



Influence of organic amendments on the sorption of pentachlorophenol on soils

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Received 22 April 2008; revised 22 May 2008; accepted 28 May 2008

Abstract

The influence of pH on the sorption of pentachlorophenol (PCP) onto three organic amendments, char, humic acid (HA) and peat, and the effect of organic amendments on PCP sorption to three kinds of soils were evaluated. The sorption of PCP on these sorbents fitted the Freundlich model well, suggesting that PCP sorption isotherms were nonlinear with exponential coefficient (N) value lower than 1. The PCP sorption capacity on three organic amendments and the N values increased with decreasing pH. The sorption capacities were in the order: char > HA > peat. Organic amendments resulted in an enhancement of sorption capacities of soils. The N values of PCP sorption on soils were decreased by char amendment and increased by HA and peat amendments. This study demonstrated that application of traditional organic amendments led to the enhancement of PCP sorption by soils. This information may aid both in predicting environmental fates of hydrophobic ionizable organic compounds and in developing remediation strategies for them.

Key words: sorption; pentachlorophenol; char; peat; humic acid; pH

DOI: 10.1016/S1001-0742(08)62294-9

Introduction

Soil is regarded as the ultimate sink for large number of organic contaminants in terrestrial (Davies *et al.*, 1999; Skrbic and Durisic-Mladenovic, 2007). Various forms of natural organic matter (NOM) associated with soils serve as dominant “compartments” for sorption and sequestration of hydrophobic organic chemicals (HOCs). The sorption and desorption behaviors of HOCs to different NOMs vary markedly. The leaching behaviors and bioavailability of organic pollutants in soil are affected mainly by soil organic matter concentration and composition (Hatzinger and Alexander, 1995; Dercova *et al.*, 2006).

Organic amendment is a common practice in agriculture to improve the physical and chemical properties of soils at low cost. It increases soil organic matter content and offers many benefits, such as improvement of soil aeration, water infiltration, nutrient-holding capacity, and adjustment of soil pH (Mbagwu and Piccolo, 1989). Most of the traditional organic amendments, such as peat, char, and humic acid, are naturally occurred and environmentally friendly. Therefore, organic amendment is regarded as one of the most suitable technologies for the sustainable agriculture.

In addition to the soil property modification, organic amendment also affects the sorption of organic contaminants. The amendment of both natural and engineered natural materials significantly increases the sorption and

decreases the extractability and bioavailability of polycyclic aromatic hydrocarbons (PAHs) from contaminated soil (Tang and Weber, 2006; Weber *et al.*, 2006; Tang *et al.*, 2007). Amendment with both humic acid (HA) and peat was reported to increase the adsorption and decrease leaching of ethametsulfuron-methyl in soils (Si *et al.*, 2006). However, Hernández-Soriano *et al.* (2007) found that HA could induce an adsorption increase of diazinon, dimethoate, malathion, and methidathion, while peat did not affect pesticide adsorption significantly. Char has been proven to be a highly effective sorbent for organic contaminants (Cornelissen *et al.*, 2004; Zhu *et al.*, 2005). Sheng *et al.* (2005) found that wheat char could adsorb diuron, bromoxynil, and ametryne effectively. Therefore, char could significantly influence the environmental fate of pesticides.

Pentachlorophenol (PCP) and its salt have been worldwide applied for more than 50 years as a biocide in both industry and agriculture, which led to serious soil contamination. In China, PCP was used extensively from 1960s until 2000 as a major molluskicide to kill *Oncomelania hupensis*, which is the intermediate host of schistosomes (Ge *et al.*, 2007). Thus, it is interesting to predict the environmental fate of PCP and to develop potential remediation technologies for PCP contaminated soils. The aim of this study is to evaluate the influence of pH on PCP sorption onto three common organic amendments including char, HA, and peat, and the sorption enhancement of PCP onto three different kinds of soils amended with char, HA or peat. The related mechanisms were also discussed.

