

# Use of Rice Straw Biochar Simultaneously as the Sustained Release Carrier of Herbicides and Soil Amendment for Their Reduced Leaching

Jinhong Lü, Jianfa Li,\* Yimin Li, Baozhu Chen, and Zhangfeng Bao

Department of Chemistry, Shaoxing University, Zhejiang 312000, China

**S** Supporting Information

**ABSTRACT:** The sustained release and reduced leaching of herbicides is expected for enhancing their efficacy and minimizing their pollution. For this purpose, the rice straw biochar made at a relatively low temperature (350 °C) (RS350) was used simultaneously as the carrier for incorporating herbicides besides as the soil amendment. In this way, the sustained release of herbicides acetochlor and 2,4-D was obtained in the release experiments, due to the high and reversible sorption by RS350 biochar. Besides, the RS350 biochar significantly reduced the leached amount of herbicides by 25.4%–40.7% for acetochlor, and by 30.2%–45.5% for 2,4-D, depending on the depth (50 or 100 mm) of biochar-amended soil horizon. The high retention of both herbicides in the biochar-amended topsoil makes it possible to extend their efficacy. The results suggest a potential way of using low temperature biochars to reduce the leaching of herbicides without impacting their efficacy.

**KEYWORDS:** *biochar, pesticide, sustained release, leaching, sorption*

## INTRODUCTION

The movement of pesticides in soil is decisive for their efficacy and potential pollution to environment. The leaching of pesticides in soil generally greatly reduces their efficacy and makes them an important source of groundwater pollution.<sup>1</sup> Despite this environmental problem, the use of pesticides is still essential for agronomic practice in most regions so as to maintain enough food supply for increasing population in an efficient way.<sup>2</sup> Therefore, how to enhance the efficacy of pesticides and minimize their pollution is always an important issue in both agricultural and environmental chemistry, and many attempts in this subject have focused on regulating their release and leaching behaviors in soil.<sup>3–11</sup> One practical path is to control the release of pesticides by incorporating them using some sorbents. For example, the montmorillonite clay showed high sorption to pesticides after modification by ion exchange reaction with inorganic or organic cations, and the modified products have been used as the carrier in the controlled release formulations of pesticides.<sup>3–5</sup> Because of the enhanced sorption by modified clays, the release of active ingredients (a.i.) from the formulations was slowed.<sup>3,4</sup> So the efficacy of soil applied herbicides at the topsoil was extended and their application dose reduced.<sup>6,7</sup> At the same time, the amount of pesticides available for leaching was reduced, and their pollution to groundwater was minimized.<sup>8,9</sup> Another potential path is to improve the pesticides' retention in soil by enhancing their sorption on soil. For this purpose, using some organic soil amendments such as olive waste<sup>10</sup> and peat<sup>11</sup> could help to control the movement of some pesticides in soil and reduce their leaching, although the performance would be affected by some other factors like dissolved organic matters.<sup>12,13</sup>

In recent years, biochars, produced by thermal decomposition of biomass under limited supply of oxygen, have received increasing attention as soil amendment. Besides the

great potential on carbon sequestration, introduction of biochars in soil will provide multiple benefits including improved soil properties, enhanced retention and availability of nutrients, and increased water holding capacity, etc.<sup>14–16</sup> Being good sorbents for many organic molecules,<sup>17,18</sup> biochars will surely influence the movement of organic pesticides in soil if they were applied as soil amendments. Until now, most of the published results have shown the enhanced sorption of pesticides by soil amended with biochars or charcoals and suggested the extended retention and reduced leaching of pesticides in soil.<sup>19–23</sup> However, the strong sorption by biochars is not always desirable for pesticide application in agronomic practice, as particularly the efficacy of pesticides would be impacted.<sup>24</sup> The nearly irreversible sorption of pesticides by biochars made at high pyrolysis temperature (>800 °C) may decrease the pesticides' phytoavailability<sup>23</sup> and reduce the efficacy of soil-applied herbicides.<sup>25</sup>

In this context, the biochars as soil amendment should be well selected and properly used to obtain a compromise between the release and leaching behaviors of herbicides in soil, so as to maintain their efficacy at the same time as controlling their pollution.<sup>24</sup> For this purpose, the rice straw biochars made by slow pyrolysis at relatively low pyrolysis temperatures (200–500 °C) are adopted in this study to regulate the release and leaching of herbicides. The pyrolyzed products are acid washed, dried, and directly used without further post-treatment in view of production cost, so the biochar samples may contain some stable minerals from the rice straw. Next, the biochars are used as the adsorptive carrier for incorporating herbicides, and also

