Sorption properties for black carbon (wood char) after long term exposure in soils

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ABSTRACT

Amending soil with black carbon (BC) can change the sorption properties of the soil. However, there is some concern based on studies that deal with newly produced BC and barely consider the possible changes in sorption properties for BC after being amended in soil. This study uses newly produced BC and historical BC samples, along with soils containing high levels of historical BC and adjacent soils without visible BC, to compare their diuron, atrazine and Cu^{2+} sorption properties. Compared with newly produced BC, historical BC exhibited reduced (56–91%) sorption capacity for diuron and atrazine but 2–5 times enhanced sorption capacity of Cu^{2+}. These changes in sorption properties can be interpreted via the formation of surface functional groups in BC. Whereas the sorption capacity for diuron and atrazine was reduced with historical BC, the sorption capacity of BC-containing soils was higher than for the adjacent soils, indicating that BC possessed stronger sorption capacity than non-BC material. A biological assay revealed reduced herbicide efficiency for the newly produced BC, and even the historical BC still exerted an influence on reducing herbicide efficiency. Along with its recalcitrance in environments, BC has a significant long term effect on the toxicity of contaminants and soil fertility.

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1. Introduction

Black carbon (BC) is the byproduct of the pyrolysis of biomass. Because it is stable, it can persist in nature for long periods of time. Therefore, researchers have proposed charring biomass to BC as a way to divert carbon (C) from a rapid biological C cycle to a slow geological C cycle and BC soil amendments can effectively sequester atmospheric CO_2 in soil (Lehmann, 2007). BC amendments also provide the agronomical benefits of enhancing soil fertility and increasing crop yield (Lehmann, 2007; Sohi et al., 2010) and have recently been implemented in many experiments worldwide (Chan et al., 2007; Kimetu et al., 2008; Atkinson et al., 2010; Major et al., 2010; Spokas et al., 2012).

BC is a strong sorbent for organic compounds. The sorption of hydrophobic organic compounds by BC can be up to 10–100× greater than sorption by other types of organic matter (OM; Cornelissen et al., 2005b). Sorption of diuron by BC is up to 400–2500× more effective than that of soil (Yang and Sheng, 2003a). Thus, BC

amendments to soils have the potential to cause significant changes in the sorption properties of the soils. The amendments enhance herbicide sorption and affect the efficiency, movement and degradation of herbicides in soils (Yang et al., 2006; Yu et al., 2006; Kookana, 2010; Jones et al., 2011; Nag et al., 2011; Graber et al., 2012). The reduction in herbicide efficiency is important for weed control in agricultural management practices because farmers must apply more herbicide to BC-amended soils to compensate for the decreased herbicide efficiency. This activity subsequently increases commercial expense and environmental risk.

Much of the concern with the reduction in herbicide efficiency arises from studies that treat newly produced BC as a surrogate. However, these studies barely consider the possible change in BC characteristics after amendment. Research has shown that the structure of BC in soils is changed and may undergo biotic and abiotic oxidation on the short term (months) and continually over the long term (years, decades or centuries) (Cheng et al., 2006, 2008a; Cheng and Lehmann, 2009; Zimmerman et al., 2010). The natural oxidation of BC forms surface functional groups such as carboxylic and phenolic species, causing a reduction in surface positive charge and a substantial increase in surface negative charge (Cheng et al.,

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2006, 2008a). Because the surface properties of BC substantially affect its sorption properties, changes produced by natural oxidation may profoundly affect these sorption properties (Moreno-Castilla, 2004; Kookana, 2010). In addition, BC can interact with various soil components after it is added. Pore blockage and direct site competition with non-BC material may also affect the sorption properties of BC (Kwon and Pignatello, 2005; Cornelissen and Gustffsson, 2006). To date, no information is available on the sorption properties for BC after long term exposure in soils. Because of the long term persistence of BC in nature and its promising applications for environmental practices, it is important to understand its sorption properties and how they change after long term exposure.