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1 Methods

1.1 Chemicals and materials

Reference standard of PCP was purchased from AccuStandard Inc. (USA) and stored in sealed volumetric flasks (1.0 mg/mL in methanol and preserved at 4°C). Methanol (Fisher, USA) was of HPLC grade. Calcium chloride dehydrate (Beijing Chemical Reagents Company, China) were of analytical grade. Sodium azide (Dongyang Tianyu Chemical Ltd., Zhejiang, China) was of chemical grade. Acetic acid (Siuopharm Chemical Reagent Co., Ltd., Zhejiang, China) was of guaranteed grade.

Stock solution of PCP was mixed with background electrolyte (0.01 mol/L CaCl₂ containing 100 mg/L NaN₃) to make an initial aqueous concentration in the range of 20–8000 µg/L for sorption experiments.

Three cultivated soils were collected from Jiangxi Province, South China (Jiangxi soil); Beijing, North China (Beijing soil); Hebei Province, North China (Hebei soil). The soils were air-dried, ground, and passed through a 60-mesh sieve to remove stones, plant roots, and other large particles. Soil pH was measured in 0.01 mol/L CaCl₂ solution 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 particle size distribution was measured by the Beijing Forest University Soil Testing Laboratory using pipet method (Day, 1965) (Table 1).

Three organic amendments including char, peat, and HA, were used. Char was prepared by atmospheric pyrolysis according to the method by Braida *et al.* (2003). Willow-wood shavings were placed in a 15-cm watch-glass-covered crucible and heated at 400°C for 2 h. Peat 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). The obtained char, HA, and peat were dried, pulverized gently in a mortar to pass through a 0.25-mm sieve, and stored in a glass vial at room temperature.

Char, HA, and peat were added into three soils, respectively, at a ratio of exact 2% soil (W/W) and mixed thoroughly on a rotary shaker for 24 h for sorption experiments.

1.2 Characteristics of char, HA, and peat

The elemental compositions (C, H, N) of char, HA, and peat were determined with a high-temperature combustion method (PE 2400 SERIES II analyzer, Pekin-Elmer, Inc., USA). Oxygen content was calculated by the mass difference. Ash content was determined by combustion of char, HA, and peat at 800°C for 4 h. Surface area of char

was measured by N₂-BET method (ASAP 2010 surface area analyzer, Micromeritics Instrument Corp., USA). pH values of char, HA, and peat were measured in 0.01 mol/L CaCl₂ solution using a sample/solution ratio of 1:5 (W/V).

Char, HA, and peat were subjected to ¹³C NMR analysis to obtain their chemical group distribution. Solid-state ¹³C NMR data were acquired using a cross-polarization and magic angle spinning (CPMAS) on a 300-MHz NMR spectrometer (Varian, USA). Spectra were acquired at a frequency of 75 MHz, for ¹³CP MAS spinning rate of 13 kHz, contact time of 2 ms, 5 s recycle delay. The number of scans was ranged from 5000 to 10000 per sample.

1.3 Sorption isotherms

A batch equilibration technique with 10.0 mg of each organic amendment (char, HA, or peat) or 0.500 g soil as sorbent and 30 mL solution were utilized for all sorption experiments. A mixture of 0.01 mol/L CaCl₂ and 100 mg/L NaN₃ was used as background electrolyte in all sorption experiments to prevent any biological degradation of PCP. In brief, 40-mL glass tubes with Teflon-lined caps were used as batch reactors. Our preliminary tests indicated that apparent equilibrium was reached before 14 d for char and char amended soils, and 4 d for other sorbents. The initial aqueous-phase PCP concentrations (C₀) were selected to yield a set of isotherm data for each sample that distributed evenly on a (q_e vs. C_e) plot to span approximately 2 orders of magnitude in aqueous-phase solute equilibrium concentrations (C_e). The amount of sample in each tube corresponded to a sample-to-solution ratio that would result in 30%–85% uptake of PCP. Reactors filled with sorbent and initial aqueous solution were mixed at 100 r/min, (20 ± 1)°C for 14 d in the dark. The pH was adjusted to 4.0, 6.0 and 8.0, respectively with 0.1 mol/L HCl or NaOH solution. During the shaking, the pH values were measured at certain intervals and readjusted if necessary. At the end of the shaking period, the pH of suspension was measured again. After centrifugation at 1667 ×g for 20 min, PCP in the supernatant solution was determined using high performance liquid chromatography (HPLC).

