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Assessment of herbicide sorption by biochars and organic matter associated with soil and sediment

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ABSTRACT

Sorption of two herbicides, fluridone (FLUN) and norflurazon (NORO), by two types of biochars, whole sediment, and various soil/sediment organic matter (OM) fractions including nonhydrolyzable carbon (NHC), black carbon (BC) and humic acid (HA) was examined. The single-point organic carbon (OC)-normalized distribution coefficients (K_{OC}) of FLUN and NORO at low solution concentration ($C_e = 0.01S_W$, solubility) for HA, NHC, and BC were about 3, 14, and 24 times and 3, 16, and 36 times larger than their bulk sediments, respectively, indicating the importance of different OM fractions in herbicide sorption. This study revealed that aliphatic moieties of the hydrothermal biochars and aromatic moieties of NHC samples, respectively, were possibly responsible for herbicide sorption. The hydrothermal biochar and condensed OM (i.e., NHC and BC) showed relatively high or similar herbicide sorption efficiency compared to the thermal biochar, suggesting that the hydrothermal biochar may serve as an amendment for minimizing off-site herbicide movement.

1. Introduction

Extensive and worldwide herbicide usage has increased dramatically during the last two decades due to changes in farming practices and increasingly intensive agriculture. It has been estimated that 2.5 million tons of pesticides are applied worldwide each year and the application rates are increasing with the passage of time (Tariq et al., 2007). The pesticide industry is very big because pesticides are an integral component of intensive world agriculture. World-wide pesticide sales in 2004 were a record $32.7 billion. Herbicides accounted for 45.4% of the pesticide market (Pacanoski, 2007). The use of herbicides has created considerable controversy worldwide. It has been reported that herbicides are lost from agricultural fields and aquatic sediments to surface- and groundwater by run-off and leaching (Konstantinou et al., 2006). Herbicide run-off and leaching are recognized as serious environmental concerns and a primary source of pollution for surface- and groundwater (Carter, 2000). To alleviate the environmental risk of leached herbicides, innovative strategies are needed to reduce the amount lost from application sites and transported to surface waters. Sorption process can retard or even prevent the movement of herbicide and affect its availability for plant or microbial uptake; it is one of the main processes reducing the mobility of herbicides in soils (Morillo et al., 2002). Moreover organic matter (OM) associated with soil and sediment has been known to play an important role in pesticide sorption. It is well known that the OM has highly heterogeneous structures (Chefetz and Xing, 2009; Cornelissen et al., 2005; Xing and Pignatello, 1997). To ascertain the chemical structures of OM, it is commonly separated from solid phases into various extracted fractions and black carbon (BC) (Gelinas et al., 2001; Kang and Xing, 2005; Ran et al., 2007). The knowledge of herbicide sorption capacity of these OM fractions and black carbon is very important in understanding of the herbicide leaching and transport characteristics. However, knowledge on herbicide sorption on these individual OM fractions from the same soil or sediment sample is very limited (Cornelissen et al., 2005; Sun et al., 2010a).

In addition to natural OM, herbicide leaching can be reduced by intentionally enhancing the sorption potential of soil by adding biochar (Yang and Sheng, 2003). Biochar is the solid charred and carbon-rich residue from pyrolysis or incomplete combustion of biomass (Cao et al., 2009; Giusquiani et al., 1995; Sun et al., 2011). Biochar has attracted widespread attention because of its potential use as a soil amendment to improve soil quality (Lehmann, 2007;

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Renner, 2007), reduce anthropogenic emissions of CO_2 to the atmosphere (Laird, 2008; Lehmann, 2007; Novak et al., 2009), and to enhance the adsorptivity of the soil for pesticides (Yang and Sheng, 2003). Therefore, addition of biochar to soils or aquatic systems can be a potential management strategy for reducing herbicide leaching. However, the sorption efficiency of biochar strongly depends on the original feedstock used and the pyrolysis conditions employed (Brown et al., 2006; Chen et al., 2008; James et al., 2005; Zhou et al., 2010). In this study, four biochars derived from two feedstocks under two different pyrolysis conditions were selected to investigate their sorption potential to two selected herbicides: norflurazon (NORO) and fluridone (FLUN).

The nonionic herbicide NORO is a fluorinated pyridazinone aquatic herbicide registered for soil-applied use in cotton, soybean, tree fruit, nut crops, citrus, and cranberries, and is frequently detected in groundwater (Morillo et al., 2004; Senseman et al., 1996). The weakly basic FLUN is a fluorinated pyridazinone herbicide used to control common nuisance plants such as pond weed and water mil foil. Sorption capacities of these selected herbicides in soils are directly related to soil organic matter (OM) content (Morillo et al., 2002; William et al., 1997; Xing and Pignatello, 1997). The importance of organic matter as well as pH of the aquatic sediment for sorption and transport of sediment-associated contaminants has been emphasized (Gao et al., 1998). These factors, however, have not yet been studied in detail for the two herbicides selected for this study.

To our knowledge, the sorption behavior of NORO and FLUN in different OM fractions, i.e., humic acid (HA), nonhydrolyzable carbon (NHC), and BC has not been yet reported. Sorption of the two herbicides on these different OM fractions can be a pivotal interaction that determines their fate and behavior in the both soil and aquatic ecosystems.