This study investigates newly produced BC (fresh BC) samples and historical BC samples that had been left in soils since the late 19th century to compare their sorption properties. Diuron, atrazine and Cu^{2+} served as the model sorbates. The objectives were to (i) identify the changes in BC sorption properties after long term exposure in soils, (ii) compare the sorption properties of soils containing high levels of historical BC and adjacent control soils without visible BC and (iii) conduct a biological assay to assess the survival rates of ryegrass seeds grown under diuron and Cu^{2+} applications on a cultivated soil amended with/without BC.

2. Material and methods

2.1. BC and soil samples

The BC samples included two contrasting types: fresh and historical. The fresh BC sample was newly produced from the Hopewell Furnace National Site in Pennsylvania, where BC is produced by the same traditional charcoal-making method used in the 19th century. The fresh BC was sampled ca. 1 month after charring and the pieces ground to pass through a 2 mm sieve and stored in a sealed glass jar (Cheng et al., 2008a,b). The historical BC samples were the remnant charcoal from historical charcoal blast furnaces, in which BC was left in the soil in the mid-19th century. One historical BC sample was collected from Trois-Riviera, Quebec (denoted as QC) and the other was collected from Dickson, Tennessee (TN). Both historical BC samples were collected from the surface soils and BC was obtained by carefully picking large fragments (> 4 mm) from the soil at a depth of 10–20 cm. The fragments were gently rinsed with distilled water until the electric conductivity was close to the background distilled water. The rinsed BC fragments were oven dried at 70 °C for 24 h and ground to pass through a 2 mm sieve for the chemical measurements. The fresh BC sample was expected to have properties close to the "original" status of the historical BC samples because it was produced via the same traditional method, as carried out by charcoal workers in the 19th century (Cheng et al., 2008a,b).

A laboratory-oxidized BC sample was also examined to assess the effect of oxidation. The ground fresh BC sample was incubated at 70 °C for 6 months and referred to as BC6M (Cheng and Lehmann, 2009). Although a temperature of 70 °C is unrealistic for naturally occurring processes, it was used to represent the long term oxidation of BC (Cheng and Lehmann, 2009). In addition, the soils that contained high levels of BC (BC-containing soils) and without visible BC (adjacent control soils) in the historical charcoal blast furnaces in QC and TN were subjected to the same sorption experiments as the BC samples to enable accurate comparison of the sorption properties of BC-containing soils and adjacent soils.

2.2. Properties of BC and soil

Table 1 lists some of the physicochemical properties of BCs based on the findings of previous studies (Cheng et al., 2008a;

Cheng and Lehmann, 2009). The C, N and H elemental compositions were measured using an elemental analyzer; pH was measured at a BC/water ratio of 1:10 (w/v); surface negative charge, surface positive change and point of zero net charge were measured by ion index. Table 1 also lists the soil properties of the BC-containing soils and adjacent soils in the blast furnaces in QC and TN.

Cheng et al. (2008a) and Cheng and Lehmann (2009) presented the surface C speciation and functionalities of the BC samples determined using X-ray photoelectron spectra (XPS). This study used synchrotron-based near edge X-ray adsorption fine structure (NEXAFS) at the carbon K adsorption edge. The C (1s) NEXAFS spectra were obtained on beamline 24A at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. Duplicate scans ranging from 275 to 340 eV were obtained on the freshly cut cross section of BC particles. Energy steps of 0.5 eV were run from 275 to 282 eV, followed by 0.1 eV from 282 to 295 eV, 0.2 eV from 295 to 322 eV and 0.5 eV up to 340 eV. The dwell time for each energy point was 1 s. The incident beam intensity was recorded with an Au mesh reference monitor (I_0) and the NEXAFS signal was detected in total electron yield (I_{TEY}). The NEXAFS spectra were obtained by calculating the ratio I_{TEY}/I_0 for the sample current mode. Peak assignment for NEXAFS spectra was based on studies by Haberstroh et al. (2006), Solomon et al. (2009) and Heymann et al. (2011). Thus, 284.9–285.5 eV was assigned to aromatic C, and 288.0–288.5 to carboxylic C.

