Journal of Hazardous Materials 190 (2011) 474–479

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Impact of black carbon originated from fly ash and soot on the toxicity of pentachlorophenol in sediment

Liping Lou[a,*], Ling Luo[a], Wei Wang[b], Xinhua Xu[a], Jiaai Hou[a], Bei Xun[a], Yingxu Chen[a,**]

[a] *Department of Environmental Engineering, Zhejiang University, Hangzhou, 310029, China*
[b] *Division of Analytical and Environmental Toxicology, Department of Laboratory Medicine and Pathology, University of Alberta, Edmonton, AB, Canada T6G 2G3*

ARTICLE INFO

Article history:
Received 13 October 2010
Received in revised form 18 March 2011
Accepted 21 March 2011
Available online 29 March 2011

Keywords:
Black carbon (BC)
Pentachlorophenol (PCP)
Extractability
Toxicity

ABSTRACT

The widely existing fly ash and soot produced during the process of combustion, which are often known as waste but also an important source of black carbon (BC) in the environment, were treated by HCl and HF solution for this study, and recorded as FC and SC, respectively. A series of experiments were carried out to investigate the toxicity of pentachlorophenol (PCP) in sediment, influence of various BCs in sediment with different contents (0%, 0.5%, 1%, 2%, 5% and 10%) on the extractability and toxicity of PCP (50 mg/kg), and toxicity of various BC in sediment. The results demonstrated that the PCP exposure to wheat seed exhibited a dose-dependent behavior, and the extractability and toxicity of PCP decreased with the increasing content of BC in sediment. The PCP extractable rate was significantly ($P < 0.01$) influenced by the higher content of BCs. Noticeably, each BC had no toxic but stimulative effect on root elongation and early seedling growth. Furthermore, it was found that the inhibitive effect on the extractability and toxicity of PCP and the stimulative effect on root elongation and early seedling growth caused by SC were more evident than FC.

1. Introduction

Black carbon (BC), accounting for approximately 9% of the total organic carbon (TOC) in sediments, originates from incomplete combustion of biomass and fossil fuels [1–4]. It is ubiquitously present in the environment due to its wide-spread production and its chemical and microbiological inertness [5,6]. There is an extensive body of literature in which BC dominated the sorption and desorption of organic pollutants to BC in soil/sediment, such as polychlorinated naphthalenes (PCNs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), octachlorostyrene (OCS), hexachlorobenzene (HCB), hexachlorocyclohexane (HCH), 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT), and some pesticides [6–13]. Furthermore, it has been reported that the addition of biochar in soil/sediment could reduce toxicity/bioavailability of organic contaminants (such as PAHs, PCBs, diuron, chlorpyrifos, pyrethroid, carbofuran, etc.) [6,14–18], but the effect of BC in wastes of fly ash and soot on toxicity of contaminants has received relatively little attention in the environment.

Fly ash, produced during the combustion of coal in the electricity generation process, is mainly collected from thermal power plants and disposed predominantly in landfills [19,20]. A survey about fly ash production and utilization in different countries during 2005 showed that China generated higher production of fly ash (100 million tonnes/year) and utilized lower percentage of fly ash (45%) comparing to other countries except India [19]. Soot, produced as an unwelcome byproduct in many practical combustion systems, usually generates from the exhaust of the diesel engine and has been found to make up a significant fraction (2–20%) of the total carbon in marine sediments [8,21–23]. Emissions of fly ash and soot were known to cause major environmental problems (e.g. contributing to the global warming, carrying carcinogenic compounds and causing serious health risks) [6], because they have been reported to contain toxic elements (as B, Se, Ni, Mo and Cd) [19] and PAHs [22]. However, in recent years, fly ash and soot have been suggested to be important sorbents for organic contaminants in various environments, since they are low cost, ubiquitous, and have strong affinities for organic chemicals [22,24–28]. Moreover, fly ash has been reused for building material and soil amendment [19,24,29], but like soot, it has rarely been applied to reduce the toxicity of organic pollutants in soil/sediment. Consequently, owing to the ubiquity and large mass of BC, it is necessary to investigate the feasibility of applying BC in wastes to reduce the mobility and toxicity of organic pollutants in soil/sediment, and the combined effect between BC and organic contaminants in the environment.

Our former research showed that BC is a supersorbent for contaminants [30], and to provide a basis for the feasibility of applying BC in wastes to control the contaminant of organic pollutants in

---

[*] Corresponding author. Tel.: +86 571 88982502; fax: +86 571 88982502.
[**] Corresponding author.
E-mail addresses: loulp@zju.edu.cn (L. Lou), yxchen@zju.edu.cn (Y. Chen).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.03.073

Table 1
Physical and chemical properties of the tested sediment.