Our objectives were: 1) to characterize sorption behavior of the two herbicides (FLUN and NORO) by a variety of OM fractions and quantify the relative contribution of each organic fraction to the overall sorption capabilities by soils and sediments; 2) to assess the potential of the four biochars for sorbing the two herbicides (FLUN and NORO) and determine their suitability as a potential amendments to reduce groundwater contamination of herbicides; and 3) to determine the most important OM or biochar-specific parameters influencing the sorption of FLUN and NORO.

2. Materials and methods

2.1. Chemicals

NORO (4-chloro-5-methylamino-2-(α, α, α)-trifluoro-m-tolylpyridazin-3-(2H)-one) was purchased from ChemService company (USA) with a reported purity > 98.6%. ^{14}C-labeled and unlabeled FLUN (1-methyl-3-phenyl-5-[3-(trifluoromethyl)-phenyl]-4(1H)-pyridinone) was purchased from Sigma-Aldrich Chemical CO (Riedel-de Haen). Their selected properties were listed in Table S1.

2.2. Biochar and soil/sediment organic matter samples

Two kinds of biochar were used in this study including thermal and hydrothermal biochars with processing conditions previously reported (Sun et al., 2011). Briefly, the two thermal biochars T-PL and T-WS were produced from poultry litter and wheat straw feedstocks, respectively, at 400 °C until no visible smoke was emitted from the reactor. They were washed with 0.1 M HCl followed by water till neutral pH, subsequently oven-dried at 105 °C, gently ground, and homogenized to pass through a 250 μm sieve. The two hydrothermal biochars (H-SS and H-PL) were produced by carbonizing poultry litter and swine solids in tubular stainless steel reactors with deionized water at 250 °C under autogenic pressures for 20 h. Afterwards, biochars were dried at 105 °C, gently ground and homogenized to pass through a 250 μm sieve. Because biochars were produced at 250 °C in the presence of water, they were named as hydrothermal biochars to distinguish them from the thermal ones produced at 400 °C in the absence of water.

Three surface sediment samples (ST1, ST2, and ST3) and two surface soil samples (SL4 and SL5) were collected in north China (Sun et al., 2010a). The isolation method of different OM fractions was modified from a reported procedure (Gelinas et al., 2001) and was described in previous studies (Ran et al., 2007; Sun et al., 2010a,b). Briefly, soil/sediment samples were initially treated to isolate NHC fractions with a mixture of 1 M HCl and 10% (v/v) HF, and 2 × 2 M, followed 4 M, and 6 M trifluoroacetic acid (TFA), and finally 6 M HCl, respectively, to remove minerals and hydrolysable carbon in soils and sediments. After the above treatment, the residues (NHC) were freeze-dried and stored in glass vials for further study. BC fraction was obtained from the combustion of the NHC sample at 375 °C for 24 h with sufficient air (Cornelissen et al., 2005; Gelinas et al., 2001). HA fraction was isolated by a progressive alkali-extraction method (Kang and Xing, 2005). The HAs from sediment were extracted with 0.1 M $Na_4P_2O_7$ for five times and with 0.1 M NaOH for five times under N_2 protection, respectively. These extracts were combined, de-ashed with 0.1 M HCl/0.3 M HF solution, washed with DI water, freeze-dried, gently ground to pass through a 100 μm sieve, and stored for subsequent use.

2.3. Characterization of OM fractions

The acid-treated (1 M HCl) original soil or sediment samples, OM isolated samples, and biochars were analyzed for their C, H, N, and O contents using an Elementar Vario El elemental analyzer (Table 1). The acid treatment was used to remove inorganic carbon in the soil or sediment samples. Among the soil and sediment samples tested in this study, only the sediment sample 1 (ST1) contained sufficient OC content to provide adequate masses of each recovered organic fraction (HA, NHC, and BC) for subsequent sorption experiments. Therefore, only ST1 was fractionated completely while other soil and sediment samples were partially fractionated for the NHC fraction only. The elemental compositions (w/w) present in 2 soil and 3 sediment bulk samples (Table 1) were corrected with their corresponding carbonate contents. The solid-state cross-polarization (CP) and magic angel spinning (MAS) ^{13}C NMR spectra of the isolated samples were obtained using a Bruker DRX-400 NMR spectrometer operated at a ^{13}C frequency of 100.63 MHz and a magic-angle-spinning (MAS) rate of 8.0 kHz. The NMR spectra for the 5 NHC samples, one HA1 sample (isolated from ST1), and 4 biochars were presented in Fig. S1a, and the functional group assignments were listed in Table S2.

2.4. Fluridone and norflurazon sorption experiment

All sorption experiments were conducted by mixing sorbents in solutions containing various sorbate concentrations (400–18,000 $\mu g\ L^{-1}$ for NORO according to its detection limit and solubility in water) in 8 mL, 15 mL, or 40 mL vials containing 0.01 M $NaNO_3$ to maintain a constant ionic strength. The solid (g)/solution (mL) (w/v) ratios were 1:6–1:2000 for NORO and 1:30–1:5000 for FLUN for the tested sorbents. These samples were shaken for 2 days according to the preliminary kinetics experiment (Fig. S2). After shaking, the suspensions were centrifuged, and

Table 1
Elemental composition, atomic ratio, ash content, aromaticity, BET-N_2 surface area (SA-N_2) of samples.