This study used ^{13}C solid state nuclear magnetic resonance (NMR) spectra to assess the bulk chemical composition of BC. The spectra were obtained from a Bruker Avance III 400 NMR spectrometer operating at a ^{13}C frequency of 100 MHz and run using standard ramp cross-polarization magic angle spinning (CPMAS) spectroscopy. The sample was packed in a 4 mm diameter zirconia rotor and spun at 10 kHz. A contact time of 3 ms and a pulse delay of 1 s were used. A total of 10,000 scans was recorded. The chemical shift regions assigned for the major C types were 0–45 ppm for alkyl C, 45–110 ppm for O-alkyl C, 110–145 ppm for aryl C, 145–165 ppm for O-aryl C and 165–190 ppm for carboxyl C (Baldock and Smernik, 2002).

The physical structure of BC samples was determined from surface area and microscale morphology. The specific surface area of BCs and soils was determined from N_2 adsorption isotherms at 77 K using an ASAP 2200 system (Micromeritics, Norcross, GA, USA). Prior to adsorption experiments, the BC and soil samples were degassed at 378 K under a pressure of $< 10^{-4}$ Pa for at least 15 h. Applying the BET model to the N_2 adsorption isotherms afforded the specific surface area (S_{BET}). The microscale morphological characterization of BC was examined using scanning electron microscopy (SEM) with a Hitachi TM-3000. The BC particles and freshly cut cross sections were examined under an Au coating.

2.3. Sorption isotherms

Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea; > 98%], atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine; > 98%) and Cu^{2+} ($CuCl_2$) were selected as the model sorbates to evaluate the sorption properties of BC and soils. Diuron and atrazine are commonly used as non-selective herbicides for pre-emergent and post-emergent weed control, and Cu^{2+} is heavily used in industry and agriculture. These three species are frequently detected as organic (diuron and atrazine) and inorganic (Cu^{2+}) contaminants in soil and water.

The sorption experiments were performed using the batch equilibrium technique in duplicate for each sorption test. A BC sample of 0.01 g or soil of 0.02 g was suspended in 10 ml aliquots

Table 1
Characteristics of fresh BC, fresh BC after incubation at 70 °C for 6 months (BC6M) and historical BCs collected from charcoal blast furnaces in Quebec (QC) and Tennessee (TN).

	C^a (mg/g)	N^a (mg/g)	H^a (mg/g)	O^a (mg/g)	pH^b	AEC (at $pH_{3.5}$) (mmole/kg C)	CEC (at $pH_{7.0}$) (mmole/kg C)	$PZNC^c$	Surface area (m^2/g)
Fresh BC	908	2	22	68	8.5	+99	+9	7.4	122
BC6M	871	2	29	98	7.9	+15	96	3.9	109
QC	721	2	42	236	4.8	Nil	956	2.0	2.1
TN	690	2	39	269	4.8	Nil	2144	1.8	2.3
QC BC soil	404	6.4	$-^d$	–	4.1	Nil	1423	< 2	2.2
TN BC soil	225	3.3	–	–	5.3	Nil	1269	< 2	8.7
QC adjacent soil	32	2.4	–	–	4.8	Nil	211	< 2	4.7
TN adjacent soil	13	0.9	–	–	5.1	Nil	209	< 2	8.9

[a] Ash-free dry basis.
[b] Measured at 1:10 (w/v under water) for BC samples and 1:2.5 (w/v under 0.01 N $CaCl_2$) for soil samples.
[c] Point of zero net charge.
[d] Not detected.

of aqueous sorbent solution containing an initial concentration ranging from 1 to 20 mg/l for diuron and atrazine and 5–300 mg/l for Cu^{2+}. The aqueous phase of the diuron and atrazine solution received 200 mg/l NaN_3 to inhibit aerobic microbial degradation. The suspensions were shaken on a rotary shaker at 120 rpm at 27 °C in the dark for 24 h. Preliminary kinetic experiments had shown that the sorption of diuron, atrazine and Cu^{2+} reached equilibrium within 24 h. The solution was then filtered using a 0.45 μm membrane (PALL, Millipore Millex-GS; Millipore, Billerca, MA). An aliquot of the filtrate was transferred to an amber vial and analyzed for the remaining amount of each sorbate. Diuron and atrazine were quantified using high performance liquid chromatography (HPLC) with a Waters X-Bridge RP-18 TM column and a Water Alliance 2695 series. The mobile phase was 70:30 MeOH/H_2O (v:v) at 1 ml/min, and the injection volume was 50 μl. The UV wavelength used to detect diuron and atrazine was 254 nm. Cu^{2+} in the filtrate was measured using atomic adsorption spectroscopy (Sensa AA, GBC, Victoria, Australia).

