PCP from soil. $CaCl_2$ extractable amount of organic pollutants was regarded as closely related with leaching and bioavailability to organisms (Bergknut et al., 2007), though results obtained by Kelsey et al. (1997) showed that water extraction would cause underestimation of bioavailability. Butanol is suggested to remove the weakly associated fraction of HOCs in soil in a single extraction (White et al., 1999). Liste and Alexander (2002) and Kelsey et al. (1997) proposed that butanol extraction was a feasible method for earthworm accumulation and bacterial mineralization prediction. While several studies have shown that

Fig. 2. Extractable fractions of PCP in soils amended with carbonaceous materials after aging of 7 days using $CaCl_2$, BuOH and DCM as extractants. Error bars represent one standard deviation. Bars with same letter or letters imply no significant difference ($p < 0.05$).

butanol is an exhaustive extractant and largely overestimate microbial mineralization (Reid et al., 2000; Northcott and Jones, 2003). The butanol extractable PCP from unamended S1, S2, S3 and F soils was 55.2, 60.6, 37.6, and 50.9% of total PCP in soil, respectively (Fig. 2). After char, HA and peat amendments, butanol

extractability was not significantly changed for all soils except that butanol extractable PCP increased for soil S1 amended with HA.

Harsh extractants, such as DCM, are generally used to quantify the total amount of HOCs in soil by a single extraction (Macleod and Semple, 2003), which overestimate the contaminant fraction available to soil biota (Hatzinger and Alexander, 1995; Reid et al., 2000). In this study, DCM was used as a final sequential extractant after CaCl_2 and *n*-butanol extractions. It is obvious that after char amendment, PCP extracted by DCM increased ($p < 0.05$) for all soils (Fig. 2). The decrease of CaCl_2 extractable and increase of DCM extractable PCP indicated that a fraction of PCP became more strongly associated with soil after carbonaceous materials addition.

3.3. Effect of carbonaceous material amendments on PCP desorption kinetics

PCP desorption from soil S2 is shown in Fig. 3. The lines obtained by two-compartment first order kinetics fits are included in the graphs. Corresponding desorption rate parameters with 95% confidence intervals are listed in Table 2. The first-order kinetic model provides an acceptable description of PCP desorption from soil with and without amendment, with all R^2 values higher than 0.980. Amendment with char significantly decreased the labile fraction of PCP (ϕ_1 value) from 0.342 to 0.196, and the labile and resistant desorption rate constants were also decreased from 19.1 to 5.86 d^{-1} (k_1), and from 0.113 to 0.012 d^{-1} (k_2), respectively ($p < 0.05$). Similar decreases of k_1 and k_2 values were observed for HA and peat amendments, though ϕ_1 values were not significantly changed as compared to soil without amendment. Such decreases suggested that PCP binding shifted from easy desorption to relatively difficult desorption sites as a result of carbonaceous material addition. This is in conformity with the observations to indicate the impact of carbonaceous material amendments on PCP leaching ability and bioaccumulation by earthworms.

The above results are strongly supported by current knowledge that SOM controls the fate and transport of organic contaminants in soils. Results obtained by van Noort et al. (2003) showed that the rapid desorption rate of HOCs was correlated natively with SOM content. Accordingly, amendments with carbonaceous materials would increase SOM content, resulting in lower desorption rate of labile fraction of PCP. Johnson et al. (2001) found that rates and extents of desorption of HOCs are strong functions of the type of natural organic matter that soil contains. Pignatello and Xing

Table 2

Desorption rate parameters for the biphasic first-order model with 95 % confidence intervals of PCP from soil S2.