Sample	C%	N%	H%	O%	C/N	H/C	O/C	SA-N_2[b] ($m^2\ g^{-1}$)	Aromaticity[c] (%)
ST1	3.39	0.36	0.83	nd[a]	11.00	2.94	nd	nd	nd
ST2	0.88	0.07	0.47	nd	14.31	6.43	nd	nd	nd
ST3	1.05	0.10	0.51	nd	12.05	5.81	nd	nd	nd
SL4	1.03	0.09	0.64	nd	13.05	7.51	nd	nd	nd
SL5	1.15	0.09	0.64	nd	14.61	6.68	nd	nd	nd
HA1	36.98	4.05	4.08	18.93	10.65	1.32	0.38	nd	28.0
BC1	6.47	0.21	0.42	nd	36.83	0.78	nd	nd	nd
NHC1	22.38	1.03	2.36	6.65	25.30	1.26	0.22	6.0	35.7
NHC2	10.85	0.73	0.92	3.90	17.30	1.02	0.27	nd	61.4
NHC3	10.73	0.57	1.58	2.58	22.00	1.77	0.18	nd	37.2
NHC4	15.71	1.25	1.22	6.78	14.70	0.93	0.32	nd	63.8
NHC5	12.12	0.92	1.55	4.31	15.30	1.53	0.27	12.0	55.6
H-SS	47.46	1.25	5.72	20.7	44.35	1.45	0.33	4.0	34.0
H-PL	40.20	1.67	3.86	22.1	28.01	1.15	0.41	8.7	32.8
T-PL	53.45	2.80	3.71	15.0	22.30	0.83	0.21	6.7	72.4
T-WS	65.79	0.21	3.43	20.4	370.50	0.63	0.23	2.0	81.6

HA, humic acid; NHC, nonhydrolyzable carbon; BC, black carbon. HA1, BC1 and NHC1 were isolated from ST1 bulk sediment sample, and NHC2, NHC3, NHC4, and NHC5 fractions were isolated from bulk sediments (ST2 and ST3) and bulk soils (SL4and SL5), respectively.

Hydrothermal poultry litter (H-PL); Thermal poultry litter (T-PL); Hydrothermal solid swine (H-SS); Thermal wheat straw (T-WS).

[a] Represents not detected.

[b] Calculated using the Brunaer–Emmett–Teller (BET) equation for data in the range from 0.05 to 0.3 of relative pressure.

[c] Aromaticiy = 100 × aromatic C(108–165 ppm)/[aromatic C (108–165 ppm) + aliphatic C(0–108 ppm)], the data of aromatic C (108–165 ppm) and aliphatic C (0–108 ppm) were listed in Table S2.

the concentrations of NORO in the supernatant were determined using HPLC (HP model 1100, reversed phase C18, 15 cm × 4.6 mm × 4.6 μm). The mobile phase was a mixture of 65:35 (v:v) of acetonitrile and deionized (DI) water. NORO was analyzed using a fluorescence detector at an excitation and an emission wavelength of 310 and 405 nm, respectively. The detection limit of this analytical procedure was 50 $\mu g\ L^{-1}$. Headspace was kept minimal to reduce solute vapor loss. Because of low volatility of these herbicides, the difference between the initial and final equilibrium concentrations was assumed to be due to sorption. The amount of NORO retained by the sorbents was calculated by multiplying the concentration difference with its solution volume. All experiments including the blanks were run in duplicate and performed at room temperature (25 ± 1 °C).

The FLUN sorption experimental procedure was similar to that of phenanthrene in a previous study (Ran et al., 2007) using a batch equilibration technique. The stock solutions of both ^{14}C labeled and non-labeled FLUN were used to make the sorption solutions containing 0.01 M $NaNO_3$. The adsorbent sample masses added to each of the vials were selected to obtain 20–80% uptake of sorbate at equilibrium. The vials were then placed on a rotary shaker for 2 days at 25 ± 1 °C. After centrifugation (3000 rpm for 20 min), about 1.0 mL of the supernatant was added to 6 mL of Scintiverse cocktail (Fisher Scientific Co.) for liquid scintillation counting (Beckman LS6500). Solute ^{14}C labeled FLUN concentrations of control ($C_{0\text{-label}}$) and equilibrium solutions ($C_{e\text{-label}}$) were analyzed by the result of liquid scintillation counting as above. The concentration of non-labeled FLUN ($C_{0\text{-non-label}}$) in control solution has been known due to precise measurement from its stock solution using proper scale-injectors. So the final equilibrium concentrations were obtained from the following equation,

$$C_e = (C_{0-\text{label}} + C_{0-\text{non-label}}) \times \frac{C_{e-\text{label}}}{C_{0-\text{label}}}$$

2.4.1. *Data analysis*

The Freundlich model (FM) was used to fit the sorption data (Xing, 2001),

$$\log q_e = \log K_F + n \log C_e \quad \text{(FM)}$$

where q_e [$\mu g\ g^{-1}$] is the equilibrium sorbed concentration; C_e [$\mu g\ L^{-1}$] is the equilibrium aqueous concentration; K_F [$(\mu g\ g^{-1}/(\mu g\ L^{-1})^n$] is the Freundlich affinity coefficient; and n is the Freundlich exponential coefficient.