Because of the minimal sorption of the vials and the apparent lack of biodegradation, the amount of sorbed diuron, atrazine and Cu^{2+} (Q_e, mg/g) was calculated on the basis of the difference between the equilibrium concentration and the initial concentration:

$$Q_e = (C_o - C_e)[V/m] \qquad (1)$$

The term Q_e is the amount of sorbed diuron, atrazine or Cu^{2+}; C_o and C_e represent the initial and equilibrium concentrations of diuron, atrazine or Cu^{2+} in the aqueous solution; V is the solution volume and m the weight of BC or soil. The variation in duplicate experiments was generally < 5%, and the average data are reported. The sorption isotherm was fitted with the commonly used Freundlich and Langmuir equations:

$$Q_e = K_f C_e^n \qquad (2)$$

$$Q_e = q_m K_L C_e/(1 + K_L C_e) \qquad (3)$$

Q_e is the amount of sorbed diuron, atrazine or Cu^{2+}. C_e is the equilibrium concentration. K_f ($[mg/g] [mg/l]^n$) and n (dimensionless) are the Freundlich parameters for the corresponding system, and q_m (mg/g) and K_L (l/mg) are the Langmuir parameters related to the maximum capacity of sorption and the binding energy of sorption, respectively. This study adopted the model achieving the greatest degree of fit.

The sorption experiments were performed under the natural pH of diuron, atrazine and Cu^{2+} solution. The pH of the BC-suspended diuron, atrazine and Cu^{2+} solutions ranged from 5.7 to 7.3, 5.4 to 6.9 and 4.0 to 5.5, respectively. The fresh BC solutions displayed the highest pH values, whereas the QC solutions had acidic values. Under this pH range, diuron and atrazine were electrically neutral and Cu^{2+} was cationic. The surface charge on fresh BC was positive because the point zero net charge (PZNC) of fresh BC was at pH 7.4 (Table 1), whereas the BC6M and historical BC samples were primarily negative because the PZNC for these samples was < 3.9 (Cheng et al., 2008a).

2.4. Biological assays for diuron and Cu^{2+}

Two diuron levels of 1.5 and 6 mg/kg soil were used to assess the effects of herbicide on the growth of ryegrass in soil with and without BC amendment. The 1.5 mg/kg soil was at the low end of the recommended use range and the 6 mg/kg soil was at the high end. The BC samples of fresh BC and QC were added to the soil at a rate of 0.1% and 1%, respectively. A cultivated soil from Taoyung County, Taiwan, at a depth of 0–15 cm served as the control soil (Hseu and Chen, 1996). It developed in an alluvial fan terrace derived from Quarternary materials and is classified as a Typic Plinthaquic Paleudalf with loam texture (14% clay, 41% silt and 46% Sand) and 1.4% organic carbon (OC) content.

The diuron was prepared at 60 and 240 mg/l in acetone. An aliquot (5 ml) of solution was added to 200 g soil with and without BC amendments to achieve diuron levels of 0 (acetone with no diuron), 1.5 and 6 mg/kg soil. The soil was thoroughly mixed and placed to a round plastic pot 10 cm wide and 8 cm high. For each pot, ten pregerminated ryegrass seeds with extended radicles and hypocotyls 5–15 mm in length were placed evenly on the surface of the soil. The pots were then placed in a completely randomized block design in a greenhouse. The growth of the ryegrass seeds was monitored daily and maintained with adequate water throughout. The mortality of the seeds influenced by diuron was visually observed starting after 7 days and the survival rate (no injury) was evaluated after 21 days. A 100% survival rate indicated no effect of herbicide and a 0% rate complete herbicide effect.