Control reactors prepared similarly but no sorbent were run simultaneously to assess the loss of PCP. Results of triplicate sorption at each C₀ level showed that average solution-phase concentrations of each solute were consistently within 98%–102% of the respective initial concentration of the same solution, indicating that microbial degradation and volatilization during the sorption and the uptake to the glass walls were negligible. Hence, no correction was made during sorption experiments.

1.4 Determination of pentachlorophenol

The concentrations of PCP were determined using an Agilent 1200 series HPLC with a UV detector and a C18 reversed-phase column (250 × 4.6 mm, 5 µm). Methanol and 1% acetic acid (95:5, V/V) were used as a mobile phase at a flow rate of 1 mL/min. The UV wavelength for detection of PCP was set at 220 nm. Under such HPLC conditions, PCP showed a single peak with a retention time of 5.2 min. The relative standard deviation (RSD) of

Table 1 Characteristics of soils

Soil	Sand (%)	Silt (%)	Clay (%)	pH	Organic matter (%)
Hebei	13.7	59.0	27.3	7.15	4.53
Jiangxi	20.3	47.4	32.3	5.65	1.53
Beijing	37.6	51.6	10.8	7.73	1.35

triplicate determinations were less than 4.8%.

1.5 Data analysis

The data reported are averages for triplicate measurement. The amounts of PCP adsorbed were determined by mass differences between the initial and final equilibrium concentrations. The experimental data were fitted by Freundlich model (Eq. (1)):

$$q_e = K_F C_e^N \quad (1)$$

where, q_e (mg/kg) is the PCP sorbed concentration on sorbents, C_e (mg/L) is the equilibrium concentration of PCP in the aqueous phase, K_F ((mg/kg)/(mg/L)^{*N*}) is the affinity coefficient and N is an exponential coefficient. The higher the K_F , the higher the sorption capacity of a sorbent; while the lower the N value, the more nonlinear is an isotherm. Both K_F and N were determined by regression of the experimental data.

The concentration dependent sorption coefficient (K_d) was calculated based on the following Eq. (2).

$$K_d = K_F C_e^{N-1} \quad (2)$$

where, K_d is the concentration rate of the sorbed PCP on the solid phase to that on the aqueous phase.

The concentration dependent organic carbon-normalized sorption coefficient K_{OC} (L/kg OC) was calculated based on the following Eq. (3).

$$K_{OC} = K_{FOC} C_e^{N-1} \quad (3)$$

where, the organic carbon-normalized sorption coefficient (K_{FOC}) was calculated by dividing K_F by the respective fraction of organic carbon (F_{OC}). The values of K_{OC} can be used to denote directly the sorption characteristics of sorbents.

Statistical analyses were conducted with the software origin 7.5 for Windows (OriginLab Corporation, USA). Parameter sets for Eq. (1) were optimized by nonlinear regression at 95% confidence. The values including soil pH, total concentrations of PCP in aqueous solutions, organic amendments, soils and organic amended soils are reported as mean \pm standard error.

2 Results and discussion

2.1 Elemental compositions, ash contents and pH values of char, HA, and peat

Elemental compositions of three organic amendments and surface area of char are shown in Table 2. Ash contents

were lower than 10% for all amendments. The H/C ratios followed the order: char < HA < peat. A higher H/C ratio may suggest a higher degree of aliphaticity. The polarity (N+O)/C was found to be the highest for peat and the lowest for char. A lower (N+O)/C ratio suggests a lower polar-group content in char, reflecting a higher hydrophobicity. The pH order was: HA < peat < char.