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applied as soil amendment for retaining herbicides in the topsoil. Their influence on the release and leaching of herbicides is investigated with release experiments through a thin soil layer and with soil column experiments. Two herbicides investigated are 2,4-D (2,4-dichlorophenoxyacetic acid) and acetochlor (2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl) acetamide). Both of them are widely used in croplands and have relatively high leaching potential,<sup>26,27</sup> and then pose a threat of surface and groundwater contamination.<sup>28,29</sup>

## MATERIALS AND METHODS

**Herbicides and Soil.** Technical grade herbicides 2,4-D (98.2% purity, acid form) and acetochlor (96.2% purity) were kindly supplied by Hangzhou Qingfeng Agrochemicals Co. Ltd., China. The soil used was collected locally from the top layer of red soil, a kind of ferrallitic soil widely distributed in Southern China. The soil has a pH of 4.8 (determined in a 1:2.5 soil/water (w/w) suspension using a Sartorius-PB10 pH meter), organic matter content of 0.6% (by Walkley-Black acid digestion method<sup>30</sup>), and CEC of 0.11 mmol g<sup>-1</sup> (by barium acetate method<sup>31</sup>). The soil was air-dried and sieved through a 2 mm screen before use.<sup>26</sup>

**Preparation and Characterization of Rice Straw Biochars.** The rice straw biochars were prepared with a thermal decomposition process at relatively low temperatures under oxygen-limited condition.<sup>17</sup> First, the rice straw collected locally was pretreated by a procedure of rinsing, drying, and cutting into chips of 2 mm × 2 mm in size. The rice straw chips (10 g) were added in a ceramic pot fitted with a lid, and then the pot was placed in a Muffle furnace at a set temperature. After thermal treatment of 6 h, the solid residue was soaked in 100 mL of 1 mol L<sup>-1</sup> hydrochloric acid solution at room temperature four times (4 h each time), and then washed with distilled water another four times, then the solid char was oven-dried at 70 °C to a constant weight. The resulting product was mechanically ground to less than 0.15 mm in size. The samples obtained at different pyrolysis temperatures of 200, 350, or 500 °C are referred to hereafter as RS200, RS350, and RS500, respectively. The yield of biochars was calculated on the basis of the initial weight of dried rice straw chips. The Brunauer–Emmett–Teller (BET) specific surface area (SSA) of biochar samples was obtained from nitrogen adsorption data at 77 K in an ASAP 2020 system (Micromeritics). The elemental (C, H, N, O, S) contents in the biochars were determined in a PE2400-II elemental analyzer (Perkin-Elmer). ATR-IR spectra were recorded in the 4000–675 cm<sup>-1</sup> region using a Nicolet Nexus FTIR spectrophotometer. Ash content was measured by heating the samples at 800 °C for 4 h.

**Sorption and Desorption Experiments.** 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 ( $C_0$ , μmol L<sup>-1</sup>), which ranged from 100 to 600 μmol L<sup>-1</sup> for acetochlor ( $C_s = 826$  μmol L<sup>-1</sup> (25 °C)<sup>32</sup>), and from 270 to 1360 μmol L<sup>-1</sup> for 2,4-D ( $C_s = 1360$  μmol L<sup>-1</sup> at pH = 1 (20 °C) and increases with pH<sup>33</sup>), respectively. The sorption experiment was carried out in a thermostatic shaker bath at 25 ± 0.1 °C for 24 h. Preliminary experiments on sorption kinetics confirmed that the sorption equilibration had been reached within 24 h (Figures S1 and S2, Supporting Information). After which, the pH in the dispersion was measured (the results are shown in Tables S1 and S2, Supporting Information). Next, the dispersion was centrifuged, and the supernatant solution filtered through a 0.22 μm microporous membrane was sampled for analysis of herbicide concentration. The analysis was conducted in an Agilent 1200 HPLC system equipped with an ultraviolet detector. The herbicides acetochlor and 2,4-D were analyzed at 225 and 282 nm, respectively, with detection limits of 0.3 μmol L<sup>-1</sup> for acetochlor and 0.5 μmol L<sup>-1</sup> for 2,4-D. The amount adsorbed ( $Q_e$ , μmol g<sup>-1</sup>) was calculated from the difference in concentration between the initial ( $C_0$ , μmol L<sup>-1</sup>) and the equilibrium ( $C_e$ , μmol L<sup>-1</sup>) solutions. Blanks without herbicide and triplicates of each sorption point were used in

every series of experiments. Desorption experiments were performed immediately after sorptions at the highest equilibrium concentrations. Ten milliliters of supernatant was removed for analysis, and replaced with 10 mL of distilled water. After being shaken at 25 ± 0.1 °C for 24 h, the dispersion was centrifuged, and another 10 mL of supernatant was replaced by distilled water. This desorption cycle was repeated four times.