Similar biological assays were also conducted using Cu^{2+} at 0, 30, 150 and 350 mg Cu/kg soil. The ryegrass shoot biomass of each pot served as an indicator for assessing the effect of BC amendments under Cu^{2+} application. The ryegrass shoots were clipped after 28 days and dried at 60 °C until constant wt. The biological assays for both diuron and Cu^{2+} tests were performed in triplicate.

2.5. Statistics

Curve fitting was conducted using SigmaPlot 10.0. Means testing of biological assay was tested using one-way ANOVA and the Tukey test in SAS software (version 9.1).

3. Results

3.1. BC properties

The long term exposure of BC in soils produced a higher O content and lower C content than fresh BC (Table 1). NEXAFS spectra of BC pieces indicated that the formation of surface functional groups, especially the carboxylic groups at 288.0–288.5 eV, caused the increase in O content (Fig. 1). The formation of these surface functional groups raised the surface negative charge of BC and reduced the surface positive charge, shifting the point of zero net charge from pH 7.4 for fresh BC to 3.9 for BC6M and < 2 for QC and TN (Table 1). However, these changes in BC structure seemed to be less significant for the bulk chemical structure. The NMR spectra for QC and TN showed only a slight enhancement in O-aryl C (145–165 ppm) and carboxyl C (165–190 ppm) and a dominant peak from aromatic C in fresh BC at 129 ppm (Fig. 2).

The specific surface area of BCs decreased from 122 m²/g for fresh BC to 109 m²/g for BC6M and then significantly decreased to 2 and 1 m²/g for QC and TN, respectively (Table 1). The SEM images in Fig. 3a and b show that the external surfaces of historical BC particles were covered with a mixture of minerals, soil OM, or other tiny BC particles, whereas Fig. 3c and d show an interior wood-like morphology in historical BC particles. The SEM images of fresh and historical BC did not display significant differences in the interior morphology (Fig. 3c–f), suggesting that the reduction in surface area of historical BC may occur at the nanoscale of molecular structure.

The BC-containing soils had higher C and N contents and surface negative charge than the adjacent soils. However, the surface area for the BC-containing soils at QC and TN was 2.2 and 8.7 m²/g, respectively, and comparable with their adjacent soils.

3.2. Sorption of diuron, atrazine and Cu²⁺

Fig. 4 shows sorption data for diuron, atrazine and Cu²⁺. Table 2 shows Freundlich parameters for organic compounds and Langmuir parameters for Cu²⁺. The sorption isotherms of diuron and atrazine on fresh BC exhibited greater sorption capacity than BC6M and historical BCs. At an equilibrium concentration between
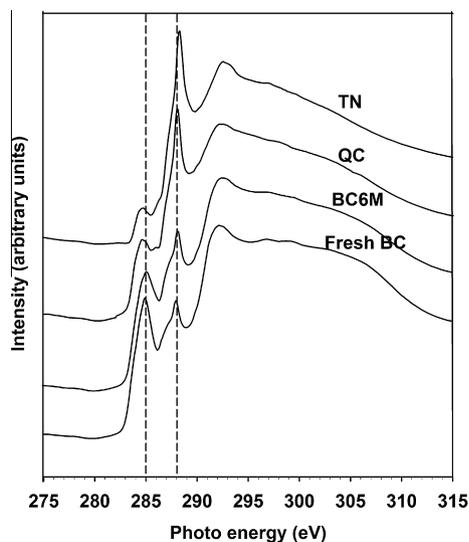
Fig. 1. Carbon near edge X-ray absorption fine structure (NEXAFS) spectra for fresh BC, fresh BC incubated at 70 °C for 6 months (BC6M) and historical BC (QC and TN). Vertical dashed lines indicate energy absorbance of aromatic C at 285 eV and carboxylic C at 288 eV.
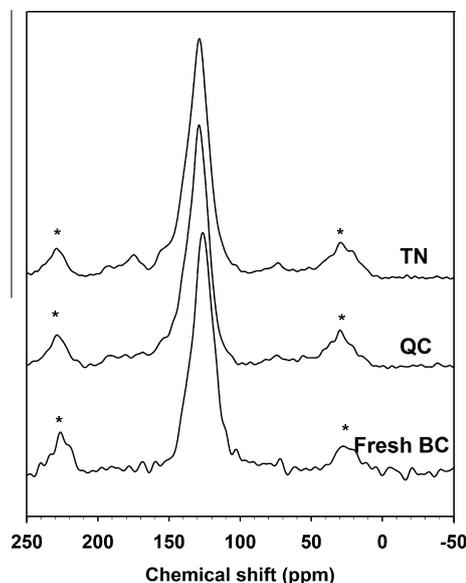
Fig. 2. Solid state ^{13}C NMR spectra for fresh and historical (QC and TN) BC. The asterisk refers to spinning side bands at ca. 100 ppm from the dominant aromatic C resonance at 129 ppm.