HA	KG (%)	BC	Moisture content (%)	CEC (cmol/kg)	OM (g/kg)	pH	Sand	Silt (%)	Clay
0.57 ± 0.04	1.72 ± 0.13	0.37 ± 0.04	55.01 ± 0.61	10.94 ± 0.22	9.64 ± 0.08	6.76 ± 0.05	7.12 ± 1.6	13.84 ± 1.9	79.04 ± 6.8

soil/sediment, the influence of fly ash and soot on the toxicity and extractability of HOCs was investigated, and the toxicity of fly ash and soot themselves was also studied. In this paper, pentachlorophenol (PCP) was chosen as a representative HOC because of its stable aromatic ring structure and high chlorine content [31–34]. The wheat seed germination, root elongation and early seedling growth were adopted as toxicity of PCP and BC tests according to the U.S. EPA [10]. The water extraction was studied in order to validate the effect of BC on the mobility of PCP. Lastly, the discrepancies between fly ash and soot were also studied.

2. Materials and methods

2.1. Sediment and BC particles

The sediment was obtained with a clam sampler from the Qiantang River. The sampling depth was 1–10 cm from the surface of the sediment. The fresh sediment was air dried, ground, and sieved through a 0.15-mm mesh to remove stones, other particles, etc. A comprehensive procedure consisting of major steps of demineralization, base extraction, and chemical oxidation, was developed in this study to quantify contents of humic acid (HA), kerogen (KG), and BC [13]. Oven-dry moisture content was determined by drying the soils for 48 h at 105 °C [10]. The $NH_4Cl–C_2H_5OH$ method and $K_2Cr_2O_7$ oxidation method were used to determine the cation exchangeable capacity (CEC) and the organic matter content (OM), respectively [35]. Sediment pH was measured in deionized water using a 1:1 (w/v) soil-to-solution ratio [36]. The physico-chemical properties of the sediment are shown in Table 1. Moreover, there was pollution in the sediment, such as PCB (0.0459 mg/kg), Cr (0.0429 mg/kg), Zn (0.1683 mg/kg), Cd (0.0021 mg/kg), and Cu (0.0764 mg/kg), but the sediment did not contain a detectable quantity of PCP [37].

The fly ash, produced during the combustion of coal (at 1400 °C), was collected on electrostatic filters (Hangzhou Thermoelectric Plant, Zhejiang province, China). Soot was purchased from Degussa Company, Germany. To get purified BC, these samples were treated in 2 M HCl and 1 M:1 M HCl–HF solutions, then thoroughly washed with distilled water five times [38,39]. The treated fly ash and soot were oven-dried overnight at 105 °C, and recorded as FC and SC, respectively.

The elemental composition (C, H, and N) of each BC was determined with an Element Analyzer (EA 1110, USA). The Brunauer–Emmerr–Teller (BET) surface area and pore volume of BCs were measured with a 100CX surface area analyzer (Coulter Omnisorp, USA) and calculated by the BET equation and monobuoy cohesion (at $P/P_0 = 0.981$), respectively. The surface acidity and basicity were determined using the Boehm's titration method [30]. The characteristics of FC and SC, determined before, are shown in Table 2.

2.2. Chemicals and seeds

Pentachlorophenol (PCP), with a purity of >98%, was purchased from Sigma Aldrich (China) and prepared to a concentrated stock solution with methanol. A solution consisting of distilled water (pH 7.0 ± 0.1), 1 mM $CaCl_2$, 1 mM $MgCl_2$, and 0.5 mM $Na_2B_4O_7·10H_2O$ was used to extract PCP in sediment amendments. Wheat seeds, named as Yangmai 12, were purchased from the seed technique extension station of Hangzhou, Zhejiang province, China.

2.3. Toxicity of PCP in sediment

PCP was spiked in the sediment to get a series of concentrations ranging from 0 (control) to 100 mg/kg using the prepared PCP methanol solution. After methanol volatilized completely, 30 g contaminated sediments with different concentrations of PCP were weighed in Petri dish (90-mm diameter) and adjusted the maximum water holding capacity (WHC) to 60% using distilled water, then each dish was placed at 25 °C for 24 h in the dark to make PCP equilibrium. Each treatment was conducted in triplicate. Prior to testing, fifteen wheat seeds were sown evenly throughout each Petri dish. After that, all the Petri dishes were incubated in a controlled environment chamber (model 102F Electrolab), with the conditions of 25 °C/20 °C day/night temperature, 14 h/10 h day night cycle and 65% air humidity. In our test, the experiments were terminated after 72 h of growth on the basis that the primary root of the control group was 18.2 mm, which was up to the standard of ending experiment. At the end of incubation, germinated seeds, the root and shoot lengths of emerged seedlings were determined [10,40]. In order to make toxicity of PCP clear, the inhibition rate (%) of germination, shoot and root length of seedlings growing in the test sediments was calculated as follows:

$$\text{Inhibition rate } (\%) = \frac{\text{control value} - \text{sample value}}{\text{control value}} \times 100\% \quad [41].$$