Although both Dubinin–Ashtakhov (DA) and Polanyi–Manes (PMM) models are based on the Polanyi theory, only the DA model was employed to fit the adsorption isotherms in this study. In the DA model, molar volume (V_S) was used as a constant in the regression analysis despite the fact that V_S values of the compounds could not be given (Sun et al., 2010b),

$$\log q_e = \log Q^0 + (\in/E)^b \quad \text{(DA)}$$

$$\log q_e = \log Q^0 + a(\in/V_S)^b \quad \text{(PMM)}$$

where Q^0 [$mg\ g^{-1}$] is the saturated adsorption capacity; $\in = -RT\ln(C_e/C_s)$ is the effective adsorption potential [$KJ\ mol^{-1}$]; C_s [$mg\ L^{-1}$] is the water solubility at 25 °C (12 $mg\ L^{-1}$ for FLUN, and 33.7 $mg\ L^{-1}$ for NORO); R [8.314×10^{-3} KJ/(mol K)] is the universal gas constant; and T [K] is absolute temperature; E [$KJ\ mol^{-1}$] is the "correlating divisor"; a and b are fitting parameters.

3. Results and discussion

3.1. *Chemical characterization of OM and biochars*

The ten samples including soil/sediment, OM, and biochars varied substantially in OC content and atomic ratios (H/C and O/C) (Table 1). It was noted that H/C and O/C atomic ratios of biochar produced from poultry litter decreased with increasing pyrolysis temperature (Table 1), which was consistent with a previous result that the biochars were most polar (high O/C and O + N/C ratios) at lower pyrolysis temperatures (Novak et al., 2009). Substantial differences occurred in their solid state ^{13}C NMR spectra (Fig. S1). The NMR spectra of five NHC samples were dominated by two broad alkyl and aryl carbons resonances centered at 30 ppm and 128 ppm, respectively, which was characteristic of the NHC fractions. In contrast, both HA1 and hydrothermal biochars (H-PL and H-SS) exhibited diversified OC structures, including alkyl carbon (0–45 ppm), methoxy carbon (45–63 ppm), carbohydrate (63–108 ppm), aryl carbon (108–148 ppm), and carboxyl carbon (165–187 ppm) (Fig. S1). The spectral area for the O-containing polar groups accounted for 26.4–38.6% of total OC in NHC samples, whereas in HA1 and hydrothermal biochars, these groups accounted for 34.4–62.7% of the spectral area. These % C distributions were consistent with the atomic ratio (O/C) results (Table 1). Finally, compared to HA, hydrothermal biochars, and NHC samples, the spectra of thermal biochars (T-PL and T-WS) were devoid of peaks from other O-containing functional groups, but were dominated by peaks at about 128 ppm assigned to aromatic-C structures with their aromaticity ranging from 72.4 to 81.6% (Table 1).

3.2. *Norflurazon and fluridone sorption by sediment 1 (ST1), OM fractions (HA, NHC, and BC) and biochars*

3.2.1. *Sorption isotherms of fluridone and norflurazon*

The sorption isotherms and Freundlich model fitting parameters of FLUN and NORO by HA, NHC, BC, sediment (ST1) and biochars were shown in Fig. 1 and listed in Table 2, respectively. Herbicides sorption on ST1 and its OM fractions displayed different nonlinear isotherms with n values from 0.51 to 0.79 and from 0.64 to 0.97 for FLUN and NORO, respectively (Table 2). The substantial nonlinearity in sorption manifested at low concentrations of FLUN and NORO might be related to preferential sorption by the BC fraction with high-surface area carbonaceous materials (e.g., soot or wood chars) (Chiou, 1995; Gustafsson et al., 1997). These materials can be encased within BC fractions (Table 1) and can significantly influence the sorption behavior of the two herbicides. The BC fraction had comparable sorption capacity (K_d) of FLUN and NORO to that of NHCs, but exceeded that of HA despite the fact that it had the lowest OC among all OM fractions (Table 1). There was no positive relationship between herbicide sorption capacity (K_d) of OM fractions and OC content (Fig. S3). This finding was surprising considering the fact that FLUN and NORO sorption by soil has been positively related to OC content (Weber et al., 1986; William et al., 1997). In addition, the fact that HA had the lowest herbicides sorption capacity (K_d) among all OM fractions and it had the highest oxygen (O) contents (Tables 1 and 2 and Table S4) suggested that O should be one of the dominant factors influencing herbicide sorption capacity of HA. However, with the exception of HA and BC, the NHC samples' sorption capacity ($\log K_d$) related positively with their O-containing polar C content (Fig. S4d). This finding indicates that O-containing polar C within NHC samples may have some influence on herbicide sorption capacity of NHC samples at least for FLUN and NORO. All herbicides isotherms of NHC samples with the exception of NORO on NHC1 exhibited similar nonlinearity within the range of 0.62–0.73 and 0.64–0.77 for FLUN and NORO, respectively (Table 2).

Similar to the OM sorption, hydrothermal and thermal biochars used in this study showed large differences in sorption nonlinearity as their n values deviated widely from unity. Thermal biochars generally exhibited relatively higher nonlinearity compared to hydrothermal biochars especially for FLUN. It has been reported in the literature (Chefetz and Xing, 2009) that aromatic moieties in OM cause nonlinearity of hydrophobic organic contaminants (HOCs) sorption isotherms. Significantly negative correlations between the n values and the aromaticity of NHC and biochar samples (Fig. 2a) suggest that the nonlinearity in sorption of these herbicides increases with the aromaticity of sorbents.