1 and 10 mg/l, the sorption capacity of BC6M and historical BC decreased by 56–91% over the concentration range. Fresh BC had a greater degree of sorption nonlinearity, although it decreased in BC6M and historical BC, such that the n values of the diuron sorption isotherms increased from 0.19 for fresh BC, which was highly nonlinear, to 0.5 for historical BCs, which was moderately nonlinear. Table 2 also shows the OC normalized distribution coefficient K_{OC} (mg/l), defined as $K_{OC} = (Q_e/C_e)/OC$ on an OC basis, for BCs and soils. At an equilibrium concentration of both $C_e = 1$ mg/l and 10 mg/l, the K_{OC} values for diuron and atrazine sorption were highest for fresh BC and decreased by 44–88% for BC6M and historical BCs. These results suggest the important effect of long term exposure in soils on BC quality.

Unlike the sorption of diuron and atrazine, the fresh BC had the lowest sorption capacity of Cu²⁺. However, the capacity increased with the progressive change from BC6M to QC and TN. Because the sorption isotherm of Cu²⁺ formed a plateau at an equilibrium concentration beyond 15 mg/l, the Langmuir model produced better fitting results (Fig. 4 and Table 2). The maximum sorption capacity of Cu²⁺ in QC and TN reached 12.9 and 30 mg/g, respectively, compared with 6.0 and 7.5 mg/g for fresh BC and BC6M.

The sorption capacity of diuron, atrazine and Cu²⁺ in BC-containing soils were all greater than those for the adjacent soils (Fig. 4). At an equilibrium concentration of 1 mg/l for both diuron and atrazine solutions or 10 mg/l for the Cu²⁺ solution, the sorption capacity of the BC-containing soils was 7–160 times that of the adjacent soils. The nonlinearity and K_{OC} values for diuron and atrazine sorption and the maximum sorption capacity for Cu²⁺ sorption in the BC-containing soils were also greater than that of the adjacent soils. The Freundlich n values for diuron sorption were ca. 0.5 vs. 0.8, K_{OC} for diuron sorption at 1 mg/l were 3.5 vs. 0.5 l/mg C, and maximum sorption capacity of Cu²⁺ was 13 vs. 3 mg/g for the BC-containing and adjacent soils, respectively.