2.4. Extractability of PCP by BC

To achieve amendment rates of 0% (control), 0.5%, 1%, 2%, 5% and 10% (dry weight basis), the sediment was mixed with specific quantities of FC and SC, respectively. The sediment amendments were thoroughly mixed and then spiked with the PCP stock solution to achieve a concentration of 50 mg/kg [42,43]. After that, the spiked sediment amendments were incubated in the dark at 25 ± 1 °C for the same period of time as in the germination test [10,36], then the aqueous extract of PCP was conducted with prepared distilled water based on the ratio of soil/water to 1:2.5. The mixture was shaken on a horizontal shaker at 200 rpm at 25 ± 1 °C for 24 h (enough for the reaction to reach the apparent equilibrium) in the dark and the resulting slurry was separated by centrifugation at 3000 rpm for 20 min. An aliquot of 1 mL of the supernatant liquid was filtered through a 0.45 μm Millipore membrane and then analyzed using high performance liquid chromatography (HPLC, Agilent 1100, USA). A mixture of methanol and 1% acetic acid (90:10, v/v) was used as a mobile phase at a flow rate of 1.0 mL/min, and the injection volume was 20 μL [35].

2.5. Influence of BC in sediment on toxicity of PCP

The sediments amended with FC and SC (the content ranged from 0% to 10%) were spiked with the PCP stock solution to achieve a final concentration of 50 mg/kg. Then, the germination test was conducted following the same protocol as described in Section 2.3 except that the sediment was replaced by sediment amended with FC and SC, and each treatment was repeated three times. The germination rate, shoot and length of seedlings were expressed to observe the effect of BC on toxicity of PCP directly.

Table 2
Physical and chemical properties of two BCs.

BC	Elemental composition (%)			Surface area (m^2/g)	Porosity (mL/g)	Average pore size (nm)	Acidic group (mmol/g)				Basic group (mmol/g)
	C	H	N				Carboxyl	Lactone	Phenolic	Quinonyl	
FC	29.68	0.26	0	21.0	0.0387	20.53	0.494	0.000	0.000	0.490	0.000
SC	91.46	0.97	0	50.5	0.170	19.87	1.014	0.240	0.161	0.016	0.000

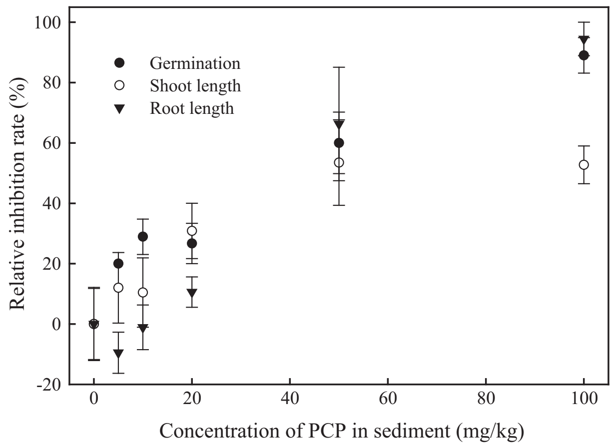

Fig. 1. Inhibitive effects of PCP concentrations on the germination, shoot and root length of wheat seeds. Error bars represent standard deviations ($n = 3$).

2.6. *Toxicity of BC in sediment*

Germination tests of FC-amended and SC-amended sediments without PCP were carried out to examine whether BC would show toxicity to seed germination. Germinated seeds, root and shoot length of emerged seedlings were determined in the same way as described above. Each treatment was also done in triplicate.

3. Results and discussion

3.1. *Toxicity of PCP in the sediment*

The inhibition rate of germination, shoot and root length in the PCP contaminated sediment is plotted in Fig. 1. It is showed that the inhibitive effects of germination and root length were quite evident and enhanced along with increasing PCP concentration, but a weaker inhibitive effect of shoot length was shown. Moreover, it is found that the inhibition rate of germination was below 0 when the concentration of PCP in sediment was 5 and 10 mg/kg. This suggested that the toxicity of PCP was stimulatory at low concentrations but toxic at higher concentrations, which was accordance with “hormesis” effect (a dose–response phenomenon that is characterized by low-dose stimulation and high-dose inhibition) [44,45].

Compared a concentration of 50 mg/kg to the control group (PCP = 0 mg/kg), the inhibition rate of germination showed significant difference ($P < 0.05$), the root length exhibited extremely significant difference ($P < 0.01$), whereas the shoot length had no obvious significant difference at 5% level. At a concentration of 100 mg/kg, the inhibition rate of germination and root length was nearly 90% toxic to wheat seed in the sediment, and showed extremely significant differences ($P < 0.01$) in comparison with the control group.

Linear regression analysis was conducted to data in Fig. 1, and the obtained equation is shown in Table 3. The corelationship analysis showed that there was significant correlation between PCP

Table 3
Linear relation between PCP concentrations(C_{PCP}) in sediment and the inhibition rates of germination (I_G), shoot (I_S) and root (I_R) length of wheat seeds, respectively.

Inhibition rate	Linear equation	R^2	P
Germination	$I_G = 0.806C_{PCP} + 12.586$	0.923	0.0014
Shoot	$I_S = 0.430C_{PCP} + 12.309$	0.783	0.0128
Root	$I_R = 1.058C_{PCP} - 10.508$	0.983	$6.95449E^{-5}$

$P < 0.05$ means significant correlation, $P < 0.01$ means extremely significant correlation.