**Release Experiment through a Thin Soil Layer.** The release experiment was carried out in a Buchner funnel (80 mm inner diameter) paved with a thin soil (red soil or biochar-amended soil) layer (ca. 20 mm thick) at the bottom.<sup>34,35</sup> For the release experiment through the biochar-amended soil layer (the schematic installation is shown in Figure S3, Supporting Information), the biochar sample was mixed with red soil (116 g), in which the biochar accounted for 0.5% and 1.0%, respectively, by weight. Next, the biochar-amended soil was deposited on a nylon filter cloth (0.05 mm in mesh size) paved in the funnel. The herbicide was incorporated to the biochar before application on the soil layer. 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-loading biochar was air-dried in a ventilation cabinet and mixed with 10 g of red soil. In this way, the ratio of biochar in the herbicide-loading mixture is also nearly 0.5% or 1.0% by weight, the same ratio as that used in the biochar-amended soil layer. The herbicide-loading soil mixture then was applied uniformly on the top of the soil layer. The dose of herbicide is equivalent to the application of 400 mg m<sup>-2</sup>, a value much higher than ordinary application in field. The high dose is selected due to the consideration of detection accuracy by HPLC methods mentioned above. In the release experiments, the funnels were sprayed with distilled water nine times with a 1 h interval, and the volume of water for each spray was 40 mL (completely sprayed within 8–10 min). The rinsed solution was collected, and the amount of herbicide released ( $M_i$ , mg) was calculated from its concentration in the solution. Next, the cumulative percentage of herbicide released after watering  $n$  times ( $(\sum_{i=1}^n M_i/M_0) \times 100\%$ ) was calculated. The experiment for each treatment was performed in triplicates. For comparison studies, two control experiments were designed, respectively, as: Control-I, the technical herbicide (acetochlor or 2,4-D) was applied directly on the red soil layer, and no biochar was used in the experiments; Control-II, the technical acetochlor was applied directly on the biochar-amended soil layer, in which the biochar was used only in the soil layer at the ratio of 0.5% by weight.

**Leaching Experiment in the Soil Column.** The soil column was prepared by filling red soil (or amended soil with biochar at the ratio of 1.0% by weight) in a polyvinyl chloride (PVC) pipe (400 mm length, 46 mm internal diameter).<sup>36,37</sup> A piece of nylon filter cloth was laid at the bottom and every 50 mm segment of soil in the pipe, to redistribute the flow and separate the soil layer. Each column contained, from the bottom to the top, a layer of acid washed sand (20 mm), soil layer of six segments (6 × 50 mm = 300 mm, with biochar-amended soil used in the top one or two segments, respectively), and a top sand layer (20 mm) (the schematic column is shown in Figure S4, Supporting Information). The bottom sand layer was used to prevent the displacement of soil, and the top sand layer to distribute the dripping water evenly around the cross-section of soil column. The bulk density of soil filled in the column was estimated to be 1.26 g cm<sup>-3</sup>, 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 mol L<sup>-1</sup> CaCl<sub>2</sub> aqueous solution and then left for draining overnight.

The herbicide containing a.i. of 2.0 mg ( $M'_0$ ) was applied uniformly on the top of sand layer in a mixture with 100 mg of biochar and 10 g of red soil, and the mixing procedure was the same as that used in the release experiments. After herbicide application, an additional sand layer (10 mm) was added to the top of the column. Next, the column was eluted with distilled water using a peristaltic pump at a flow rate of 10 mL h<sup>-1</sup>. The leachate was collected in fractions of 100 mL each day, and total elution of 12 days was conducted in duplicates. Next, the leachate was further concentrated under vacuum to a volume of 10 mL, and the herbicide concentration was analyzed with the HPLC method mentioned above. The amount of herbicide leached ( $M'_i$ , mg)

Table 1. Characteristics and Compositions of Biochars

sample	yield (%)	SSA <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	ash (%)	compositions of organic elements							
				C (%)	H (%)	N (%)	O (%)	S (%)	H/C <sup>b</sup>	O/C <sup>b</sup>	
RS200	68.9 ± 0.4	2.1	11.5	46.7	5.00	0.790	34.3	0.705	1.29	0.551	
RS350	27.8 ± 1.2	20.6	31.0	46.9	1.34	2.08	12.3	0.075	0.342	0.197	
RS500	17.3 ± 0.9	128	48.4	40.7	0.15	1.18	4.14	0	0.044	0.076	

<sup>a</sup>Specific surface area. <sup>b</sup>Atomic ratios.

each day was calculated by multiplying the herbicide concentration with the volume of concentrated leachate. The percentage of herbicide leached each day was calculated as  $(M'_i/M'_0) \times 100\%$ .

