REGULAR ARTICLE

Effectiveness of low-temperature biochar in controlling the release and leaching of herbicides in soil

Jianfa Li · Yimin Li · Mingjun Wu ·
Zheying Zhang · Jinhong Lü

Abstract

Aims Biochars, being good sorbents of organic compounds, can reduce the mobility of pesticides in soil and subsequent pollution to groundwater, but may also impact on the efficacy of soil-applied herbicides. The aim of this study is to seek a potential solution to this problem.

Methods We prepared a wood biochar at a relatively low heat treatment temperature (350 °C), and used it as an adsorptive carrier for incorporating the herbicides 2,4-D and acetochlor, and also as a soil amendment. Release experiment through a thin soil layer and leaching experiment through a soil column were used to evaluate the effectiveness of the biochar for controlling the release and leaching of herbicides in soil.

Results The release experiments demonstrated that the low-temperature biochar could control the release of herbicides in soil, and the leaching experiments showed that this biochar significantly reduced the leached amount of herbicides by 1/2∼3/4, depending on the depth (5∼15 cm) of biochar-amended topsoil.

High retention of herbicides in the biochar-amended topsoil was observed.

Conclusions The results suggest that the low temperature biochar, if applied properly in soil, may be useful for extending the efficacy of herbicides while controlling their potential pollution.

Keywords Biochar · Pesticide · Controlled release · Leaching · Sorption

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J. Li (✉) · Y. Li · M. Wu · Z. Zhang · J. Lü
Department of Chemistry, Shaoxing University,
Huancheng Xi Lu 508,
Zhejiang, Shaoxing 312000, China
e-mail: ljf@usx.edu.cn

Introduction

Biochars, the charred organic matters intended for carbon sequestration and soil improvement, have received increasing attentions in recent years (Lehmann et al. 2006; Lehmann 2007). Besides their great potential for mitigation of climate change, biochars as a soil amendment can provide multiple benefits for nutrient retention (Glaser et al. 2002; Lehmann et al. 2003; Ding et al. 2010; Taghizadeh-Toosi et al. 2012) and crop productivity (Graber et al. 2010; Major et al. 2010; Zhang et al. 2012). Biochars are prepared by thermal decomposition of various types of biomass including wood, manure, grass and straw, so their compositions and properties are diverse depending on the feedstock and thermal decomposition conditions (Laird et al. 2009; Uchimiya et al. 2011). Generally, biochars obtained at relatively high heat treatment temperatures (HTT>600 °C) show a high degree of carbonization, as indicated by low H/C

atomic ratios and high specific surface areas (Chun et al. 2004; Chen et al. 2008). Similarly to activated carbons, these biochars show high sorption capacity, and can be used for remediation of both organic and inorganic pollutants (Chen et al. 2011; Hale et al. 2011; Uchimiya et al. 2011; Debela et al. 2012). As a potential soil amendment, biochars also exhibit good sorption of many organic pesticides (Yang and Sheng 2003; Yu et al. 2006; Qiu et al. 2009; Zheng et al. 2010; Sun et al. 2011; Uchimiya et al. 2012), and influence the mobility of soil-applied herbicides. Until now, most of the published results have shown extended retention and reduced leaching of pesticides in biochar-amended soils (Wang et al. 2010; Jones et al. 2011), which is beneficial for controlling their environmental pollution. However, biochars of high maturity may show nearly irreversible sorption of pesticides, thus reducing their plant availability and efficacy (Yu et al. 2010; Graber et al. 2011; Nag et al. 2011; Graber et al. 2012). Therefore, further research is needed to seek an appropriate compromise between sorption capacity and release ability of pesticides by biochars, so as to maximize the benefits of biochars as a soil amendment, without impacting the efficacy of soil-applied herbicides (Kookana 2010).

Compared with biochars obtained at high temperatures, their counterparts made at relatively low temperatures (<500 °C) generally contain some residual organic matter existing as condensed tars in the carbonaceous matrix (Schnitzer et al. 2007; Cao et al. 2009). These biochars may absorb organic molecules mainly through a partition mechanism, which is different from the surface adsorption mechanism occurring in highly matured biochars (Chun et al. 2004; Chen et al. 2008). In this way, the absorbed organic molecules may be re-released by the driving force of concentration differences when the organically-loaded biochars are put into water. Thus the biochars made at relatively low temperatures may have the potential to control the release of some soil-applied herbicides, just as some clay sorbents do (Celis et al. 2002; Li et al. 2008). When the soil-applied herbicides were incorporated in these clay sorbents, controlled release of active ingredients was obtained, so the efficacy of herbicides was extended, and the amount of herbicides available for leaching was reduced in the interim (El-Nahhal et al. 1998; Hermosín et al. 2001; Sánchez-Verdejo et al. 2008). If the active ingredients can be released sustainably at a rate suitable for weed control, the pollution of herbicides could be minimized and the cost of herbicide applications reduced.

In this study, we prepared biochars by thermal decomposition of a wood residue, namely poplar branches, at relatively low temperatures (200–500 °C). Among these biochars, we attempted to find a suitable sorbent of herbicides, and to develop a practical method of using this biochar sorbent for controlling the release and leaching of herbicides in soil. The two herbicides tested were 2,4-D (2,4-dichlorophenoxyacetic acid) and acetochlor (2-chloro-N-(ethoxymethyl)-N-(2ethyl-6-methylphenyl) acetamide). Both herbicides are widely applied in croplands, and have relatively high leaching potentials (Li et al. 2009; Lü et al. 2012), therefore posing a potential threat of groundwater contamination.