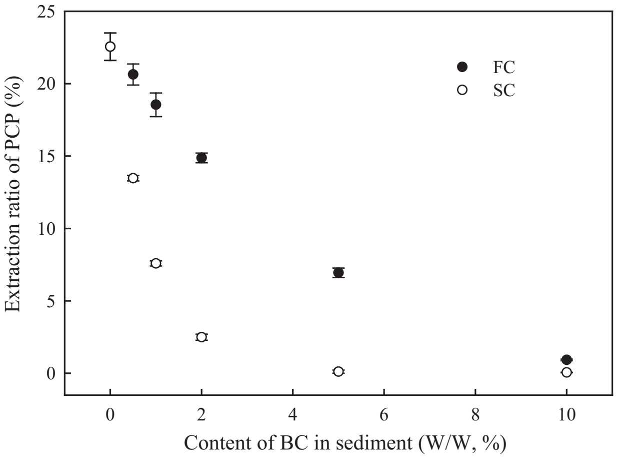

Fig. 2. Extraction ratio of PCP (50 mg/kg) to sediment associated with black carbon (FC and SC). Error bars represent standard deviations ($n = 3$).

concentrations and inhibition rates of shoot length ($P < 0.05$), and extremely significant correlation between PCP concentrations and inhibition rates of germination or root length ($P < 0.01$).

In addition, the LC_{50} (lethal concentration of 50%) of PCP in the sediment was 46.42 mg/kg calculated by the linear equation between PCP concentrations and the inhibition rates of germination, and based on this, a PCP concentration of 50 mg/kg was chosen for all subsequent experiments.

3.2. Influence of BC on extractability of PCP

The extractable rates of PCP by aqueous solution extraction decreased with the increasing content of BC and decreased to almost 0% as the addition of BC up to 10% (Fig. 2). The variance analysis indicated that all the sediment amendment rates except FC content of 0.5% had extremely significant effects ($P < 0.01$) on the extractability of PCP compared to the control group (sediment without adding BC at 50 mg PCP/kg).

It was proposed that BC in soils or sediments could act as supersorbent for contaminants because of its special physical and chemical properties [2,4,6–8,38,39]. In the current study, the native BC in the sediment was only 0.37% and the additional BCs were rich in surface area, porosity and functional group. Owing to the addition of FC and SC to the sediment, the liquid phase (bioavailable concentration) of PCP might decrease due to its adsorption and binding to BCs [4,7,38,46]. Moreover, because of the dissociation of acidic groups of BC (–OH, –COOH, etc.), the pH value of system might decrease. Thus, the proportion of species-PCP^n and PCP^- was altered as well, and the neutral form of PCP, highly sorptive, might increase in sediment amended with FC and SC [47,48].

Additionally, the extractability of PCP in sediment amended with SC was lower than FC, which was mainly caused by the higher surface area, porosity, and functional group of SC.

3.3. Influence of BC on toxicity of PCP

The influence of BC on the toxicity of PCP (50 mg/kg) in the sediment is shown in Fig. 3. The germination rate, shoot and root length exhibited a growing tendency along with the increasing BC content in sediment ranging from 0% to 10%. In comparison with the control group (the sediment without adding BC at 50 mg PCP/kg), the addition of FC to the sediment had no statistically significant effect on the germination rate; whereas FC content up to 5% and 10%, extremely significant difference ($P < 0.01$) was found in shoot and root length test. In the SC amendment groups, there was extremely significant difference ($P < 0.01$) in germination rate, shoot and root length at SC content from 2% to 10% compared to the control group; while SC content of 1% had no statistically significant effect on the germination rate, but extremely significant effect ($P < 0.01$) on shoot length and significant effect ($P < 0.05$) on root length.