On completion of leaching experiment, each segment of soil and the top layer for herbicide application was removed from the column separately, and dried at room temperature. Samples (10 g) of soil and sand were extracted in conical flasks with 30 mL of methanol–water mixture (80: 20, V/V) four times. The total extractive solution was filtered and concentrated under vacuum to a volume of 5 mL. Finally, the herbicide concentration in the condensed solution was analyzed with the HPLC method, the residual amount of herbicide ( $M''_i$ , mg) in each layer was calculated, and the percentage of residual herbicide was obtained as  $(M''_i/M'_0) \times 100\%$ . In the duplicated control leaching experiments, the technical herbicides (2.0 mg a.i.) were dissolved in methanol and applied to the top of each soil column packed with the red soil.

## RESULTS AND DISCUSSION

**Biochar Characterizations.** The compositions and properties of biochar were greatly influenced by process conditions of thermal treatment, as well as those of pre- and post-treatment. Among which, the heat treatment temperature (HTT) was generally recognized to be the most important. Thermal decomposition of lignocellulosic materials at high HTTs (>600 °C) results in biochars with high aromaticity and maturation, while the products treated at relatively low HTTs may vary apparently in their compositions and properties.<sup>38</sup> The elemental compositions and specific surface areas (SSA) of rice straw biochars obtained at three treatment temperatures (200, 350, and 500 °C) are shown in Table 1. Corresponding infrared spectra of these three products are given in Figure 1.

Despite the higher content of minerals in rice straw than other lignocellulosic materials such as wood, the thermal decomposition of rice straw at the relatively low temperature

mainly occurred on the organic matters. In general, thermal degradation of lignocellulosic materials begins at dehydration, followed by depolymerization, fission, and carbonization, etc. The accompanying vaporization of gasified matters increases with increasing treatment temperature, which results in the decreased yield of biochar products.<sup>17,39</sup> The higher H/C atomic ratio of RS200 biochar, less than but close to that of lignocellulosic polymers (ca. 1.3–1.6), indicates the dehydration of biopolymers in the rice straw. The absorption bands at 3379, 2925, and 1056 cm<sup>-1</sup> in the IR spectrum of RS200 biochar represent the vibrations of hydroxyl, and methylene and ether groups in the biomass.<sup>37</sup> The peak at 1716 cm<sup>-1</sup> is assigned to C=O groups generated by dehydration of biopolymers.<sup>39</sup> For RS350 biochar, the H/C and O/C ratios decreased in comparison with RS200 biochar, indicating the increased degree of aromaticity and carbonization.<sup>17</sup> In the IR spectrum of RS350 biochar, we can observe the intensifying absorptions at 1616 and 799 cm<sup>-1</sup> that belong to the aromatic structure.<sup>17,39</sup> The diminishing absorptions at 3379 and 2925 cm<sup>-1</sup> imply the intensive depolymerization at this temperature (350 °C), accompanied by the significant mass loss and creation of porous C matrix, as indicated by the increased specific surface area (Table 1). At the treatment temperature of 500 °C, the biopolymers were completely depolymerized as that indicated by the disappearance of absorption bands at 2925 and 1716 cm<sup>-1</sup> in the IR spectrum of RS500 biochar. The stronger band at 1079 cm<sup>-1</sup> should be ascribed to the overlapped absorptions of both C–O bonds<sup>17,39</sup> and Si–O structure of minerals<sup>7</sup> that had not been washed away during the acid treatment of biochar samples. The absorptions corresponding to the aromatic C=O, C–O, and –OH structures were observed in the IR spectra of both RS350 and RS500 biochars, implying the presence of aryl carboxylic acids in both biochar samples. The acidity of these biochar samples can also be confirmed by low pH in their aqueous dispersions (Table S1, Supporting Information). The residue of stable minerals in the biochar samples RS350 and RS500 is confirmed by the high ash content in these samples. The amount of these minerals in the biochars increased with the increasing treatment temperature, indicating little loss of these minerals during the thermal treatment at relatively low temperature. Despite this, the high specific surface area of RS500 indicates that the development of porous C structure has not been hindered by these minerals.

### Sorption and Desorption of Herbicides on Biochars.

Figures 2 and 3 show sorption isotherms of herbicides acetochlor and 2,4-D on three biochars. For both herbicides, the isotherms display increasing nonlinearity with the increase of treatment temperature for preparing biochars, corresponding to the increasing deviation from 1 of Freundlich  $n_f$  values (Table 2). The sorption isotherms of both herbicides on RS200 biochar are nearly linear, with respective Freundlich  $n_f$  close to 1. The linear sorption on RS200 suggests a mechanism of partition of herbicides in the organic phase of this biochar,<sup>40</sup>