Materials and methods

Preparation of poplar wood biochars

As the biomass material for preparing the biochars, poplar (*Populus euramericana*) branches without leaves were collected locally and rinsed with water. After drying, the wood branches were cut into chips of 2 mm×2 mm in size for heat treatment under oxygen-limited conditions (Chen et al. 2008; Cao et al. 2009). Typically, the dried wood chips (10 g) were added to a ceramic pot fitted with a lid, after which the pot was placed in a muffle furnace. After heat treatment at a set temperature (200 °C, 350 °C or 500 °C) for 6 h, the solid residue was washed in 100 mL of 1 mol/L HCl solution four times, so as to remove soluble salts. After rinsing with distilled water, the solid biochar was oven dried at 70 °C to constant weight. The resulting biochar product was then ground to less than 0.15 mm in size. The samples obtained at the different heat treatment temperatures of 200 °C, 350 °C or 500 °C are referred to hereafter as PW200, PW350 and PW500, respectively.

Characterization of biochar samples

The Brunauer-Emmett-Teller (BET) surface area of the biochar samples was obtained from nitrogen adsorption data at 77 K in an ASAP 2020 system (Micromeritics). The elemental (C, H, N and O) compositions of the biochar samples were determined in a PE2400-II elemental analyzer (PerkinElmer). Ash

content was measured by heating the samples at 800 °C for 4 h. ATR-IR spectra were recorded in the 4,000~675 cm^{-1} region using a Nexus FTIR spectrophotometer (Thermo Nicolet).

Sorption experiments of herbicides on biochars

Sorption isotherms were used to compare the sorption capacity of herbicides by the various biochars. For this purpose, aqueous herbicide solutions were obtained by dissolving technical grade herbicides 2,4-D (98.2 % purity, acid form) and acetochlor (96.2 % purity) purchased from the Hangzhou Qingfeng Agrochemicals Co. Ltd., China. The sorption isotherms were determined by batch equilibration of solid biochar samples (0.1 g for sorption of acetochlor, and 0.2 g for sorption of 2,4-D) in 25 mL of aqueous solutions of various initial herbicide concentrations (C_0, mgL^{-1}), which ranged from 30 to 160 mg L^{-1} for acetochlor, and from 60 to 300 mgL^{-1} for 2,4-D. The aqueous phase for sorption studies of both herbicides was acidic, with a pH of ca. 4.0 in the acetochlor solutions, and a pH of 3.1~3.5 in the 2,4-D solutions depending on 2,4-D initial concentrations (see Fig. S1 in the online supplementary material for details). The sorption experiment was carried out in a thermostatic shaker bath at 25 ± 0.1 °C for 24 h (Lü et al. 2012). The amount adsorbed (Q_e, mgg^{-1}) was calculated from the difference in concentration between the initial (C_0, mgL^{-1}) and the equilibrium (C_e, mgL^{-1}) solutions. Desorption experiments were performed immediately after sorption equilibrium at the highest equilibrium concentrations, by replacement of 10 mL of the supernatant solution with an equal volume of distilled water (Pu and Cutright 2006; Yu et al. 2006). After shaking the diluted suspension at 25 ± 0.1 °C for 24 h (a period equal to that used in the sorption procedure), another 10 mL of supernatant was sampled and replaced again with distilled water. The desorption cycle was repeated four times, after which the herbicide concentration in the liquid has dropped apparently enough for observing the desorption behavior of herbicides.

Release experiment through a thin soil layer

In order to investigate the potential of biochars for regulating the release of herbicides, a release experiment was carried out by using the biochars as both the adsorptive carrier of herbicides and a soil amendment. The experiment was carried out in a Buchner funnel paved with a thin soil layer (ca. 2.0 cm thick) (Radian and Mishael 2008; Lü et al. 2012) (see Fig. S2(a) in the online supplementary material for the schematic installation). The soil used was collected locally from the top layer of a red soil, a kind of ferrallitic soil widely distributed in Southern China. It has a pH of 4.8, organic matter content of 0.6 % and CEC of 0.11 $mmolg^{-1}$. The soil was air-dried and sieved through a 2 mm screen before use. Before being added to the funnel, the red soil (116 g) was amended with the biochar by mixing them together, at a biochar dose rate of 0.5 % (w/w) or 1.0 % (w/w) of the red soil. Then the soil mixture was deposited evenly on a nylon filter cloth (0.05 mm in mesh size) in the bottom of the funnel (8.0 cm inner diameter).

The herbicides were applied on the thin soil layer after being incorporated into the biochar as the carrier. First, the herbicide containing active ingredient (a.i.) of 2.0 mg (M_0) was dissolved in 3 mL of methanol and mixed with 50 or 100 mg of a biochar sample. The herbicide-loaded biochar sample was air-dried in a ventilation cabinet, and then mixed with 10 g of red soil. The resulting herbicide-containing soil mixture has a biochar content of 0.5 % (w/w) or 1.0 % (w/w), respectively, corresponding to the biochar dose rate in the thin soil layer. Finally, the herbicide-containing soil mixture was added evenly onto the top of the thin soil layer. Control treatments of both 2,4-D and acetochlor were performed by application of the technical grade herbicides directly onto the thin soil layer of the original red soil.