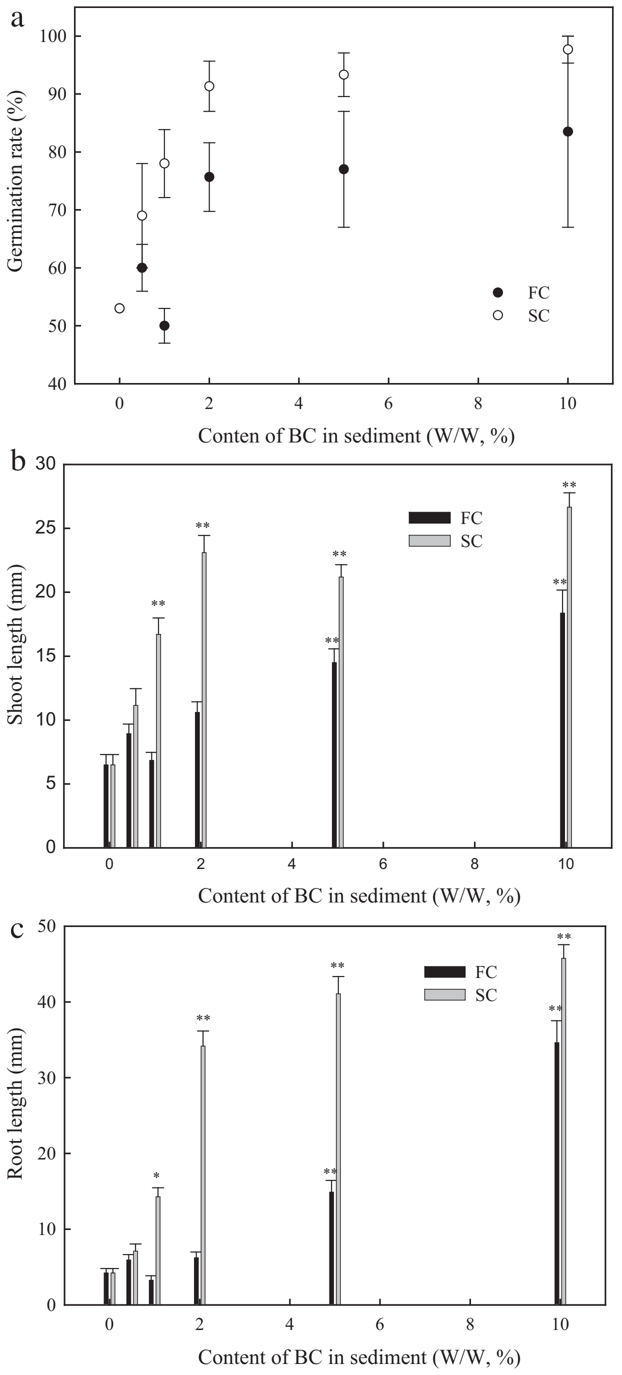

Fig. 3. Effects of 50 mg PCP/kg and added BCs (FC and SC) on the germination (a), shoot (b) and root length (c) of the wheat seeds. Error bars represent standard deviations ($n = 3$); compared with the control, ** represent a significant difference for $P < 0.01$ and * represent a significant difference for $P < 0.05$.

In general, it has been hypothesized that the strong sorption and desorption hysteresis caused by BC could be considered as one of the key factors regulating the bioavailability and the toxicity of organic contaminants in soil/sediment [5–7,27,43,49]. In this study, due to the addition of FC and SC in sediment, the liquid phase (bioavailable concentration) of PCP gradually decreased with

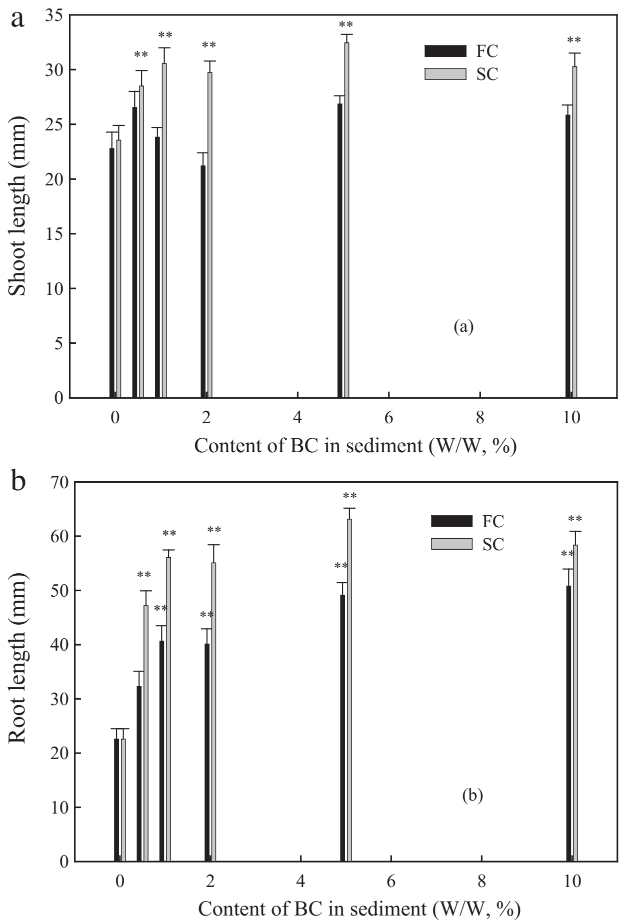

Fig. 4. Effects of various BC on the shoot length (a) and root length (b) were determined in samples including wheat seeds and sediment associated with BC only. Error bars represent standard deviations ($n = 3$); compared with the control, ** represent a significant difference for $P < 0.01$ and * represent a significant difference for $P < 0.05$.

the increasing content of BC and the toxicity of PCP was reduced accordingly. Therefore, it is concluded that the addition of FC and SC could reduce the toxicity of PCP in the sediment.