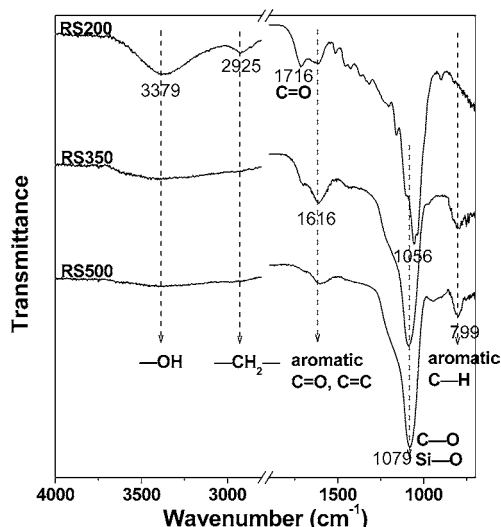
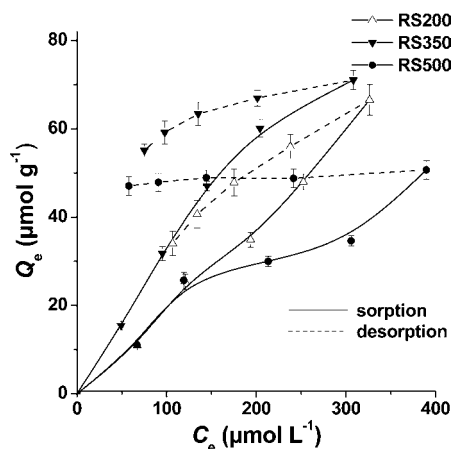
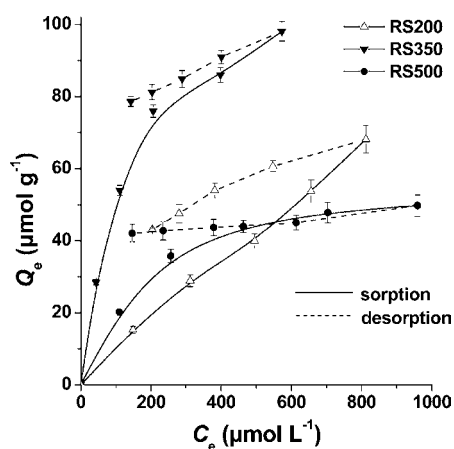


Figure 1. ATR-IR spectra of biochars.



**Figure 2.** Sorption and desorption of acetochlor on biochars at 25 °C (error bars represent the standard deviation of triplicates).



**Figure 3.** Sorption and desorption of 2,4-D on biochars at 25 °C (error bars represent the standard deviation of triplicates).

which has the highest content of organic matter among the three biochars, as indicated by the high H/C and O/C ratios (Table 1). In comparison, the decreased Freundlich  $n_f$  values for sorption isotherms on RS500 biochar indicate the transition to surface adsorption on the carbonaceous matrix.<sup>17,40</sup> The enhanced sorption to acetochlor at high equilibrium concentration ( $>300 \mu\text{mol L}^{-1}$ ) was observed on RS500 biochar, which may be related to the improved hydrophobicity of this biochar after presorption of some acetochlor.<sup>3,4</sup> Within the low to moderate herbicide concentrations (e.g.,  $C_e/C_s = 0.05\text{--}0.5$  for acetochlor), the highest sorption is observed on RS350 biochar for both herbicides (Figures 2 and 3), with moderate Freundlich  $n_f$  and high  $K_f$  of sorption isotherms. The high sorption on RS350 biochar may be attributed to a mechanism

combining the surface adsorption and partition, because this biochar has a higher surface area than RS200 sample, and a higher content of organic phase than RS500 sample (Table 1). It is worth mentioning that the sorption to 2,4-D may be influenced by pH in aqueous phase, because 2,4-D as an organic acid will dissociate partly at high pH.<sup>41</sup> Yet in our sorption studies, the pH values in the dispersions of various biochar samples were very close to each other, if the dispersions of same initial 2,4-D concentration were compared (Table S2, Supporting Information). So the high sorption to 2,4-D by RS350 biochar did not result from the pH difference.

Many previous studies indicate the higher sorption of organic pollutants on biochars obtained at higher treatment temperature.<sup>17,40</sup> However, a higher sorption of herbicides on RS350 biochar than on RS500 biochar was observed in this study. The reasons may be related to the difference in chemical compositions between biochars from various origins and made by different processes. The biochars used in this study contain a considerable part of stable minerals that has not been removed during the post-treatment. The washing with dilute hydrochloric acid may remove some soluble minerals such as carbonates, but most insoluble silicon compounds from the rice straw were left in the biochar samples. This is particularly obvious for RS500 biochar, in which the stable minerals (ash) account for nearly one-half mass of the sample. The poor adsorption of herbicides by these minerals should be one reason for the lower sorption by RS500 biochar in overall than RS350 biochar. Besides, the removal of some functional groups in carbonization of organic matters at higher treatment temperature may also result in the decreased sorption to herbicides by biochars.<sup>39,42</sup>