The funnel was sprayed with water nine times at 1 h intervals. The volume of each watering was 40 mL and it was completed within 8–10 min. This rate of rinsing is equivalent to a rainfall of 8.0 mm per hour, which is higher than the moderate rain (2.6 mm to 7.6 mm per hour according to the classification of American Meteorological Society (2012)). The quick rinsing was chosen to shorten the experimental period, so as to minimize the influence of herbicide degradation in soil. The rinsed solution was collected after each watering, and sampled using a syringe and filtering through a 0.22 μm microporous membrane. The amount of herbicide released (M_i, mg) was calculated from the herbicide concentration in the solution sample. The cumulative percentage of herbicide released after watering n times $\left(\left(\sum_{i=1}^{n} M_i / M_0 \right) \times 100\% \right)$ was obtained for each treatment in triplicate.

Leaching experiment through the soil column

The performance of biochars in reducing the leaching of herbicides was evaluated with leaching experiments through a soil column. The soil column was prepared by filling soil (or amended soil with biochar at a dose rate of 1.0 %(w/w)) into a polyvinyl chloride (PVC) pipe (40 cm length, 4.6 cm internal diameter) (Cox et al. 2000; Fernández-Pérez et al. 2011; Lü et al. 2012), with a piece of nylon filter cloth applied at the bottom and at each 5 cm segment of soil in the pipe, so as to re-distribute the water flow. Each column contained, from the bottom to the top, a layer of acid washed sand (2.0 cm), a soil layer of a total of 6 segments (6× 5.0 cm=30 cm, including 0~3 segments packed with biochar-amended soil at the top end), and a top sand layer (2.0 cm) (see Fig. S2(b) in the online supplementary material for the schematic installation). The bottom sand layer was used to prevent the displacement of soil, and the top sand layer to distribute the dripping water evenly across the cross-section of the soil layer. The bulk density of the soil in the column was $1.26 \ \mathrm{g\,cm^{-3}}$, which resulted in a pore volume of ca. 250 mL for the soil layer. Prior to herbicide application, the column was saturated with $0.01 \ \mathrm{mol\,L^{-1}}$ $CaCl_2$ aqueous solution and then left to drain overnight.

The herbicide containing the a.i. of 2.0 mg (M'_0) was applied evenly onto the top of the sand layer in a mixture with 100 mg of biochar and 10 g of red soil. The mixing procedure was the same as above de-scribed for the release experiment. After herbicide application, a sand layer (ca. 1.0 cm) was added to the top of the column. The column was then irrigated with distilled water (100 mL each day) using a peri-staltic pump at a flow rate of $10 \ \mathrm{mL\,h^{-1}}$ (equivalent to a rainfall of 6.0 mm per hour). The total period of irrigations was 12 days. The leachate was collected each day, and then condensed under vacuum for anal-ysis of the herbicide concentration. The amount of herbicide leached (M'_t, mg) was calculated by multi-plying the concentration by the volume (ca. 10 mL) of condensed leachate. Finally, the percentage of herbi-cide leached ((M'_t/M'_0)×100 %) at each irrigation was calculated in duplicate.

On completion of the leaching experiment, each segment of soil layer was removed from the column separately, and weighed (m_{soil}) after drying in air. The dried soil sample of 10 g was extracted in conical flasks with 30 mL of methanol four times (with recovery rates of above 95 % from spike-in experi-ments). The total extractive solution was filtered and the most of the solvent was vaporized under vacuum. Finally, the herbicide concentration in the condensed extractive solution (ca. 5 mL) was analyzed, and the residual amount (M'_r, mg) of herbicide in each soil segment was estimated by scaling up the extractable amount of herbicide in the soil sample of 10 g to the total soil weight (m_{soil}) in the segment. The residual percentage of herbicide ((M'_r/M'_0)×100 %) in each soil segment was obtained in duplicate.

Control leaching experiments, in which no biochar was used, were conducted by applying technical her-bicides (2,4-D or acetochlor) onto the top of columns packed with the original red soil. Before herbicide application, both herbicides were dissolved in metha-nol, and the solutions were mixed with 10 g of red soil. The mixture was left to dry overnight at room temper-ature before being added to the soil column.

HPLC analysis of herbicides in solution samples

The analysis was conducted using an Agilent 1200 HPLC system equipped with an ultraviolet detector and an HP Hypersil C18 column (150 mm×4.6 mm i.d, particle size 5 μm). The mobile phase used was an acetonitrile–water mixture (70:30, V/V), with the pH adjusted to 2.0 for 2,4-D analysis. The herbicides acetochlor and 2,4-D were analyzed at 225 nm and 282 nm, respectively, with a detection limit of 0.08 mg L^{-1} for acetochlor and 0.10 mg L^{-1} for 2,4-D.

Results

Elemental analysis and IR characterization of biochars

The biochars obtained at three HTTs (200 °C, 350 °C and 500 °C) were different in some physical character-istics. For example, the PW200 biochar was brown in color and difficult to grind into a powder, but the other two biochars were black and fragile. The results of elemental analysis of the three biochars are presented in Table 1. As can be seen, the carbon content of biochars increased with the HTT, while the content of both hydrogen and oxygen decreased. Therefore the H/C and O/C ratios of the biochars decreased with the increasing HTT, in accordance with that illustrated in van Krevelen diagrams (Mahinpey et al. 2009). In

Table 1 Characterizations of biochars

Sample	Yield (%)	SSA[a] ($m^2 g^{-1}$)	Ash (%)	Organic elemental compositions					
				C(%)	H(%)	N(%)	O(%)	H/C[b]	O/C[b]
PW200	75.5±0.7	n.d.	2.23	51.6	5.06	0.95	36.2	1.18	0.526
PW350	39.0±1.4	4.03	3.85	68.9	1.67	1.84	16.5	0.290	0.179
PW500	20.1±1.6	30.5	8.05	74.5	1.17	1.13	6.56	0.189	0.066