Soil	ϕ_1	k_1 (d^{-1})	k_2 (d^{-1})	R^2	N^a	MWSE ^b
Unamended	0.342 ± 0.025	19.1 ± 0.8	0.113 ± 0.009	0.983	36	0.0087
Char	0.196 ± 0.008	5.86 ± 0.06	0.012 ± 0.001	0.986	36	0.0014
HA	0.324 ± 0.014	12.9 ± 1.2	0.058 ± 0.003	0.990	36	0.032
Peat	0.331 ± 0.020	12.5 ± 0.8	0.073 ± 0.006	0.985	36	0.020

^a N : number of data point.

^b MWSE: mean weight square error, calculated as $1/v \sum [(q_{\text{measured}} - q_{\text{model}})^2 / q_{\text{measured}}^2]$, $v = N - 3$.

(1996), and Huang and Weber (1998) hypothesized that rigid parts of the organic matter matrix could be responsible for slow desorption of HOCs. Cornelissen et al. (2005) suggested that the “rigid” or “glassy” parts of SOM is in fact the same as the carbonaceous geosorbents (CG), such as black carbon, char, and kerogen, and thus that sorption to CG probably causes slow desorption. Therefore, addition of char would cause sorption of PCP from SOM to char, thereby resulting in the most pronounced slow desorption. Moreover, char was also regarded as an ideal sorbents for anion (Daifullah et al., 2007), thus it could immobilize deprotonated PCP.

3.4. PCP bioavailability to earthworms in soils

During the accumulation experiments, no mortality was observed. The average weight of earthworms decreased by 12–22%, but no significant weight difference was found for those in soils with and without amendment (data not shown). It is evident from the data presented in Fig. 4 that the bioavailability of PCP to earthworms in char amended soils decreased most significantly ($p < 0.05$), more specifically, values of BAF decreased by factors of 4.0–26.1. Similarly, for HA amended soils, significant reductions of BAF were found for all soils studied except soil S3. For peat amendment, the average BAF values were lower than those without amendment. However, significant reduction ($p < 0.05$) of BAF was only found for soil S2. These results suggested that carbonaceous material amendment reduced PCP bioavailability quickly. Among the amendments described in this study char appeared to be the most promising one. The above results implied that PCP bioavailability is dependent on the properties of soils and the amendments.

Fig. 3. PCP desorption from soil S2 amended with carbonaceous materials (lines fit Eq. (1)).

Fig. 4. Bioaccumulation factors (BAFs) for PCP present in soils amended with carbonaceous materials. Error bars represent one standard deviation. Bars with same letter or letters imply no significant difference ($p < 0.05$).

Fig. 5. Extractable fractions of PCP in soil S2 amended with carbonaceous materials for aging of 250 days using CaCl₂, butanol and DCM as extractants. Error bars represent one standard deviation. Bars with same letter or letters imply no significant difference ($p < 0.05$).

3.5. Long-term effect

When the aging time increased to 250 days, total PCP concentration remained unchanged in soil S2, which showed the negligible biodegradation and volatilization during the incubation. No significant difference ($p > 0.05$) of soil pH was found when compared with those of 7 days incubation.

A comparison of PCP fractionation of 250-day aging treatment (Fig. 5) with that of control indicates that the CaCl₂ extractable PCP decreased significantly ($p < 0.05$) for all amendments. The butanol extractability decreased significantly ($p < 0.05$) for char and HA amendments, but not for peat amendment. An obvious ($p < 0.05$) increase of DCM extractable PCP was found for all amendments. The different PCP fractionation distribution patterns revealed tighter PCP binding with increasing aging time. The average BAF values of 250-day aging were 0.78, 0.60 and 2.29 for char, HA and peat amendments, respectively, which were significantly lower than those of control (3.98) ($p < 0.05$). Results obtained from this experiment demonstrated that the PCP immobilization effect by char, HA and peat amendments is enduring and enhanced as time goes by.