Besides, the influence of SC on toxicity of PCP was found to be more pronounced than FC. This might be mainly due to the surface area, porosity, and functional group of SC which are superior to FC (Table 2). It is inferred that PCP molecules in sediment amended with SC were better to be locked by the manner of adsorption and binding of micropore, which was determined by the surface area and porosity. Consequently, the toxic effect of PCP in sediment added in SC was lower than FC on the basis of the higher ability of locking PCP.

3.4. Toxicity of BC in sediment

Effects of BC on the germination test were determined in sediments amended with BC only. The results demonstrated that the germination rate was almost 100% in all sediment amendments, and was not statistically significantly different; that FC had no significant effect on the shoot length whereas SC showed extremely significant effect ($P < 0.01$) in all amendment rates; and that extremely significantly affect ($P < 0.01$) on root length in all sediment amendments apart from sediment amended with FC at rate of 0.5% (Fig. 4). Hence, it can be concluded that there was no toxic but stimulative effect of BC on growth of wheat seeds within the test ranges. Moreover, there was no statically significant linear correlation ($P > 0.05$) between BC content and growth promoting action caused by BC.

Meanwhile, the more obvious facilitation was found in SC-amendment groups compared with that in FC-amendments. It was reported that BC particles discharged in environment were considered both nutrient and toxic materials, and the addition of BC to soil may improve the physico-chemical properties (such as soil conductivity, organic carbon, microbial activity, soil porosity, etc.) [19,24,29,49]. In this study, due to the tested sediment was the same, the difference between FC-amendments and SC-amendments was mainly contributed to the various properties of FC and SC, which are shown in Table 2. The results may be attributed to two aspects, one is the characteristics of SC were better than FC, and SC could hold contaminants (heavy metal, PAHs, PCBs, and HOCs, etc.) more effectively; the other is FC might have more toxic elements (as B, Se, Ni, Mo and Cd) generated in process of combustion than SC. To validate the toxic elements, X-ray diffraction (XRD) analysis was carried out to determine the elements of SC and FC. The XRD pattern (figures not shown) showed that after repeated washing, there were still some residual salts like hematite, mullite and quartz in FC, and which was drawn after repeated operation and was not accidental. The existence of those substances might affect the results of the toxicity test, and the difference was also probably determined by the surface area, porosity, and functional group of BC. However, owing to the complex system, further study is still necessary to clarify the exact effect of BC on organisms.

4. Conclusion

Our experimental results showed that PCP had an obvious dose-dependent behavior for wheat seed, the toxicity of PCP was reduced gradually with the increasing content of FC and SC in sediment, and the influence of SC on the toxicity of PCP was more pronounced than FC due to the higher surface area and porosity of SC. It was also found that each BC had no toxic but stimulative effect on root elongation and early seedling growth, and the facilitation in SC-amendment groups was more obvious compared with FC-amendments. Furthermore, the addition of BC in sediment was found to be able to markedly reduce the extractable concentration of PCP.

It is commonly known that fly ash and soot produced in the process of combustion are ubiquitous, and usually classified as waste and utilized insufficiently. The emission of BC particles was attributed to part of major environmental problems. Conversely, it was reported to reduce the bioavailability and toxicity of contaminants through enhancing sorption capacity and desorption hysteresis of contaminants in soil/sediment containing BC. Therefore, the current study could provide insight into more systematic research on applying the fly ash and soot waste to reduce toxicity of contaminants and promote growth of organisms.

Acknowledgements

The work is supported by the National Natural Science Foundation of China (no. 40801198), Zhejiang Provincial Major Science and Technology Special Projects (no. 2007C13060), and Zhejiang Provincial Natural Science Foundation of China (no. R5090033).

References

[1] L. Sánchez-García, I. Cato, Ö. Gustafsson, Evaluation of the influence of black carbon on the distribution of PAHs in sediments from along the entire Swedish continental shelf, Mar. Chem. 119 (2010) 44–51.
[2] T.D. Bucheli, Ö. Gustafsson, Soot sorption of non-*ortho* and *ortho* substituted PCBs, Chemosphere 53 (2003) 515–522.
[3] J. Kumpiene, A. Lagerkvist, C. Maurice, Stabilization of Pb- and Cu-contaminated soil using coal fly ash and peat, Environ. Pollut. 145 (2007) 365–373.

[4] G. Cornelissen, O.R. Gustafsson, T.D. Bucheli, M.T.O. Jonker, A.A. Koelmans, P.A.C.M.C. Noort, Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation, Environ. Sci. Technol. 39 (2005) 6881–6895.

[5] X.H. Xia, Y.R. Li, Z. Zhou, Bioavailability of adsorbed phenanthrene by black carbon and multi-walled carbon nanotubes to agrobacterium, Chemosphere 78 (2010) 1329–1336.

[6] K. Knauer, A. Sobek, T.D. Bucheli, Reduced toxicity of diuron to the freshwater green alga pseudokirchneriella subcapitata in the presence of black carbon, Aquat. Toxicol. 83 (2007) 143–148.

[7] S. Kwon, J.J. Pignatello, Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): pseudo pore blockage by model lipid components and its implications for N_2-probed surface properties of natural sorbents, Environ. Sci. Technol. 39 (2005) 7932–7939.