[a] Specific surface area

[b] Atomic ratio of hydrogen or oxygen to carbon

addition, the yield of biochars also decreased with the increasing HTT, while the ash content and SSA increased. ATR-IR spectroscopy was used to further characterize the biochars (Fig. 1). The absorption bands at 3,377 cm^{-1} and 2,925 cm^{-1} in the IR spectrum of the PW200 biochar represent the vibrations of hydroxyl and methylene groups on the lingo-cellulosic polymers. The peak at 1,716 cm^{-1} is assigned to aliphatic C=O groups generated mainly by oxidation and dehydration of polymers. The absorptions at 1,056 cm^{-1} and 1,036 cm^{-1} are assigned to C-O stretching vibrations of alcohols on lingo-cellulosic polymers (Dong et al. 2012). The diminished absorption of these bands in the spectrum of the PW350 biochar is accompanied by intensified absorption at 1,613 cm^{-1} that belongs to aromatic and unsaturated structures, indicating greater aromaticity of this biochar (Peng et al. 2011). In the spectrum of the PW500

biochar, the absorptions at 2,990 cm^{-1}, 2,363 cm^{-1} and 799 cm^{-1} illustrate further development of aromatic and unsaturated structures in this product.

Sorption of herbicides on biochars

In comparison with the biomass feedstock, the sorption of organic molecules on biochars is always greatly improved because of the high porosity and SSA of biochar products. The sorption isotherms of herbicides by the three biochars made at different HTTs are shown in Fig. 2. As can be seen, the isotherms for both herbicides display increasing non-linearity with the increasing HTT of biochars, corresponding to the increasing deviation from 1 of n_F values in the Freundlich model (Eq. 1) (Table 2). For example, the n_F values of sorption isotherms on the PW200 biochar were closest to 1. The sorption isotherms on the PW500 biochar showed the largest deviation of n_F values from 1, and the gradual saturation of sorption was obtained with increasing equilibrium concentrations of the herbicide solutions. The PW350 biochar shows the highest sorption of both acetochlor and 2,4-D over the entire range of solution concentrations adopted in this study, with high K_F values and medium n_F values of the sorption isotherms. Desorption studies (Fig. 3, see also Fig. S3 in the online supplementary material for desorption kinetics) showed a hysteretic desorption of both herbicides from the PW350 biochar, which suggests its potential for releasing the adsorbed herbicides in a sustained way.

$$\ln Q_e = \ln K_F + n_F \ln C_e \qquad (1)$$

Controlled release of herbicides in soil

The PW350 biochar, because of its high and reversible sorption of both herbicides, was chosen as the carrier
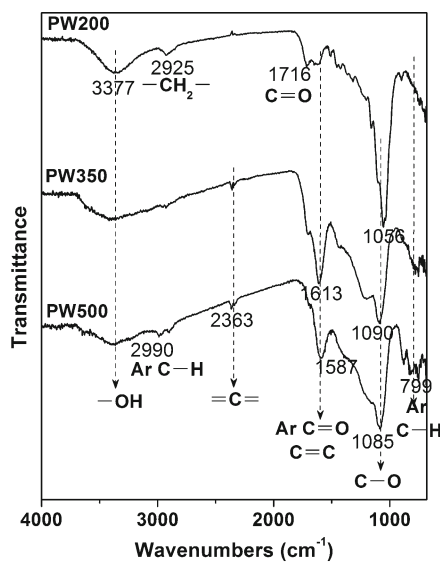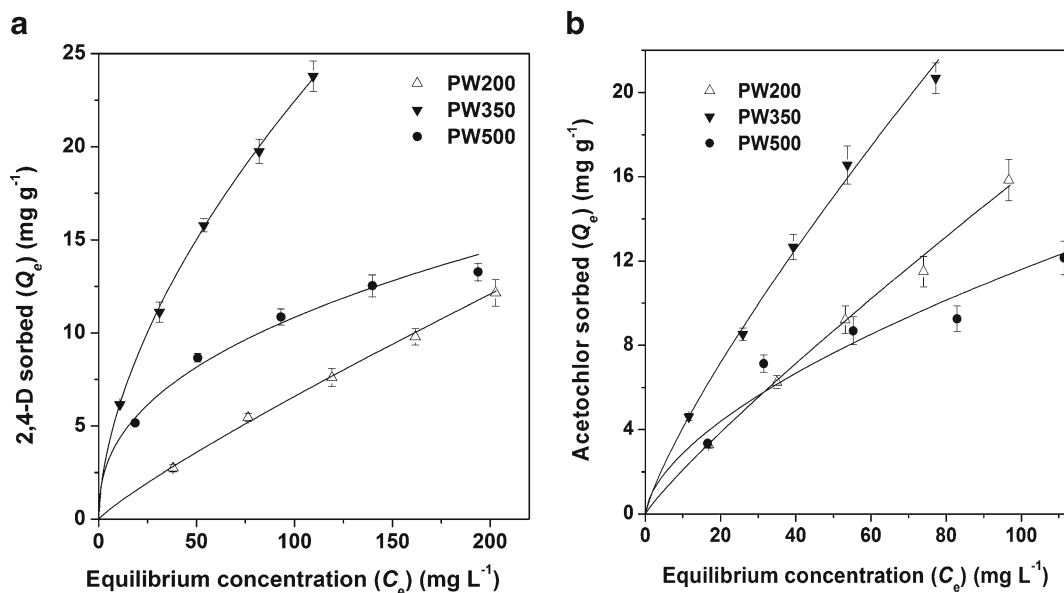