4. Environmental implication

The traditional commonly applied amendments, such as char, HA and peat, are commercially available and cost-effective. As soil amendments have a long history, the benefit of char, HA and peat amendment to soil, soil microbes and plants had been demonstrated extensively under greenhouse and field conditions (Mbagwu and Piccolo, 1989; Govindasmy and Chandrasekaran, 1992; Koelmans et al., 2006; Herrera et al., 2008). Dercová et al. (2006) demonstrated that organic amendments, such as sewage sludge or organomineral complex have the advantages of retardation of contaminant release, and enhancement of contaminant biodegradation. Results of Zhang et al. (2005) showed that biodegradation might be nutritionally simulated for severely contaminated soils in the presence of char, but pollutants would remain highly persistent in the soils due to their increased sorption as a result of char amendment. Results of the present study suggested that soil amended with various types of carbonaceous materials provides a potential strategy for *in situ* environmental remediation, restoration, and stabilization applications. Appropriate selection of amendment materials is a key to realize the remediation potential. Different kinds of organic amendments

described here and other alternatives provide a wide choice. Moreover, char, HA and peat are able to immobilize heavy metals in soil effectively (Pichtel and Bradway, 2008; Chen et al., 2006; Clemente and Bernal, 2006). Therefore, it is reasonable to regard them as a promising amendment technology, which may simultaneously stabilize heavy metals and organic pollutants in soil.

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References

- Bergknut, M., Sehlén, E., Lundstedt, S., Andersson, P.L., Haglund, P., Tysklind, M., 2007. Comparison of techniques for estimating PAH bioavailability: uptake in *Eisenia fetida*, passive samplers and leaching using various solvents and additives. *Environmental Pollution* 145, 154–160.
- Boopathy, R., 2000. Factors limiting bioremediation technologies. *Bioresource Technology* 74, 63–67.
- Boyd, S.A., Mikesell, M.D., Lee, J., 1989. Chlorophenols in Soil. Soil Science Society of America, Madison.
- Braida, W.J., Pignatello, J.J., Lu, Y.F., Ravikovitch, P.I., Neimark, A.V., Xing, B.S., 2003. Sorption hysteresis of benzene in charcoal particles. *Environmental Science & Technology* 37, 409–417.
- Chen, B., Zhu, L., Zhu, J., Xing, B., 2005. Configurations of the bentonite-sorbed myristylpyridinium cation and their influences on the uptake of organic compounds. *Environmental Science & Technology* 39, 6093–6100.
- Chen, S.B., Zhu, Y.G., Ma, Y.B., McKay, G., 2006. Effect of bone char application on Pb bioavailability in a Pb-contaminated soil. *Environmental Pollution* 139, 433–439.
- Cho, Y.-M., Smithenry, D.W., Ghosh, U., Kennedy, A.J., Millward, R.N., Bridges, T.S., Luthy, R.G., 2007. Field methods for amending marine sediment with activated carbon and assessing treatment effectiveness. *Marine Environmental Research* 64, 541–555.