[8] N.J. Persson, Ö.R. Gustafsson, T.D. Bucheli, Distribution of PCNs, PCBs, and other POPs together with soot and other organic matter in the marine environment of the Grenlandsfjords, Norway, Chemosphere 60 (2005) 274–283.

[9] K.K.C. Tse, S.L. Lo, Desorption kinetics of PCP-contaminated soil: effect of temperature, Water Res. 36 (2002) 284–290.

[10] M.K. Banks, A.P. Schwab, Ecotoxicity of pentachlorophenol in contaminated soil as affected by soil type, J. Environ. Sci. Health Part A 41 (2) (2006) 117–128.

[11] D.S. Shen, X.W. Liu, Y.H. He, Studies on adsorption, desorption and biodegradation of pentachlorophenol by the anaerobic granular sludge in an upflow anaerobic sludge blanket (UASB) reactor, J. Hazard. Mater. B125 (2005) 231–236.

[12] E. Puglisi, P. Vernile, G. Bari, M. Spagnuolo, M. Trevisan, E.D. Lillo, P. Ruggiero, Bioaccessibility, bioavailability and ecotoxicity of pentachlorophenol in compost amended soils, Chemosphere 77 (2009) 80–86.

[13] J.Z. Song, P.A. Peng, W.L. Huang, Black carbon and kerogen in soils and sediments. 1. Quantification and characterization, Environ. Sci. Technol. 36 (2002) 3960–3967.

[14] Y.N. Yang, G.Y. Sheng, M.S. Huang, Bioavailability of diuron in soil containing wheat–straw-derived char, Sci. Total Environ. 354 (2006) 170–178.

[15] Y. Yang, W. Hunter, S. Tao, J. Gan, Effects of black carbon on pyrethroid availability in sediment, J. Agric. Food Chem. 57 (2009) 232–238.

[16] X.Y. Yu, G.G. Ying, R.S. Kookana, Reduced plant uptake of pesticides with biochar additions to soil, Chemosphere 76 (2009) 665–671.

[17] X.Y. Cui, H.L. Wang, L.P. Lou, Y.X. Chen, Y.L. Yu, J.Y. Shi, L. Xu, M.I. Khan, Sorption and genotoxicity of sediment-associated pentachlorophenol and pyrene influenced by crop residue ash, J. Soil Sediment 9 (2009) 604–612.

[18] A.J. Rust, R.M. Burgess, A.E. Mcelroy, M.G. Cantwell, B.J. Brownawell, Influence of soot carbon on the bioaccumulation of sediment-bound polycyclic aromatic hydrocarbons by marine benthic invertebrates: an interspecies comparison, Environ. Toxicol. Chem. 23 (11) (2004) 2594–2603.

[19] V.C. Pandey, N. Singh, Impact of fly ash incorporation in soil systems, Agric. Ecosyst. Environ. 136 (2010) 16–27.

[20] U. Mani, A.K. Prasad, V.S. Kumar, K. Lal, R.K. Kanojia, B.P. Chaudhari, R.C. Murthy, Effect of fly ash inhalation on biochemical and histomorphological changes in rat liver, Ecotoxicol. Environ. Saf. 68 (2007) 126–133.

[21] A.D.H. Clague, J.B. Donnet, T.K. Wang, J.C.M. Peng, A comparison of diesel engine soot with carbon black, Carbon 37 (1999) 1553–1565.

[22] B.R. Stanmore, J.F. Brilhac, P. Gilot, The oxidation of soot: a review of experiments, mechanisms and models, Carbon 39 (2001) 2247–2268.

[23] S. Endo, P. Grathwohl, S.B. Haderlein, T.C. Schmidt, Effects of native organic material and water on sorption properties of reference diesel soot, Environ. Sci. Technol. 43 (2009) 3187–3193.

[24] K.V. Kumar, S. Srivastava, N. Singh, H.M. Behl, Role of metal resistant plant growth promoting bacteria in ameliorating fly ash to the growth of *Brassica juncea*, J. Hazard. Mater. 170 (2009) 51–57.

[25] M.T.O. Jonker, A.A. Koelmans, Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: mechanistic considerations, Environ. Sci. Technol. 36 (2002) 3725–3734.

[26] A.M. Accardi-Dey, P.M. Gschwend, Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments, Environ. Sci. Technol. 36 (2002) 21–29.

[27] A.R. Johnsen, J.R.D. Lipthay, F. Reichenberg, S.J. Sorensen, O. Andersen, P. Christensen, M.L. Binderup, C.S. Jacobsen, Biodegradation, bioaccessibility, and genotoxicity of diffuse polycyclic aromatic hydrocarbon (PAH) pollution at amotorway site, Environ. Sci. Technol. 40 (2006) 3293–3298.

[28] J. Dachs, S.J. Eisenreich, Adsorption onto aerosol soot carbon dominates gas-particle partitioning of polycyclic aromatic hydrocarbons, Environ. Sci. Technol. 34 (2000) 3690–3697.