OC-normalized distribution coefficients ($K_{OC} = K_d/f_{OC}$) for ST1 sediment and its different organic fractions (i.e., HA1, NHC1, and BC1) along with 4 other NHCs and biochars were listed in Table 2. The $\log K_{OC}$ values varied with different organic fractions and herbicide concentrations. The difference may be related to the change in K_{OC} with C_e because the isotherms were nonlinear. In addition, regardless of C_e levels, ST1 exhibited much lower sorption capacities (K_{OC}) than any of its OM fractions, indicating the importance of OM for FLUN and NORO sorption within the range of concentrations examined in this study. Furthermore, OM with

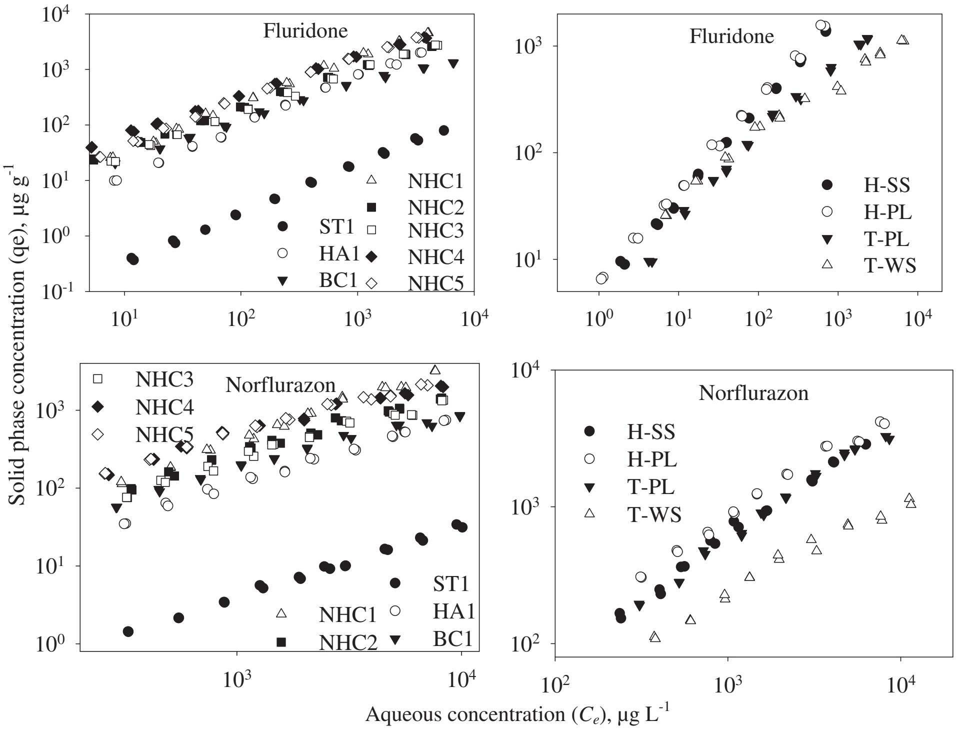

Fig. 1. Sorption isotherms of Fluridone and Norflurazon onto the bulk sediment and different forms of organic matter (HA, humic acid; NHC, nonhydrolyzable carbon; BC, black carbon: HA1, BC1 and NHC1 were isolated from ST1 bulk sediment sample, and NHC2, NHC3, NHC4, and NHC5 fractions were isolated from bulk sediments (ST2 and ST3) and bulk soils (SL4 and SL5), respectively) and hydrothermal and thermal biochars (H-SS, H-PL, T-PL, and T-WS).

Table 2
Freundlich isotherm parameters and concentration-dependent distribution coefficients (K_d) for the samples.

Samples	log K_F	n	N[a]	R^2	log K_d	K_{oc}[b] (mL g^{-1})			log K_{OC}/log K_{OW}
					$C_e = 0.01S_w$	$C_e = 0.01S_w$	$C_e = 0.1S_w$	$C_e = 1S_w$	
Fluridone (FLUN)									
ST1	0.08	0.79	20	0.996	1.51	2.98	2.77	2.56	0.81
HA1	3.20	0.79	20	0.996	3.07	3.50	3.29	3.07	1.64
BC1	16.12	0.51	20	0.990	3.18	4.37	3.88	3.38	1.70
NHC1	1.05	0.73	20	0.996	3.48	4.13	3.85	3.58	1.86
NHC2	1.09	0.64	20	0.999	3.34	4.31	3.94	3.58	1.79
NHC3	0.99	0.67	20	0.997	3.30	4.27	3.94	3.60	1.76
NHC4	1.37	0.62	20	0.997	3.57	4.38	3.99	3.61	1.91
NHC5	1.17	0.68	20	0.998	3.51	4.43	4.11	3.80	1.88
Biochar									
H-SS	4.68	0.87	20	1.000	3.40	3.72	3.59	3.46	1.82
H-PL	10.01	0.77	20	0.994	3.52	3.92	3.69	3.46	1.88
T-PL	9.42	0.62	20	0.999	3.19	3.46	3.08	2.70	1.71
T-WS	16.90	0.48	19	0.990	3.15	3.33	2.81	2.29	1.68
Norflurazon (NORO)									
ST1	0.0062	0.93	20	0.990	0.62	2.09	2.02	1.95	0.25
HA1	0.24	0.89	20	0.998	2.10	2.53	2.42	2.31	0.86
BC1	2.35	0.64	20	0.990	2.46	3.65	3.29	2.93	1.00
NHC1	0.52	0.97	20	0.996	2.65	3.30	3.27	3.24	1.08
NHC2	1.73	0.75	20	0.997	2.60	3.56	3.31	3.06	1.06
NHC3	1.25	0.77	20	0.997	2.51	3.48	3.25	3.02	1.02
NHC4	6.47	0.64	20	0.996	2.90	3.70	3.34	2.98	1.18
NHC5	4.04	0.71	20	0.997	2.87	3.79	3.49	3.20	1.17
Biochar									
H-SS	2.01	0.83	18	0.996	2.88	3.20	3.03	2.87	1.18
H-PL	6.22	0.72	18	0.980	3.10	3.49	3.22	2.94	1.27
T-PL	3.21	0.77	20	0.979	2.93	3.20	2.97	2.75	1.20
T-WS	4.13	0.60	18	0.976	2.60	2.78	2.38	1.98	1.06