Fig. 1 IR spectra of the biochars

Fig. 2 Sorption isotherms of **a** 2,4-D and **b** acetochlor on the biochars at 25 °C (error bars represent the standard deviation of triplicate measurements, and lines represent the predicted isotherms calculated with the Freundlich model)

for incorporating herbicides, along with being a soil amendment for improving the retention of herbicides in topsoil. Its performance in controlling the release of herbicides, as evaluated by release experiments through a thin soil layer, is shown in Fig. 4. The release of both herbicides was apparently slowed, in comparison with the release of technical grade herbicides through the original red soil (Fig. 4-Control). In the later case, almost all the active ingredients were released within six waterings for 2,4-D, and within eight waterings for acetochlor. The slower release of acetochlor in the Control treatment may be related to its lower solubility (223 $mg L^{-1}$ at 25 °C) and higher hydrophobicity (log K_{ow}=4.14 at 20 °C) than 2,4-D, an organic acid having enhanced solubility (c.a. 20.0 $g L^{-1}$ at pH=5 (25 °C)) and decreased hydrophobicity with increased pH in solution. The preliminary experiments (data not

included) showed a low sorption of both herbicides by the red soil, which may slightly slower the release of technical herbicides in the soil as well. As expected, the release of both herbicides was further retarded with the dose of the PW350 biochar increasing from 0.5 % (w/w) to 1.0 % (w/w). As a result of increasing the dose of biochar, the cumulative amount of herbicides released was reduced by more than 20 % after nine waterings.

Retarded leaching of herbicides in soil

As that in the release experiments, the PW350 biochar was used simultaneously as a soil amendment and adsorptive carrier for incorporating herbicides in the leaching experiments. Figure 5 shows the results of herbicides leached through the soil column packed

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Table 2 Parameters for sorption isotherms of herbicides by biochars	Herbicide	Biochar	K_{d}[a] ($L g^{-1}$)	K_{F} ($L g^{-1}$)	n_{F}	R_{F}[b]
	2,4-D	PW200	0.065±0.006	0.116±0.009	0.876±0.012	0.997
		PW350	0.336±0.141	1.55±0.11	0.580±0.019	0.993
		PW500	0.144±0.083	1.64±0.12	0.410±0.021	0.989
	Acetochlor	PW200	0.173±0.015	0.274±0.033	0.884±0.029	0.993
[a]$K_{d}=Q_{e}/C_{e}$		PW350	0.325±0.047	0.637±0.030	0.808±0.007	0.996
[b]Correlation coefficients to the Freundlich model		PW500	0.161±0.053	0.718±0.036	0.604±0.011	0.942
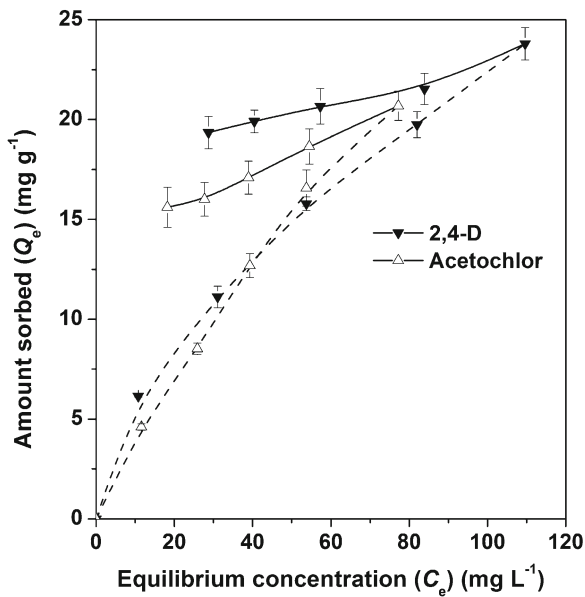
Fig. 3 Desorption of herbicides from the PW350 biochar (*error bars* represent the standard deviation of triplicate measurements)

with biochar-amended soil. The comparative leaching results of technical grade herbicides through the column packed with the original red soil (Fig 5-Control) indicate that the breakthrough appeared at the second day for 2,4-D, and at the fourth day for acetochlor. The earlier breakthrough of 2,4-D in the Control treatment is related to its higher water solubility and low hydrophobicity, and is consistent with its quicker release in

the release experiments. The breakthrough of 2,4-D was observed at the third day when using the PW350 biochar as the carrier and soil amendment, and a delayed breakthrough was obtained in comparison with the Control treatment. Meanwhile, the cumulative amount of 2,4-D leached after 12 days was greatly reduced by 1/2~3/4, depending on the depth of soil amended by the biochar. When the topsoil of 0~15 cm depth was biochar-amended, the cumulative amount of 2,4-D leached after 12 days accounted for only 20.7 % of the initial amount of herbicide applied to the soil column. The deeper the biochar-amended soil used in the column, the less 2,4-D was leached through the column. The leached amount of herbicide acetochlor was also apparently reduced by using the PW350 biochar sorbent, although no apparent delay of the breakthrough was observed. In comparison with the results in the Control treatment, the leached amount of acetochlor decreased by nearly 3/4 when the topsoil of 0~10 cm depth was amended by the biochar.