[29] B.N. Mittra, S. Karmakar, D.K. Swain, B.C. Ghosh, Fly ash—a potential source of soil amendment and a component of integrated plant nutrient supply system, Fuel 84 (2005) 1447–1451.

[30] L. Luo, L.P. Lou, X.Y. Cui, B.B. Wu, J.A. Hou, B. Xun, X.H. Xu, Y.X. Chen, Sorption and desorption of pentachlorophenol to black carbon of three different origins, J. Hazard. Mater. 185 (2011) 639–646.

[31] W.M. Law, W.N. Lau, K.L. Lo, L.M. Wai, S.W. Chiu, Removal of biocide pentachlorophenol in water system by the spent mushroom compost of *Pleurotus pulmonarius*, Chemosphere 52 (2003) 1531–1537.

[32] Y. Dudal, A.R. Jacobson, R. Samson, L. Deschênes, Modelling the dynamics of pentachlorophenol bioavailability in column experiments, Water Res. 38 (2004) 3147–3154.

[33] G. Piringer, S.K. Bhattacharya, Toxicity and fate of pentachlorophenol in anaerobic acidogenic systems, Water Res. 33 (11) (1999) 2674–2682.

[34] R. Scelza, M.A. Rao, L. Gianfreda, Response of an agricultural soil to pentachlorophenol (PCP) contamination and the addition of compost or dissolved organic matter, Soil Biol. Biochem. 40 (2008) 2162–2169.

[35] Y.X. Chen, H.L. Chen, Y.T. Xu, M.W. Shen, Irreversible sorption of pentachlorophenol to sediments: experimental observations, Environ. Int. 30 (2004) 31–37.

[36] X.Y. Hu, B. Wen, X.Q. Shan, S.Z. Zhang, Bioavailability of pentachlorophenol to earthworms (*Eisenia fetida*) in artificially contaminated soils, J. Environ. Sci. Health 40 (2005) 1905–1916.

[37] L.P. Lou, B.B. Wu, L.N. Wang, L. Luo, X.H. Xu, J.A. Hou, B. Xun, B.L. Hu, Y.X. Chen, Sorption and ecotoxicity of pentachlorophenol polluted sediment amended with rice–straw derived biochar, Bioresour. Technol. 102 (2011) 4036–4041.

[38] Y. Chun, G.Y. Sheng, C.T. Chiou, B.S. Xing, Compositions and sorptive properties of crop residue-derived, Environ. Sci. Technol. 38 (2004) 4649–4655.

[39] Y.N. Yang, G.Y. Sheng, Enhanced pesticide sorption by soils containing particulate matter from crop residue burns, Environ. Sci. Technol. 37 (2003) 3635–3639.

[40] K.L. Knoke, T.M. Marwood, M.B. Cassidy, D. Liu, A.G. Seech, H. Lee, J.T. Trevors, A comparison of five bioassays to monitor toxicity during bioremediation of pentachlorophenol-contaminated soil, Water Air Soil Pollut. 110 (1999) 157–169.

[41] J. An, Q.X. Zhou, Y.B. Sun, Z.Q. Xu, Ecotoxicological effects of typical personal care products on seed germination and seedling development of wheat (*Triticum aestivum* L.), Chemosphere 76 (2009) 1428–1434.

[42] A.H. Rhodes, L.E. McAllister, R.R. Chen, K.T. Semple, Impact of activated charcoal on the mineralisation of ^{14}C-phenanthrene in soils, Chemosphere 79 (2010) 463–469.

[43] Y. Yang, W. Hunter, S. Tao, D. Crowley, J. Gan, Effect of activated carbon on microbial bioavailability of phenanthrene in soils, Environ. Toxicol. Chem. 28 (11) (2009) 2283–2288.

[44] E.J. Calabrese, R.B. Blain, Hormesis and plant biology, Environ. Pollut. 157 (2009) 42–48.

[45] E.J. Calabrese, Hormesis: why it is important to toxicology and toxicologists, Environ. Toxicol. Chem. 27 (7) (2008) 1451–1474.

[46] W.L. Huang, P.A. Peng, Z.Q. Yu, Effects of organic matter heterogeneity on sorption and desorption of organic contaminants by soils and sediments, Appl. Geochem. 18 (2003) 955–972.

[47] Y. Shimizu, S. Yamazaki, Y. Terashima, Sorption of anionic pentachlorophenol (PCP) in aquatic environments: the effect of pH, Water Sci. Technol. 25 (1992) 41–48.

[48] M.G. Stapleton, D.L. Sparks, S.K. Dentel, Sorption of pentachlorophenol to HDTMA-clay as a function of ionic strength and pH, Environ. Sci. Technol. 28 (1994) 2330–2335.

[49] M.T.O. Jonker, A.M. Hoenderboom, A.A. Koelmans, Effects of sedimentary soot like materials on bioaccumulation and sorption of polychlorinated biphenyls, Environ. Toxicol. Chem. 23 (11) (2004) 2563–2570.