HA, humic acid; NHC, nonhydrolyzable carbon; BC, black carbon. HA1, BC1 and NHC1 were isolated from ST1 bulk sediment sample, and NHC2, NHC3, NHC4, and NHC5 fractions were isolated from bulk sediments (ST2 and ST3) and bulk soils (SL4and SL5), respectively. Hydrothermal poultry litter (H-PL); Thermal poultry litter (T-PL); Hydrothermal solid swine (H-SS); Thermal wheat straw (T-WS).

[a] Number of data.

[b] K_{oc} is the organic carbon (OC) normalized sorption distributed coefficient.

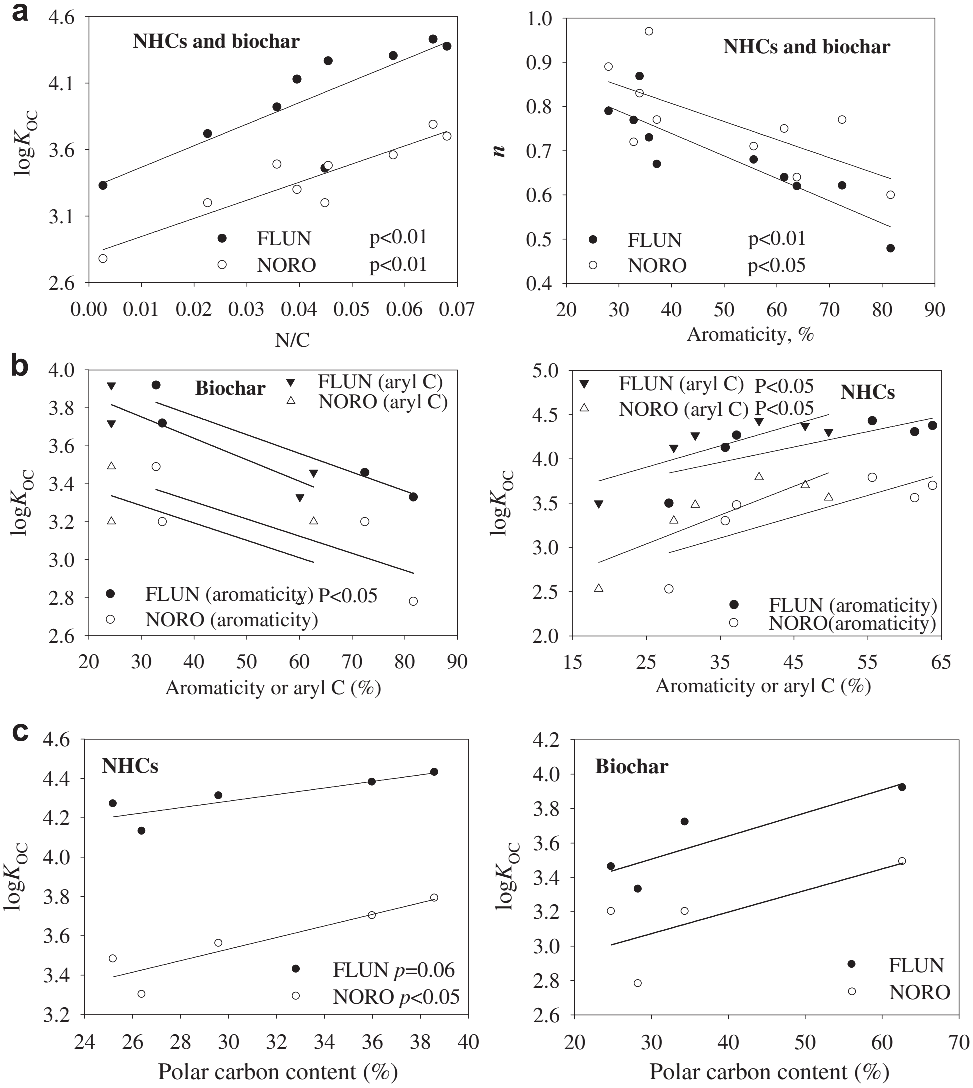

Fig. 2. The relationships between log K_{OC} and the specific parameters of sorbents including atomic ratio of N/C, aromaticity, aryl C content, and polar carbon content (sum of alkyl and aryl C); and between aromaticity of NHCs and biochars and their sorption nonlinearity *n* values for fluridone (FLUN) and norflurazon (NORO), respectively.