- Clemente, R., Bernal, M.P., 2006. Fractionation of heavy metals and distribution of organic carbon in two contaminated soils amended with humic acids. *Chemosphere* 64, 1264–1273.
- Conte, P., Agretto, A., Spaccini, R., Piccolo, A., 2005. Soil remediation: humic acids as natural surfactants in the washings of highly contaminated soils. *Environmental Pollution* 135, 515–522.
- Cornelissen, G., Gustafsson, Ö., Bucheli, T.D., Jonker, M.T.O., Koelmans, A.A., van Noort, P.C.M., 2005. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environmental Science & Technology* 39, 6881–6895.
- Daifullah, A.A.M., Yakout, S.M., Elreedy, S.A., 2007. Adsorption of fluoride in aqueous solutions using KMnO₄-modified activated carbon derived from steam pyrolysis of rice straw. *Journal of Hazardous Materials* 147, 633–643.
- Davies, N.A., Edwards, P.A., Lawrence, M.A.M., Taylor, M.G., Simkiss, K., 1999. Influence of particle surfaces on the bioavailability to different species of 2,4-dichlorophenol and pentachlorophenol. *Environmental Science & Technology* 33, 2465–2468.
- Dercová, K., Sejaková, Z., Skokánová, M., Baranciková, G., Makovniková, J., 2006. Potential use of organomineral complex (OMC) for bioremediation of pentachlorophenol (PCP) in soil. *International Biodeterioration & Biodegradation* 58, 248–253.
- Díaz-Flores, P.E., Leyva-Ramos, R., Guerrero-Coronado, R.M., Mendoza-Barrón, J., 2006. Adsorption of pentachlorophenol from aqueous solution onto activated carbon fiber. *Industrial & Engineering Chemistry Research* 45, 330–336.
- Govindasmy, R., Chandrasekaran, S., 1992. Effect of humic acids on the growth, yield and nutrient content of sugarcane. *The Science of the Total Environment* 117–118, 575–581.
- Hatzinger, P.B., Alexander, M., 1995. Effect of aging of chemicals in soil on their biodegradability and extractability. *Environmental Science & Technology* 29, 537–545.
- Herrera, F., Castillo, J.E., Chica, A.F., Lopez Bellido, L., 2008. Use of municipal solid waste compost (MSWC) as a growing medium in the nursery production of tomato plants. *Bioresource Technology* 99, 287–296.
- Hu, X.Y., Wen, B., Shan, X.Q., Zhang, S.Z., 2005. Bioavailability of pentachlorophenol to earthworms (*Eisenia fetida*) in artificially contaminated soils. *Journal of Environmental Science and Health, Part A* 40, 1905–1916.
- Huang, W.L., Weber, W.J., 1998. A distributed reactivity model for sorption by soils and sediments. 11. Slow concentration dependent sorption rates. *Environmental Science & Technology* 32, 3549–3555.
- Johnson, M.D., Keinath, T.M., Weber, W.J., 2001. A distributed reactivity model for sorption by soils and sediments. 14. Characterization and modeling of phenanthrene desorption rates. *Environmental Science & Technology* 35, 1688–1695.
- Kelsey, J.W., Kottler, B.D., Alexander, M., 1997. Selective chemical extractants to predict bioavailability of soil-aged organic chemicals. *Environmental Science & Technology* 31, 214–217.