2.2 ¹³C NMR spectra of organic amendments

The ¹³C CPMAS NMR spectra and integration results of char, HA, and peat are shown in Fig. 1 and Table 3. The spectra can be quantified by integrating the regions as follows: alkyl-C (0–50 ppm), O-alkyl-C (predominantly carbohydrates, 50–110 ppm), aromatic-C (110–160 ppm), carboxylic- and amide-C (160–190 ppm), and ketonic/aldehyde-C (190–220 ppm). The percentage of polar organic carbon (POC) was calculated as the combined fractions of 50–110 and 140–220 ppm regions of NMR spectra (Wen *et al.*, 2007).

As shown in Table 3, the differences exist among carbon-type distributions in these amendments. Peat had the highest O-alkyl carbon content (50–110 ppm), while char had the highest aromatic carbon content (110–165 ppm). Overall, the aliphatic carbon contents increased in the order: char < HA < peat, consisting with the increase in H/C ratio. POC were in the order: peat > HA > char, which is in line with the results of elemental composition (Table 2).

2.3 Effect of pH on the sorption of PCP onto char, HA, and peat

Although the solution pH values were adjusted in the beginning of experiments and readjusted during sorption, final pH values were affected by the pH of organic

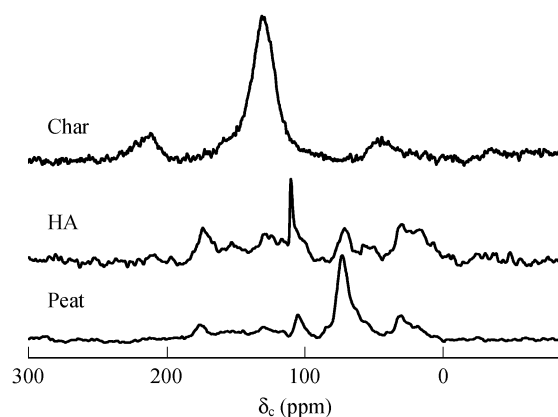


Fig. 1 CPMAS ¹³C NMR spectra of organic amendments.

Table 2 Elemental compositions, atomic ratios, ash contents, pH, and surface area of char, HA, and peat

Sample	Elemental composition (wt.%)			Atomic ratio			Ash (wt.%)	pH	SA (m ² /g)
	C	H	N	H/C	O/C	(N+O)/C			
Char	72.88	3.17	0.55	0.52	0.16	0.17	7.96	7.53	292.3
HA	51.13	5.62	2.39	1.32	0.59	0.63	0.92	2.87	0.78
Peat	45.32	6.05	1.05	1.6	0.73	0.75	3.53	4.23	ND

H/C: atomic ratio of hydrogen to carbon; O/C: atomic ratio of oxygen to carbon; (N+O)/C: atomic ratio of sum of nitrogen and oxygen to carbon. SA: surface area, determined by N₂-BET method. ND: not determined.

Table 3 Integration results of solid-state ^{13}C NMR spectra and ratios of the sum of aliphatic to aromatic peak of char, HA, or peat

	Distribution of C chemical shift (%)						Aliphaticity	POC (%)
	Alkyl-C (0–50 ppm)	O-alkyl-C (50–110 ppm)	Aromatic-C (110–140 ppm)	O-aryl-C (140–165 ppm)	Carboxyl-C (165–190 ppm)	Carbonyl-C (190–220 ppm)		
Char	10.4	7.95	57.5	13.2	2.56	8.39	0.259	32.1
HA	27.1	27.1	19.4	11.4	10.1	4.9	1.76	53.5
Peat	18.5	45.9	12.4	9.12	8.83	5.3	2.99	69.1

Aliphaticity = aliphatic-C (0–110 ppm)/aromatic-C (110–165 ppm). POC: percentage of polar organic carbon, was calculated from the peak areas listed above with an equation as $\text{POC} = (\text{O-alkyl-C} + \text{O-aryl-C} + \text{carboxyl-C} + \text{carbonyl-C}) / (\text{alkyl-C} + \text{O-alkyl-C} + \text{aromatic-C} + \text{O-aryl-C} + \text{carboxyl-C} + \text{carbonyl-C}) \times 100\%$.