The results of desorption experiments, as shown in Figures 2 and 3, indicate a nearly irreversible adsorption of herbicides on RS500 biochar. The hysteresis index (HI) for acetochlor desorption from RS500 biochar is very close to 0 that is indicative of complete irreversibility.<sup>43</sup> In comparison, the sorption on RS350 and RS200 biochars is reversible, although an obvious hysteresis was indicated by the medium HI values.<sup>43</sup> The irreversible adsorption indicates a strong bonding of herbicides on the biochar made at high temperature and with high specific surface area, which will restrain the release of herbicides and reduce their efficacy on weed control.<sup>25</sup> Instead, both biochars made at low treatment temperatures (RS350 and RS200) may be potential carriers of herbicides for their sustained release in soil.

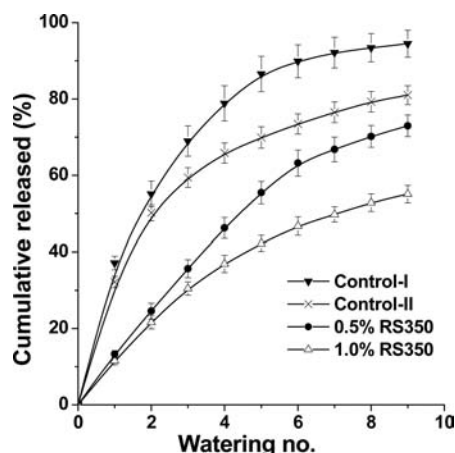
**Sustained Release of Herbicides through the Biochar-Amended Soil.** The performance of controlled release formulations of pesticides can be evaluated by release experiments through a thin soil layer.<sup>34,35</sup> In this study, the RS350 biochar showing high and reversible sorption was used for incorporating the herbicide acetochlor, and the soil used in

**Table 2.** Freundlich Parameters for Sorption/Desorption of Herbicides on Biochars

herbicide	biochar	$K_f$ ( $\text{L g}^{-1}$ )	$n_{f,\text{sorption}}$	$R_{\text{sorption}}$	$n_{f,\text{desorption}}$	HI <sup>a</sup>
acetochlor	RS200	$0.122 \pm 0.013$	$1.09 \pm 0.016$	0.987	$0.590 \pm 0.028$	0.543
	RS350	$0.648 \pm 0.091$	$0.845 \pm 0.030$	0.979	$0.175 \pm 0.009$	0.208
	RS500	$0.565 \pm 0.022$	$0.744 \pm 0.011$	0.950	$0.035 \pm 0.008$	0.047
2,4-D	RS200	$0.206 \pm 0.013$	$0.860 \pm 0.007$	0.997	$0.333 \pm 0.021$	0.342
	RS350	$5.48 \pm 0.37$	$0.467 \pm 0.008$	0.973	$0.160 \pm 0.006$	0.308
	RS500	$3.24 \pm 0.21$	$0.412 \pm 0.012$	0.954	$0.082 \pm 0.004$	0.199

<sup>a</sup>Hysteresis index =  $n_{f,\text{desorption}}/n_{f,\text{sorption}}$ .

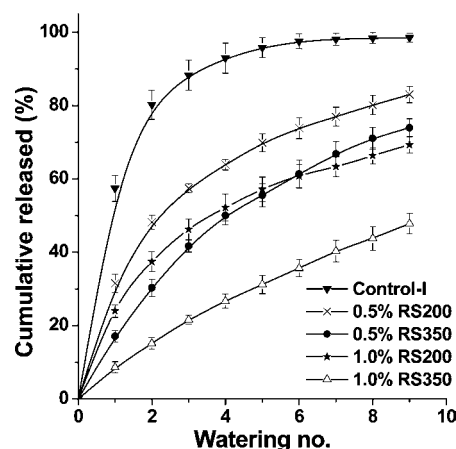
release experiments was amended with the same biochar at the ratio of 0.5% (wt) or 1.0% (wt), respectively. The release profiles are shown in Figure 4, and the results of two control



**Figure 4.** Sustained release of biochar-loaded acetochlor through the soil amended with RS350 biochar (e.g., 0.5% RS350 represents the ratio of RS350 biochar in soil accounting for 0.5% by weight) (error bars represent the standard deviation of triplicates).