different molecular structure and composition had different influences on herbicide sorption as evidenced by their wide range of K_{OC} values (2.98–4.37 log units in Table 2). The condensed OM (i.e., NHC and BC fractions) had the relatively higher log K_{OC} values than amorphous organic matter (AOM, i.e., HA) (Table 2 and Table S2). It was reported that extensive and nonlinear sorption to condensed OM (exceeding the sorption to AOM by 1–3 orders of magnitude) has been shown for polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), the pesticide diuron, benzene and chlorobenzenes, and chlorinated short-chain aliphatic compounds (Cornelissen et al., 2005). This result of herbicides sorption by OM in soils and sediments is also consistent with atrazine sorption by OM in soils and sediments (Sun et al., 2010a).

Correlations between log K_{OC} values at low concentrations of the herbicides and various specific-OM parameters were evaluated to determine their influence on sorption (Fig. 2). These OM parameters were atomic ratios (N/C), aromaticity, or content of aryl C, and polar carbon content of NHCs and biochars. Among all correlations, the atomic ratio of N/C within all sorbents including NHCs and biochar samples was significantly and positively related to log K_{OC} for both FLUN and NORO (Fig. 2a). Hydrogen (H) bonding between herbicides and the N-containing functional groups of the NHCs and biochar was speculated to cause the positive correlation. In addition, the role of aromatic moieties of sorbents as sorption domains for organic compounds remains controversial. While log K_{OC} decreased with the aromaticity of biochar samples, it increased with the aromaticity of NHCs (Fig. 2b). This suggests that aromatic domains alone did not necessarily govern the sorption capacity (K_{OC}) of all sorbents; however, they did cause nonlinearity in FLUM and NORO herbicide sorption behavior (Fig. 2a-right side). This sorption performance was consistent with previous observations in a recent review concerning the role of aromatic and aliphatic moieties on HOCs sorption (Chefetz and Xing, 2009).

The maximum OC-normalized sorption capacity (Q^0_{OC}) was estimated using the DA model. The DA model fitted experimental sorption data very well with R^2 values mostly unity (Table S3). Fig. S4 showed the plots of selected samples' Q^0_{OC} (NHC1, NHC5, H-SS, H-PL, T-PL, and T-WS) versus their surface areas (N_2-SA). As expected, there was a general trend of increasing Q^0_{OC} of both herbicides with N_2-SA. Furthermore, the significant correlation between Q^0_{OC} of NORO and N_2-SA indicates that the maximum sorption capacity of NORO by NHC and biochar with the exception of NHC1 can be influenced by their surface area alone. This might be

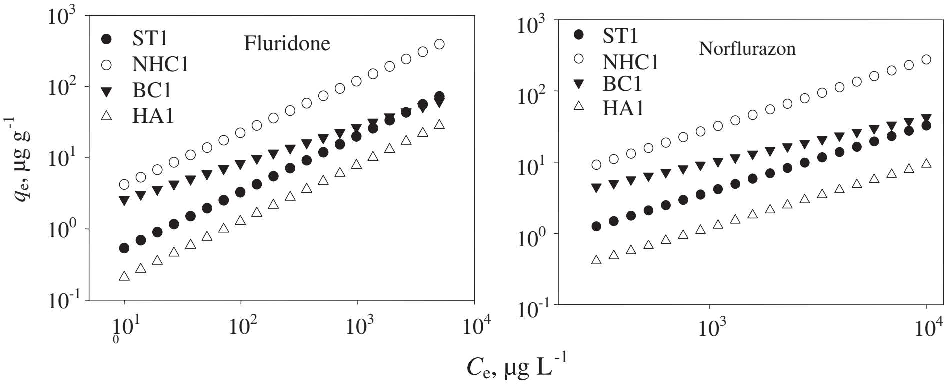

Fig. 3. Sorption isotherms of fluridone and norflurazon: Freundlich model fitting on the bulk sample, and the contribution of their nonhydrolyzable carbon (NHC), black carbon (BC) and humic acid (HA) fractions to the total sorption of fluridone and norflurazon, respectively, by the bulk sediment sample (ST1).

attributed to the fact that NORO molecules were smaller than FLUN, which made them easier to enter into pores of NHC1 (Chen et al., 2005). In addition, while both NORO and FLUN had H-bond acceptors, only NORO had one H-bond donor (i.e., methyl amino group of the NORO acting as one H-bond donor as shown in Fig. S5). This could enhance the accessibility of NORO molecules into sorption domains more than FLUN molecules.