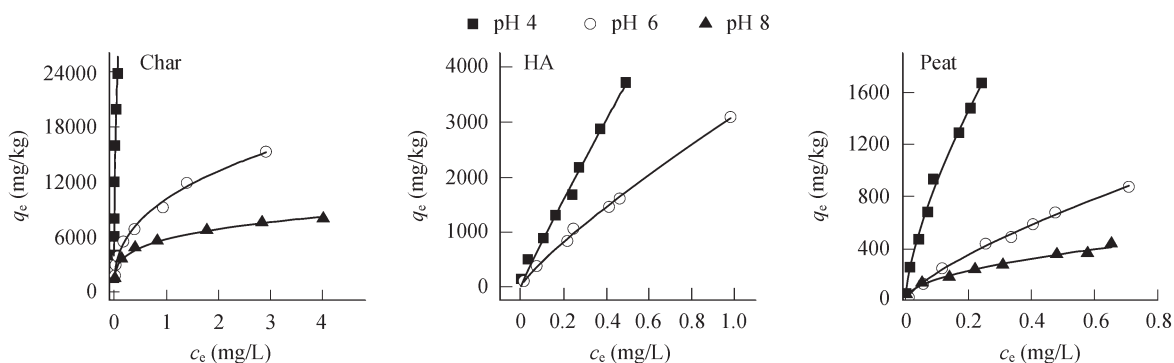
amendments. Sorption of PCP onto HA at pH 8 was not applicable because it led to substantial redissolution of HA (> 40%).

PCP sorption isotherms for the char, HA, and peat under initial pH 4, 6, and 8 fit Freundlich model well (Fig. 2), with all the correlation coefficients higher than 0.99. The resulting model parameters, along with their standard errors, and the calculated in K_{OC} values at C_e of 0.2 and 2.0 mg/L are presented in Table 4. K_F ranged from 5710 to 79948, 3114 to 7164, and 507 to 4346 for char, HA, and peat, respectively. Concentration-dependent organic carbon-normalized sorption coefficients K_{OC} at $C_e = 0.2$ and 2.0 mg/L were employed to compare the sorption capacity because the units of K_{FOC} were different as a result of nonlinearity. The K_{OC} values of char were the highest among the amendments studied. The K_{OC} of all amendments decreased with increasing initial pH.

PCP is a hydrophobic weak organic acid ($\text{p}K_a = 4.75$) and exists as either a neutral or an ionized species. The neutral species represents more than 99% of all PCP when the solution pH is below 2, whereas more than 95% of all

PCP is present as the anion when the pH is above 6 (Diaz-Flores *et al.*, 2006). The neutral form of PCP is strongly hydrophobic with a low aqueous solubility (Stapleton *et al.*, 1994). Shimizu *et al.* (1992) concluded that PCP sorption coefficients of ionized species were smaller than that of non-ionized species. Thus the species change could explain the decrease in K_{OC} values of PCP from pH 4 to 6. When pH increased from 6 to 8, the surfaces of char, peat, and HA became more negative, hence more pentachlorophenolate anions were repelled from the surfaces (Moreno-Castilla, 1995; Diaz-Flores *et al.*, 2006). In addition, HA and peat may be dissociated partially at higher pH, resulting in the increases of dissolved organic matter contents and decreases of PCP sorption (Paaso *et al.*, 2002).