experiments (Control I and Control II) are also included for comparison. As can be seen, the release of technical acetochlor through the original red soil (Control I) was very quick, with the active ingredient almost totally released within the nine times of watering. The release of technical acetochlor through the biochar-amended soil layer (Control II) was slowed. More apparently, the release rate of acetochlor through the biochar-amended soil was further decreased by incorporating it in the biochar first (see curves denoted as 0.5% RS350 or 1.0% RS350, Figure 4). As expected, the enhanced ratio of RS350 biochar in soil further decreased the release rate of acetochlor. These results display the potential of biochars on regulating the release behavior of herbicides in soil. It is worth mentioning that the biochar should be used to incorporate the herbicide besides as the soil amendment, so as to achieve the better performance on slowing its release. Although the amount of biochar used for incorporating herbicide is very low, the distinctly enhanced performance shows that the biochar made at low treatment temperature is a good choice as the sustained release carrier of herbicides. The quick release of technical acetochlor through the biochar-amended soil (Control II) may be related to the interactions between soil and the biochar when mixing them together and during the saturation of the soil layer with water. The soil components may occupy some sorption sites on the biochar surface before the herbicide molecules can reach them during the watering, and resulting in the reduced sorption of herbicide.<sup>44,45</sup> By incorporation first in the biochar carrier, the herbicide molecules were mostly adsorbed or absorbed. During the watering, the herbicide molecules desorbed and diffused gradually into the aqueous phase. During the movement in the soil layer, the herbicide molecules may have a chance to compete for sorption sites on the biochar-amended soil. In this way, the total amount of herbicide released through the soil layer is reduced gradually.

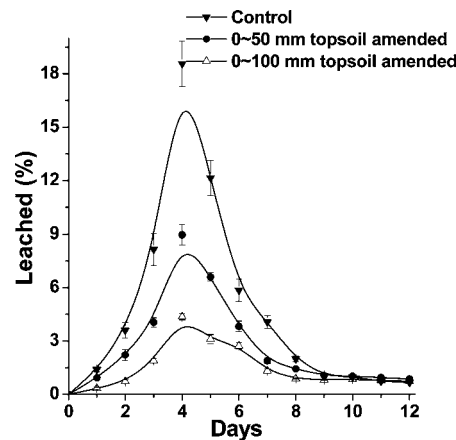
Figure 5 displays the release behaviors of 2,4-D by using RS200 and RS350 biochars in the same way as that for acetochlor treatment. The technical 2,4-D was almost completely released within six times of watering (Control I,



**Figure 5.** Sustained release of biochar-loaded 2,4-D through the soil amended with biochars (e.g., 0.5% RS200 represents the ratio of RS200 biochar in soil accounting for 0.5% by weight) (error bars represent the standard deviation of triplicates).

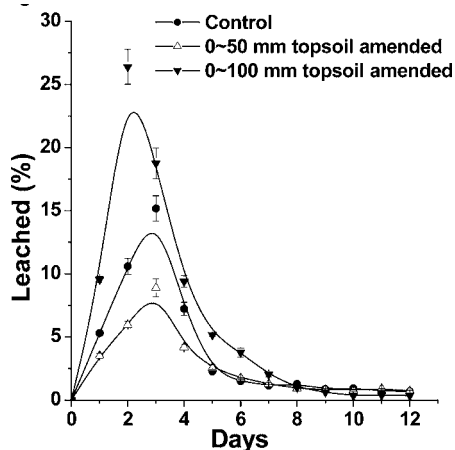
Figure 5). In comparison, its release was significantly slowed by incorporating in the biochars, then through the biochar-amended soil. At the same ratio of biochar, the quicker release of 2,4-D by using RS200 biochar is corresponding to its lower sorption capacity as compared to that of RS350 biochar. The results imply that the biochars showing relatively high and reversible sorption are useful for the sustained release of herbicides in soil, and the release rate may be regulated by choosing suitable biochars for incorporating herbicides and as the soil amendment simultaneously.

**Reduced Leaching of Herbicides in Biochar-Amended Soil.** Although some previous studies<sup>22,46</sup> have shown the reduced leaching of pesticides by using biochars as soil amendment, Cabrera et al.<sup>47</sup> indicated that not all biochars will show this effect. The uncertainty is mostly ascribed to the complex competitive sorptions within the herbicide-applied and biochar-amended soil system. In this study, considering the better performance of RS350 biochar on slowing the release of herbicides through soil when it was used simultaneously as the adsorptive carrier and soil amendment, we used it in the following leaching experiments in soil columns in a same way. That is, before application on the top of soil column, both herbicides were incorporated in the RS350 biochar. Figures 6



**Figure 6.** Biochar-loaded acetochlor leached each day in soil columns (error bars represent the standard deviation of duplicates).

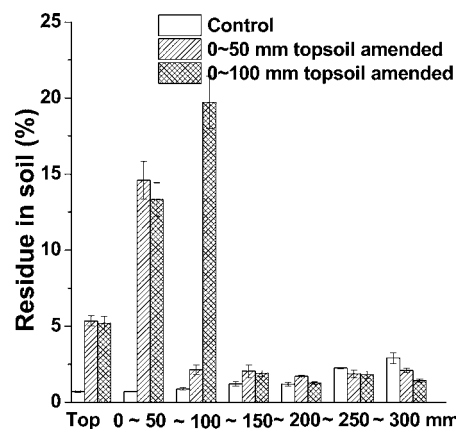
and 7 show the results of leaching experiments in the soil columns packed with different depth of biochar-amended soil.