Figure 6 shows the residual amount of herbicides recovered in the different soil segments in the soil columns after the leaching experiments. Apparent retention of both herbicides was observed in the biochar-amended soil column. The retained amount in the topsoil (0~10 cm) accounted for 27.2 % of the initial amount of 2,4-D applied to the column, while
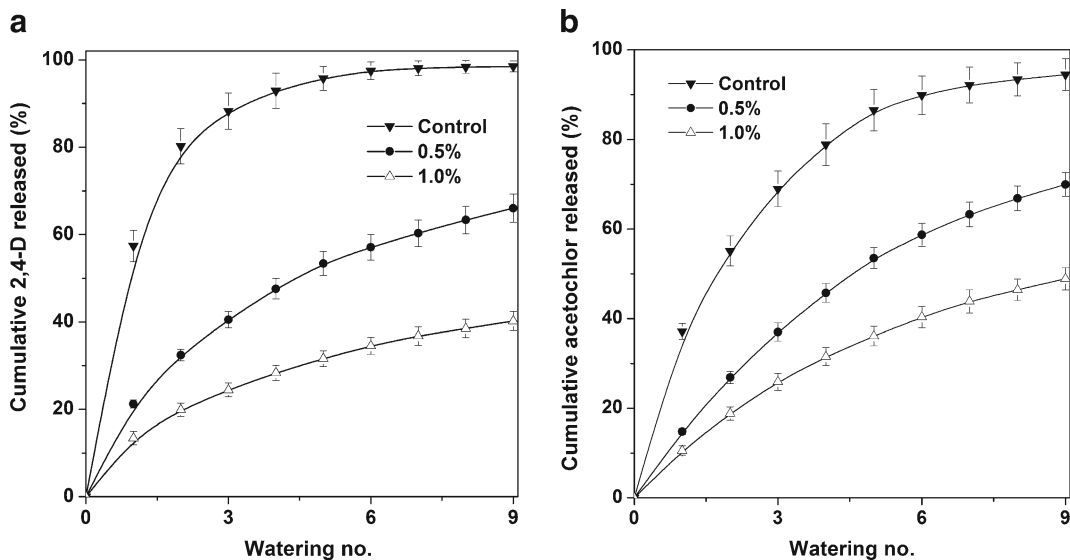

Fig. 4 Controlled release of **a** 2,4-D and **b** acetochlor in soil using the PW350 biochar as both adsorptive carrier and soil amendment (0.5 % and 1.0 % represent the dose rate of biochar in soil by weight)
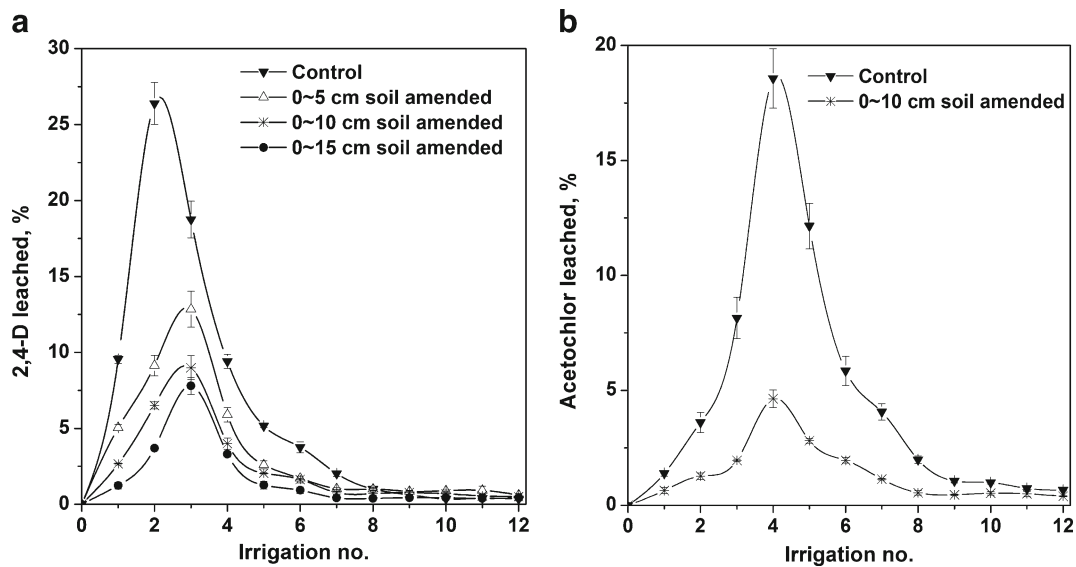
Fig. 5 Leaching of **a** 2,4-D and **b** acetochlor through the soil columns amended by the PW350 biochar (at a dose rate of 1.0 % by weight)

33.6 % of acetochlor was retained in the topsoil (0 ~10 cm). In contrast, most of the technical herbicides were leached from the column packed with the unamended red soil (Fig. 6-Control). Table 3 shows the percentage of herbicides recovered in the leachates and soil in the various treatments. The total herbicide recovered is obviously lower than 100 %, indicating loss of herbicides in the leaching experiments, presumably mainly because of herbicide degradation in the soil.