3.2.2. *Possible adsorption mechanisms for fluridone and norflurazon*

The fact that the log K_{OC} values of FLUN and NORO by OM fractions and biochars were inversely correlated with their hydrophobic carbon content (i.e., sum of alkyl and aryl carbon content in Table S2 and Fig. S4) suggests that nonspecific interaction mechanism such as van der Waals (VdW) interaction could dominate sorption of FLUN and NORO. The trend of increasing K_{OC} values of herbicides by NHCs and biochars with polar carbon contents (Fig. 2) indicates that H-bonding between herbicides and O-containing moieties in NHCs and biochars probably could play an important role in their interactions (Wang et al., 2011). At the same time, the relatively high H-bonding acceptor parameter of the two herbicides (Table S1) also supported H-bonding between FLUN/NORO (being H-bonding acceptors) and O-containing polar moieties in OM fractions and biochars, which were serving as H-bonding donors. In addition, the presence in OM of both electron-deficient and electron-rich moieties suggests the possible formation of charge-transfer complexes via electron donor-acceptor mechanisms ($\pi-\pi$ reaction). Pesticides can act as electron donors (amine and /or heterocyclic nitrogen atoms of the a-triazines, pyridines, imidazolinones) (Senesi, 1992). Thus it is, in theory, possible that FLUN and NORO are able to interact with OM fractions and biochars through $\pi-\pi$ interactions. Positive relationships between log K_{OC} values of NORO and FLUN and aryl carbon contents of NHCs (Fig. 2c) support such a mechanism. Consistent with our observations, it was reported elsewhere that K_{OC} values of atrazine by NHCs were positively correlated with their aryl carbon contents ($p < 0.05$) (Sun et al., 2010a). After log K_{OC} values of these two herbicides were normalized with their respective log K_{OW} values, log K_{OC}/log K_{OW} values of FLUN were about 1.5 times larger than that of NORO (Table 2). This could be due to a higher contribution of $\pi-\pi$ interactions between FLUN and aromatic moieties in NHCs than those between NORO and aromatic moieties because FLUN has one more electron-deficient aromatic ring than NORO (Fig. S5). In contrast, aromatic components did not play a major role in biochar sorption of these two herbicides. The K_{OC} values of these two herbicides unexpectedly increased with decreasing aromatic carbon contents of biochars. Therefore, these contrasting functions of aromatic moieties between NHCs and biochars on herbicides sorption suggest that the aromaticity alone cannot adequately explain herbicide sorption behavior of different environmental sorbents.

3.2.3. *Contribution of OM fractions to the overall sorption of fluridone and norflurazon*

Estimating the contribution of each OM fraction to the overall sorption of FLUN and NORO was one of goals in this study; therefore, we used a similar approach as described in our previous study (Sun et al., 2010a). Briefly, the isotherms for bulk sample and its fractions (i.e., NHC, BC and HA) were calculated based on the isotherm parameters (Table 2) and the mass distribution, and total OC content of different OM fractions (Table S4). Contribution of each OM fraction to the total sorption was normalized to the bulk sample mass using the equation (1). The different roles of the OM fractions in sorption by ST1 are further illustrated in Fig. 3.

$$q_{e,i} = \left[K_{F,i}(C_e)^n \phi_{oc,i} f_{oc,bulk}\right] \Big/ f_{oc,i} \qquad (1)$$

where K_{Fi} and n are the FLUN or NORO Freundlich sorption coefficients (Table 2) of a OM fraction (NHC, BC, or HA); $\phi_{oc,i}$ is the OC mass fraction of NHC, BC, or HA in the total OC of the bulk samples (i.e., NHC/OC, BC/OC, or HA/OC) (Table S4); $f_{oc,bulk}$ is the fraction OC content of the bulk sample; $f_{oc,i}$ is the fraction OC content in the OM fraction (Table S4 and Table 1).

The contributions of NHC and BC fractions per unit mass of OC exceed the overall capacity of bulk ST1, indicating the dominance of the relatively condensed OM structures for herbicide sorption. However, HA contribution to the overall sorption of herbicide was relatively low compared to other OM fractions as shown in Fig. 3. This was probably due to its low sorption capacity (Table 2) and low contribution to total OM mass (HA/OC: 12.2%, in Table S4).

4. Conclusions

Sorption behavior of FLUN and NORO on different soil and sediment bulk samples and various associated OM fractions were investigated and compared with that of two different types of biochar. The results of this study indicate sorption behavior of the herbicides FLUN and NORO in different sediment OM fractions were significantly different and highlight the importance of the condensed region in the OM-domain (i.e., NHC and BC) in regulating their sorption behavior. The single-point organic carbon (OC)-normalized distribution coefficient (K_{OC}) of FLUN and NORO for isolated HA, NHC, and BC from sediment was about 3, 14, and 24 times and 3, 16, and 36 times, respectively, greater than the whole sediment, indicating the importance of OM-fractions associated with sediment in herbicide sorption. Furthermore, their OM molecular and structure complexly influenced the sorption behavior of these herbicides. For example, the nonlinearity of sorption isotherms of FLUN and NORO was linked to the aromaticity of sorbent. However, aromaticity alone was not able to explain the opposite trends of the sorption capacity with respect to aromaticity of NHCs and biochars. Among the two types of biochars investigated in this study, hydrothermal biochar showed higher sorption efficiency due to its diverse organic functionalities compared to the thermally prepared biochar. Therefore, hydrothermal biochar is preferable for use as an amendment for minimizing off-site herbicide movement or as herbicide sorbent for spill cleanup because of its diversified organic characters and relative efficiency in adsorbing the two tested herbicides.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.envpol.2011.12.015.

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