All sorption isotherms of PCP onto sorbents were non-linear, as evidence of N values ranged from 0.26 to 0.94. N value decreased with increasing initial pH. N value could be taken as an index of site energy distribution (Weber *et al.*, 1992). Smaller N values represent more heterogeneous sorption sites in nature. DiVincenzo and Sparks

**Fig. 2** Sorption isotherms of PCP onto char, HA, and peat at different initial pH.**Table 4** Freundlich model sorption parameters and equilibrium pH for sorption of PCP onto char, HA, and peat

Sorbent	pH		R^2	Freundlich		K_{FOC}	K_d		K_{OC}	
	Initial	Final		K_F	N		$C_e = 0.2 \text{ mg/L}$	$C_e = 2.0 \text{ mg/L}$	$C_e = 0.2 \text{ mg/L}$	$C_e = 2.0 \text{ mg/L}$
Char	4.00	4.38 ± 0.06	0.918	79948 ± 18099	0.44 ± 0.03	109698	197951	54121	271614	74239
	6.00	6.94 ± 0.09	0.994	10096 ± 1689	0.38 ± 0.02	13853	27294	6579	37451	9027
	8.00	7.39 ± 0.17	0.986	5701 ± 1209	0.26 ± 0.02	7823	18791	3411	25784	4680
HA	4.00	4.00 ± 0.15	0.990	7164 ± 4809	0.94 ± 0.04	14012	7903	6867	15456	13431
	6.00	5.17 ± 0.06	0.998	3114 ± 50	0.83 ± 0.02	6091	4069	2775	7957	5428
	8.00				NA					
Peat	4.00	4.13 ± 0.05	0.994	4346 ± 265	0.68 ± 0.03	9590	7303	3476	16114	7670
	6.00	5.94 ± 0.07	0.997	1132 ± 26	0.72 ± 0.02	2498	1764	935	3894	2063
	8.00	6.26 ± 0.13	0.983	507 ± 21	0.49 ± 0.04	1119	1150	357	2537	787

NA: not applicable.

(2001) suggested that neutral form of PCP partitioned by hydrophobically binding to the soil with linear sorption isotherm, while the charged form sorbed by a more specific exothermic adsorption reaction with N value lower than 1. Char is a kind of high-surface-area carbonaceous material (HSACM) that has showed high sorption capacity and sorption isotherm nonlinearity for HOCs (Cornelissen *et al.*, 2005). The sorption of HOCs to chars is dominated by adsorptive pore-filling processes (Nguyen *et al.*, 2007). Several authors (Jung *et al.*, 2001; El-Sheikh *et al.*, 2004; Diaz-Flores *et al.*, 2006) have reported that π - π interactions control the adsorption of both neutral and anion forms of phenol and chlorophenols on granular activated carbon. This could explain the highest K_{OC} values and the lowest N values of char.

Chiou *et al.* (2000) compared the sorption of neutral dichlorophenol (DCP) on peat and HA extracted from peat. Both sorption isotherms showed distinct nonlinearity. They deemed that additional specific interactions with the active groups of sorbents are responsible for the obviously non-linear sorption of polar solutes. However, Moreno-Castilla (2004) suggested that phenol and water can compete to form H-bonds with surface active groups, such as carboxyl groups. In this competition water molecules are preferentially bound by H-bonds. Accordingly, the direct interactions between PCP and active groups of sorbents would be ignored. Wen *et al.* (2007) found that HOC sorption nonlinearity index N value was negatively correlated with the polarity of sorbents, suggesting the importance of polarity in the sorption isotherm nonlinearity. The polarity

of peat was higher than that of HA (Tables 2 and 3), which was assumed to result in the relatively low N value of peat.