- Koelmans, A.A., Jonker, M.T.O., Cornelissen, G., Bucheli, T.D., van Noort, P.C.M., Gustafsson, Ö., 2006. Black carbon: the reverse of its dark side. *Chemosphere* 63, 365–377.
- Lee, L.S., Rao, P.S.C., Nkedi-Kizza, P., Delfino, J.J., 1990. Influence of solvent and sorbent characteristics on distribution of pentachlorophenol in octanol–water and soil–water systems. *Environmental Science & Technology* 24, 654–661.
- Liste, H.-H., Alexander, M., 2002. Butanol extraction to predict bioavailability of PAHs in soil. *Chemosphere* 46, 1011–1017.
- Macleod, C.J.A., Semple, K.T., 2003. Sequential extraction of low concentrations of pyrene and formation of non-extractable residues in sterile and non-sterile soils. *Soil Biology and Biochemistry* 35, 1443–1450.
- Mbagwu, J.S.C., Piccolo, A., 1989. Changes in soil aggregate stability induced by amendment with humic substances. *Soil Technology* 2, 49–57.
- Millward, R.N., Bridges, T.S., Ghosh, U., Zimmerman, J.R., Luthy, R.G., 2005. Addition of activated carbon to sediments to reduce PCB bioaccumulation by a polychaete (*Neanthes arenaceodentata*) and an amphipod (*Leptocheirus plumulosus*). *Environmental Science & Technology* 39, 2880–2887.
- Mukherjee, S., Kumar, S., Misra, A.K., Fan, M.H., 2007. Removal of phenols from water environment by activated carbon, bagasse ash and wood charcoal. *Chemical Engineering Journal* 129, 133–142.
- Nelson, D.W., Sommers, L.E., 1982. Methods of soil analysis: part 2. In: Page, A.L. (Ed.), *Total Carbon, Organic Carbon and Organic Matter*, second ed. ASA and SSSA, Madison, WI, pp. 539–579.
- Northcott, G.L., Jones, K.C., 2001. Partitioning, extractability, and formation of nonextractable PAH residues in soil. 2. Effects on compound dissolution behavior. *Environmental Science & Technology* 35, 1111–1117.
- Northcott, G.L., Jones, K.C., 2003. Validation of procedures to quantify non-extractable polycyclic aromatic hydrocarbon residues in soil. *Journal of Environmental Quality* 32, 571–582.
- van Noort, P.C.M., Cornelissen, G., ten Hulscher, T.E.M., Vrind, B.A., Rigterink, H., Belfroid, A., 2003. Slow and very slow desorption of organic compounds from sediment: influence of sorbate planarity. *Water Research* 37, 2317–2322.
- Pichtel, J., Bradway, D.J., 2008. Conventional crops and organic amendments for Pb, Cd and Zn treatment at a severely contaminated site. *Bioresource Technology* 99, 1242–1251.
- Pignatello, J.J., Xing, B.S., 1996. Mechanisms of slow sorption of organic chemicals to natural particles. *Environmental Science & Technology* 30, 1–11.
- Reid, B.J., Stokes, J.D., Jones, K.C., Semple, K.T., 2000. Nonexhaustive cyclodextrin-based extraction technique for the evaluation of PAH bioavailability. *Environmental Science & Technology* 34, 3174–3179.
- Skrbic, B., Durisic-Mladenovic, N., 2007. Principal component analysis for soil contamination with organochlorine compounds. *Chemosphere* 68, 2144–2152.
- Stapleton, M.G., Sparks, D.L., Dentel, S.K., 1994. Sorption of pentachlorophenol to HDTMA-clay as a function of ionic-strength and pH. *Environmental Science & Technology* 28, 2330–2335.
- Tang, J., Petersen, E.J., Huang, Q., Weber Jr., W.J., 2007. Development of engineered natural organic sorbents for environmental applications: 3. Reducing PAH mobility and bioavailability in contaminated soil and sediment systems. *Environmental Science & Technology* 41, 2901–2907.
- Tang, J., Weber, W.J., 2006. Development of engineered natural organic sorbents for environmental applications. 2. Sorption characteristics and capacities with respect to phenanthrene. *Environmental Science & Technology* 40, 1657–1663.
- Tanjore, S., Viraraghavan, T., 1997. Effect of oxygen on the adsorption of pentachlorophenol by peat from water. *Water Air and Soil Pollution* 100, 151–162.
- Weber, W.J., Tang, J., Huang, Q., 2006. Development of engineered natural organic sorbents for environmental applications. 1. Materials, approaches, and characterizations. *Environmental Science & Technology* 40, 1650–1656.
- Wen, B., Zhang, J.J., Zhang, S.Z., Shan, X.Q., Khan, S.U., Xing, B.S., 2007. Phenanthrene sorption to soil humic acid and different humin fractions. *Environmental Science & Technology* 41, 3165–3171.
- White, J.C., Hunter, M., Nam, K.P., Pignatello, J.J., Alexander, M., 1999. Correlation between biological and physical availabilities of phenanthrene in soils and soil humin in aging experiments. *Environmental Toxicology and Chemistry* 18, 1720–1727.
- Zhang, P., Sheng, G., Feng, Y., Miller, D., 2005. Role of wheat-residue-derived char in the biodegradation of benzonitrile in soil: nutritional stimulation versus adsorptive inhibition. *Environmental Science & Technology* 39, 5442–5448.
- Zimmerman, J.R., Ghosh, U., Millward, R.N., Bridges, T.S., Luthy, R.G., 2004. Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments: physicochemical tests. *Environmental Science & Technology* 38, 5458–5464.