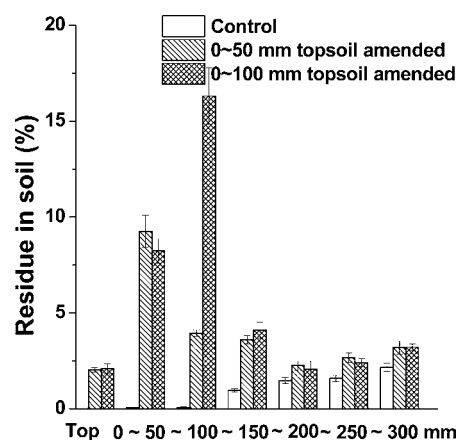
**Figure 7.** Biochar-loaded 2,4-D leached each day in soil columns (error bars represent the standard deviation of duplicates).

The comparative leaching results of technical herbicides in columns packed with the original red soil (Control) indicate that the breakthrough appeared at the fourth day for acetochlor, and at the second day for 2,4-D. The earlier breakthrough of 2,4-D is relative to its higher hydrophilicity and solubility than acetochlor. The leached amount each day of herbicide acetochlor is apparently reduced by using RS350 biochar as the carrier and soil amendment, although no apparent hysteresis of breakthrough was observed (Figure 6). The total amount of acetochlor leached after 12 days is 33.8% when the 0–50 mm topsoil was amended by biochar, and only 18.5% when the 0–100 mm topsoil was biochar-amended. In comparison with the result in control experiment, the total leached amount of acetochlor was decreased by about 25.4% and 40.7%, respectively, in the two treatments. The hysteresis of breakthrough of herbicide 2,4-D was observed (Figure 7) when RS350 biochar was used in the soil column, in comparison with the control experiment. Meanwhile, the total leached amount of 2,4-D was also greatly reduced by 30.2% and 45.5%, in columns packed with the biochar-amended soil, respectively, in the top 0–50 mm and 0–100 mm layers. These results indicate that the biochar can reduce the potential pollution of herbicides to groundwater.

Figures 8 and 9 show the residual amount of herbicides recovered in different layers of above soil columns. The apparent retention of both herbicides was observed in columns packed with the biochar-amended soil. The retained amount of acetochlor after 12 days accounted for 14.6% and 33.0% in the top 0–50 mm and 0–100 mm layer packed with amended soil, respectively. In the corresponding treatments of 2,4-D (Figure 9), there were also 9.3% and 24.5% of initial mass of herbicide retained, respectively, in the top 0–50 mm and 0–100 mm soil layer amended with the biochar, respectively. In contrast, most of the technical herbicides were leached away from the columns packed with the original red soil. The higher retention of herbicides in the topsoil may possibly help to keep their efficacy for a much longer period, as the release potential of these retained active ingredients has been confirmed by the release experiments. Despite these inspiring results, we should keep it in mind that the efficacy of herbicides, like soil-applied fertilizers, depends on many practical issues (e.g., the crop



**Figure 8.** Residual acetochlor in various soil horizons (“top” means the top layer for herbicide application).



**Figure 9.** Residual 2,4-D in various soil horizons (“top” means the top layer for herbicide application).

cycle) in agronomic operations.<sup>48</sup> The complex interactions existing in the biochar-amended soil system, such as the interactions with clay minerals, may also influence the release and leaching of soil-applied herbicides. Therefore, further investigations are definitely needed before an ideal compromise between the sustained release and reduced leaching of herbicides can be obtained by using the low-temperature biochars.

In conclusion, the rice straw biochar made at low treatment temperature (350 °C) showed high and reversible sorption to herbicides acetochlor and 2,4-D, which enable this biochar to be a good carrier for incorporating herbicides. When the biochar was simultaneously applied as the herbicide carrier and soil amendment, the sustained release and reduced leaching of herbicides were obtained. The high retention of herbicides in the biochar-amended topsoil may help to retain their efficacy for a longer period, which is worthy of further investigations. The results suggest it is possible to minimize the pollution of soil-applied herbicides at the same time as extending their efficacy by using the low-temperature biochars in a proper way.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Sorption kinetics of herbicides by biochars, pH in aqueous dispersions of biochars, pH in dispersions for sorption studies, and schematics for release and leaching experiments. This

material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*Tel.: +86 575 8832 0583. Fax: +86 575 8834 1521. E-mail: [ljf@usx.edu.cn](mailto:ljf@usx.edu.cn).

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### Notes

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