2.4 Sorption of PCP on unamended and char, HA, and peat amended soils

Figure 3 shows the PCP sorption isotherms from water by unamended and organic amended soils. All the sorption isotherms fit the Freundlich model well, with the correlation coefficients higher than 0.99 (Table 5). Effects of char, HA, and peat on sorption pH were measured because sorption of PCP was affected by pH. Amendment with HA lowered soil solution pH by 0.14, 0.26, and 0.24 units for Hebei, Jiangxi, and Beijing soils, respectively, while amendment with char increased solution pH by 0.35 and 0.62 units for Hebei and Jiangxi soils, respectively. No significant change of sorption pH was detected for all soils amended with peat and Beijing soil amended with char. Overall, the sorption pH was in the range of 5.36–7.63, and PCP was present as anionic form predominantly.

For unamended soils, the K_d values followed the order Hebei > Jiangxi > Beijing. The N values were Jiangxi > Beijing \geq Hebei. Fingler *et al.* (2004) found that the sorption of predominantly ionized chlorophenols increased linearly with increasing sorbent organic-matter content and decreased with increasing sorbent pH. Accordingly, the highest organic matter content of Hebei soil was responsible for the highest K_d value; the lowest organic matter content and the highest soil solution pH value resulted in the lowest K_d value of Beijing soil.

Amendment with char, HA, and peat significantly

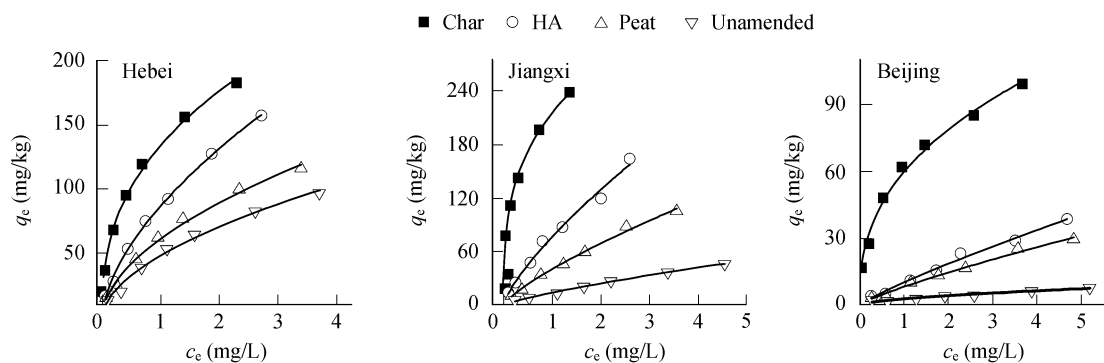


Fig. 3 Sorption isotherms of PCP onto three soils amended and unamended with organic amendments. The symbols denote experimental data points, and the lines are the Freundlich model fittings.

Table 5 Freundlich model sorption parameters and equilibrium pH for sorption of PCP on unamended and amended soils

Soil	F_{OC} (%)	Equilibrium pH	Freundlich			K_d		
			R^2	K_F	N	$C_e = 0.2$ mg/L	$C_e = 2.0$ mg/L	
Hebei	Char-amended	4.04	7.36 ± 0.06	0.984	132.0 ± 3.8	0.43 ± 0.03	330	88.9
	HA-amended	3.60	6.87 ± 0.02	0.998	87.0 ± 1.2	0.60 ± 0.02	166	65.9
	Peat-amended	3.48	7.18 ± 0.10	0.990	61.6 ± 1.8	0.54 ± 0.03	129	44.8
	Unamended	2.63	7.01 ± 0.08	0.992	48.6 ± 1.5	0.55 ± 0.03	100	35.6
Jiangxi	Char-amended	2.33	6.24 ± 0.12	0.988	217 ± 18	0.43 ± 0.08	543	147
	HA-amended	1.90	5.36 ± 0.03	0.988	77.0 ± 3.1	0.75 ± 0.05	115	64.8
	Peat-amended	1.78	5.71 ± 0.09	0.994	40.7 ± 1.5	0.77 ± 0.04	58.9	34.7
	Unamended	0.89	5.62 ± 0.05	0.996	14.3 ± 0.5	0.78 ± 0.03	20.4	12.3
Beijing	Char-amended	2.22	7.63 ± 0.06	0.992	59.7 ± 1.3	0.40 ± 0.02	157	39.4
	HA-amended	1.79	7.32 ± 0.07	0.989	10.3 ± 0.7	0.86 ± 0.06	12.9	9.35
	Peat-amended	1.67	7.40 ± 0.09	0.989	8.31 ± 0.57	0.82 ± 0.05	11.1	7.34
	Unamended	0.78	7.56 ± 0.08	0.985	2.91 ± 0.31	0.59 ± 0.03	5.63	2.19