Discussion

The changes in the physical properties and chemical compositions of the three biochars prepared at different HTT are consistent with those reported previously (Chun et al. 2004; Chen et al. 2008). The high yield of PW200 biochar indicated a low loss of mass by thermal treatment at 200 °C, and the higher H/C and O/C ratios confirmed that the loss was mainly due to the dehydration of biopolymers in the feedstock, because
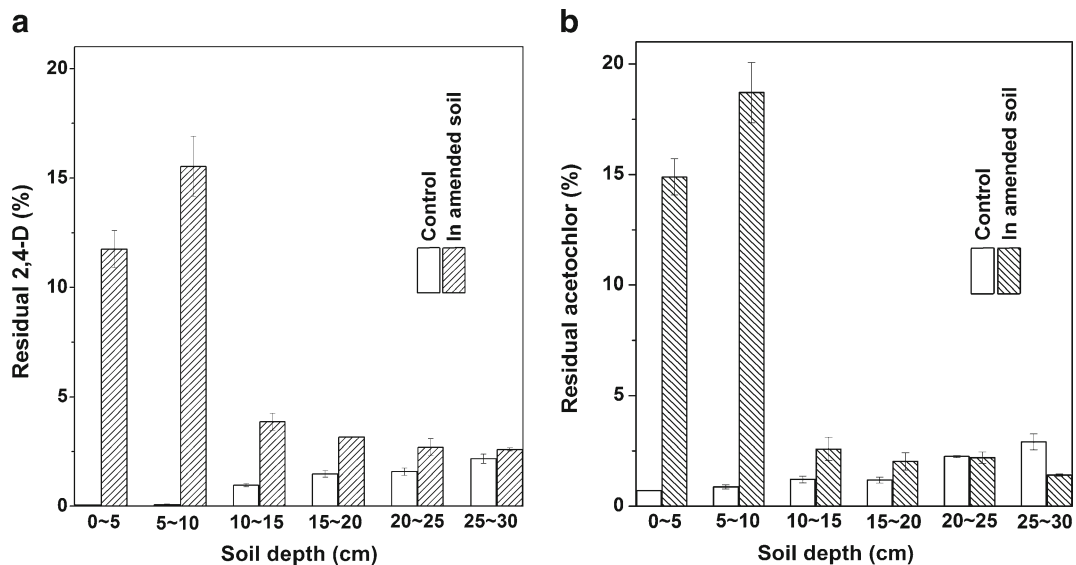

Fig. 6 Residual amount of **a** 2,4-D and **b** acetochlor in different depths of the columns with 0~10 cm topsoil amended by the PW350 biochar (at a dose rate of 1.0 % by weight), and of columns packed with the red soil (*Control*)

**Table 3** Percentage of herbicide recovered in the leachates and soil

Herbicide	Treatment	Cumulative leached (%)	Recovered in soil layer (%)		Total recovered (%)
			Biochar-amended topsoil	Red soil layer	
2,4-D	Control	77.8±2.8	–	6.32±0.05	84.1
	0~5 cm topsoil amended	42.5±1.8	16.1±1.5	15.3±0.9	73.9
	0~10 cm topsoil amended	29.8±1.6	27.2±1.3	14.7±0.6	71.7
	0~15 cm topsoil amended	20.7±1.6	44.4±2.0	6.10±0.12	71.2
Acetochlor	Control	59.2±4.2	–	9.87±0.73	69.1
	0~10 cm topsoil amended	16.9±0.7	33.6±2.2	13.2±0.6	63.7

most of the lingo-cellulosic biopolymers are thermally decomposed at temperatures above 200 °C (Özyurtkan et al. 2008; Uchimiya et al. 2011). The low H/C and O/C ratios of the PW500 biochar illustrate a low residue of the non-carbonized organic fraction, and the high SSA and IR absorption imply a high degree of carbonization and aromaticity in this product. By comparison, the PW350 biochar has a higher content of residual organic matter than the PW500 biochar, and both biochars contain porous structures that can be observed under the scanning electron microscope (Fig. 7) (Steinbeiss et al. 2009; Lee et al. 2010). The combination of these two features provides an advantage for the PW350 biochar compared with the other two biochars with respect to sorption of herbicides.

Generally, organic molecules are sorbed by biochars via two mechanisms, namely surface adsorption on the carbonized C matrix and partition in the non-carbonized organic matter (Chun et al. 2004; Chen et al. 2008), so the sorption capacity of biochars is related to both surface area and organic content. Our experimental results indicated higher sorption of herbicides by the PW350 biochar obtained at a lower HTT, although some previous reports showed enhanced sorption of organic pollutants by biochars prepared at higher HTTs (Chun et al. 2004; Chen et al. 2008; Uchimiya et al. 2010). Sun et al. (2011) attributed the high sorption of fluorinated herbicides by low temperature (400 °C) biochars to the amorphous C phase composed of small, heat-resistant aliphatic and (hetero-)aromatic elements. The IR spectrum (Fig. 1) indicates that the PW350 biochar contains increased amount of low-molecular weight aromatic compounds, which gives it greater affinity for aromatic 2,4-D and acetochlor molecules, so that high sorption was observed, even at low herbicide concentrations. The higher content of organic matter in the PW350 biochar than in the PW500 biochar results in greater sorption of both herbicides. Also, the porous structure of the PW350 biochar provides more internal space for sorption of herbicides than the PW200 biochar does. Therefore, the PW350 biochar showed higher sorption of herbicides than either the PW200 or