increased PCP sorption in all soils, which K_F of amended soils were 1.3 to 20.5 times as those of unamended soils. Amendment with char decreased the N value obviously. No significant difference of N value was found for HA and peat amendment, except that increased N values were found for HA and peat amended Beijing soil. Char-amended soil possessed the greatest PCP sorption enhancement for all soils, which was ascribed to the largest sorptive ability of char at both low and high pH. At the equilibrium concentration of 0.2 mg/L, the K_d enhancement factors were 3.3, 26.6, and 27.9 for Hebei, Jiangxi, and Beijing soils, respectively. Hebei soil had the lowest enhancement factor which may be attributed to the relatively high K_d value of unamended Hebei soil. We assume that the sorptive ability of soil for PCP did not change after the addition of char, calculation showed that 2% char contributed to more than 90% of the sorption by char-amended Jiangxi and Beijing soils, and more than 60% of the sorption by char-amended Hebei soil. This indicated the predominance of char over soil in sorbing PCP. However, the sorption was not the simple sum of the respective contributions from soil and char. NOM could sorption on char, leading adsorption site competition and pore blockage (Pignatello *et al.*, 2006). Thus, the adsorption of NOM onto char surface is assumed to reduce char adsorptivity for PCP.

Compared with unamended soils, the K_d enhancement factors of HA-amended soils were 1.7 (Hebei soil), 5.3 (Jiangxi soil), and 2.3 (Beijing soil) at the equilibrium concentration of 0.2 mg/L. These enhancement factors were slightly higher than those of peat-amended soils. Again, assume that the sorptive ability of soil for PCP did not change in the presence of HA, 2% HA contributed 39.8% (Hebei soil), 82.3% (Jiangxi soil), and 56.4% (Beijing soil) to the sorption by HA-amended soils, and 2% peat contributed 22.5%, 65.4%, and 49.3% to the sorption by peat-amended Hebei, Jiangxi, and Beijing soils, respectively. K_d of Jiangxi soil showed the largest enhancement after HA and peat addition when compared with those of Beijing soil, which was related to the high sorption ability of peat and HA at low pH.

3 Conclusions

Sorption abilities of soil organic amendments including char, HA, and peat, highly depend on pH. The sorption intensity of PCP on organic amendments decreased with increasing sorption pH, which not only due to the change of PCP species, but also the increase of the static repulsion between the sorbent surface and anionic PCP. The sorption intensity followed the order: char > HA > peat, and the nonlinearity of isotherms were: char > peat > HA. Addition of HA to soils decreased the pH of all soils, while addition of char increased the pH except that of Beijing soil. Soil organic amendments enhanced the sorption abilities of PCP significantly. The sorption enhancement factor followed the order: char > HA > peat, which was in accord with their sorption abilities. The sorption enhancement factors were soil and amendment

characteristics dependent. These results provided direct evidence that addition of traditional soil amendments could enhance the sorption of PCP. This information may aid both in predicting environmental fates of hydrophobic ionizable organic compounds, and in developing remediation strategies.

Acknowledgments

This work was supported by the Knowledge Innovation Program of the Chinese Academy of Sciences (No. KZCX-1-YW-06-03) and the National Natural Science Foundation of China (No. 40730740).

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