Fig. 7 Images of **a** PW350 and **b** PW500 biochars under the scanning electron microscope (magnified 3,000 times)
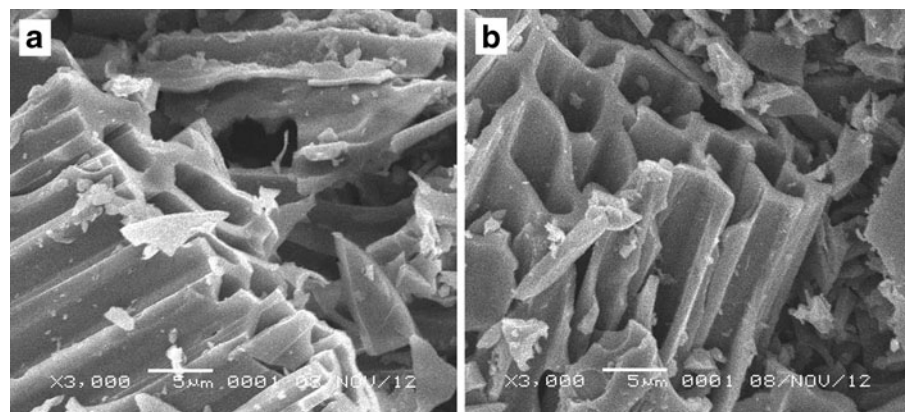
PW500 biochars. The contribution of both surface adsorption and partition can also be confirmed by the medium n_f values for the sorption isotherms of the two herbicides by the PW350 biochar (Chen et al. 2008; Li et al. 2009).

In contrast to previous reports on the nearly irreversible sorption of pesticides in soils amended with high-temperature (850 °C) biochar (Yu et al. 2006; Yu et al. 2010), the sustained release of herbicides 2,4-D and acetochlor in the biochar-amended soil was achieved by using the low-temperature biochar simultaneously as the carrier for incorporating herbicides. The release rate of herbicides could be further regulated by changing the dose of the biochar used. Such a controlled release behavior of herbicides could be explained as: firstly, the herbicides incorporated in the biochar sorbent can be released but at a slower release rate. Secondly, the released herbicides may be adsorbed again by the biochar-amended soil, and then be released again during the watering. So an overall effect similar to using controlled release formulations (CRFs) of herbicides will be obtained, and the herbicides' efficacy may be retained for a much longer period without increasing their application dose in the soil (Mogul et al. 1996; Garrido-Herrera et al. 2006; Radian and Mishael 2008; Kumar et al. 2011). As mentioned in the experimental method, the rate of rinsing used in the release experiments is higher than the intensity of moderate rain, and the cumulative amount of water (72 mm) used in one experimental cycle (9 h) is much higher than the average daily precipitation in the rainy season in most subtropical and temperate zones (Schneider et al. 2008). The high rate of rinsing means diluted herbicide concentration in soil water, which favors the desorption of herbicides and leads to the quick release of herbicides. Therefore, we can propose that the dose of biochar used in the release experiments (0.5~1.0 % in weight of soil) is adequate for significantly controlling the release of herbicides in field where lower rate of rinsing is anticipated. The results suggest a potential method for biochar application in agronomic practice, by which we may benefit from biochars as a soil amendment and worry less about their impact on the efficacy of soil-applied herbicides. However, the release behavior of herbicides in field applications will be different from that observed in the laboratory, because it is influenced by many environmental factors such as the wetting and drying cycle, soil compositions and temperature, etc. (Qiu et al. 2009; Goldreich et al. 2011). Intensive field research is required before we can determine quantitatively the ideal dose of both herbicides and biochar used, so as to retain the herbicides' efficacy and minimize their pollution.

The controlled release of herbicides by using the PW350 biochar as a sorbent makes it possible to retard the herbicides' leaching in soil, thus minimizing their potential pollution to groundwater (El-Nahhal et al. 1998; Cox et al. 2000; Fernández-Pérez et al. 2011). The results of leaching experiments indicate that the low temperature (PW350) biochar can remarkably reduce the potential pollution of groundwater by reducing the leached amount of herbicides, when it was used as the sorbent for incorporating herbicides and also for soil improvement (Wang et al. 2010; Jones et al. 2011; Lü et al. 2012). The cumulative amount of irrigation (720 mm) used in one cycle of leaching experiments (12 days with daily irrigation of 10 h) is much higher than the average month precipitation in the rainy season in most subtropical and temperate zones (Schneider et al. 2008), and also much higher than the recommended amount of irrigation for corn in its grain-filling period (2.0 in. weekly, equal to 218 mm monthly) (Rhoads and Yonts 2000). The higher rate of irrigation leads to the quicker leaching of herbicides in soil (Troiano et al. 1992), so we can propose that the dose of biochar used in the experiments (1.0 % in weight of the topsoil) is adequate for significantly reducing the leaching of herbicides in field where less precipitation or irrigation is anticipated. The higher retention of herbicides in the topsoil might serve as a reservoir for sustained release of active ingredients, and help retain their efficacy for a longer period. However, we should acknowledge that these retained herbicides in the topsoil have complex interactions with various components in the biochar-amended soil system (Kookana 2010), so further field investigations are required before we can provide definite conclusions on the releasibility and efficacy of these retained herbicides.

Conclusions

The poplar wood biochar made at a relatively low treatment temperature (350 °C) (PW350) showed high sorption of the herbicides acetochlor and 2,4-D, which makes it a good choice as an adsorptive carrier for

incorporating herbicides. When this PW350 biochar was used simultaneously as the carrier and a soil amendment, the controlled release and retarded leaching of both herbicides in soil was obtained. The results suggest that the proper application of low-temperature biochar in soil can minimize the pollution of soil-applied herbicides while extending their efficacies, which deserves further investigations in bioassay and field experiments.

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