3.3. Bioassay

Amending soil with fresh BC and QC reduced herbicide efficiency (Table 3). At the low end of the recommended herbicide application rate at 1.5 m/kg soil, 23% and 76% of the ryegrass survived when 0.1% of QC and fresh BC were used, respectively. The
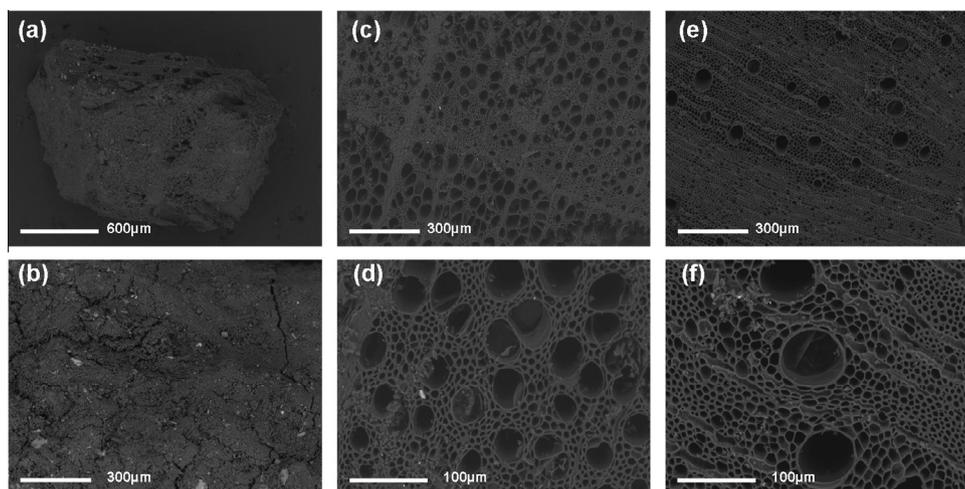
Fig. 3. Scanning electron micrographs of historical BC (a–d, collected from a charcoal blast furnace in Quebec, Canada) and fresh BC (e and f); (a and b) are typical for historical BC particles and their external surfaces are covered by mixtures of minerals, organic matter, or other tiny BC particles; (c and d) show cross-sectional views of the historical BC interior and (e and f) cross-sectional views of the fresh BC interior. A wood-like morphology is retained in historical BC particles.

survival rate increased to 76% and 100% when amendment of QC and fresh BC increased to 1%, respectively. When the herbicide application rate increased to 6 mg/kg, soil amended with 1% fresh BC still had a 26% survival rate, but the survival rate for soil amended with QC was 0%. These results show that fresh BC was more effective at reducing herbicide efficiency than aged BC as found for QC soils, which is consistent with its higher herbicide sorption capability.

Unlike the results of herbicide application, the application of Cu^{2+} did not cause the immediate mortality of ryegrass (survival rate > 90% for each pot) but displayed Cu toxicity symptoms with progressively smaller and more slender growth of the seeds as the Cu^{2+} application rate increased from 0 to 350 mg/kg soil (Table 4). Cu^{2+} application rate had no significant effect on the growth of ryegrass seed biomass for control soil, soil amended with 1% fresh BC and soil amended with 1% QC (Table 4). These results imply that the influence of BC amendment on Cu^{2+} toxicity is weak and unrelated to its Cu^{2+} sorption capability.

4. Discussion

4.1. Sorption of diuron, atrazine and Cu^{2+}

The results indicate that the long term exposure of BC in soils has a significant effect on both physiochemical structure and sorption properties. Aged (BC6M) and historical BCs (QC and TN) had diminished sorption capacity for diuron and atrazine compared with newly produced BC, whereas their sorption capacity for Cu^{2+} was enhanced. The sorption capacity of diuron and atrazine on fresh BC is in agreement with studies using carbonaceous materials (Chiou et al., 2000; Yang and Sheng, 2003a; Cornelissen et al., 2005a). The lower sorption capabilities of diuron and atrazine on historical BC corresponded well with the formation of surface O-containing functional groups during the natural oxidation of BC. O-containing surface functional groups are hydrophilic and are therefore likely to reduce the hydrophobic interaction between diuron or atrazine and the BC surface. These O-containing surface functional groups also have greater affinity for water sorption, and thus reduce the accessibility of diuron and atrazine to the sorption sites (Nguyen and Ball, 2006). Moreover, the formation of surface functional groups localizes the π electrons of the basal plane of the BC surface and weakens the π–π interaction between the aromatic ring of diuron and atrazine molecules and the basal

planes of the BC surface (Moreno-Castilla, 2004; Zhu and Pignatello, 2005). The decreased sorption capacity of BC6M vs. fresh BC does reflect the idea that the oxidation of BC contributes to a reduction in the sorption capacity of herbicides. This result is similar to studies of hydroquinone (Cheng and Lehmann, 2009) and pyrene (Hale et al., 2011) sorption.

The reduction in surface area may be another reason for the decreased sorption capacity of diuron and atrazine on historical BC. The low surface area (2 m^2/g) in this study was also reported by James et al. (2005), Pignatello et al. (2006) and Hockaday et al. (2007). This can be attributed to the blockage of pore spaces by a coating of non-BC material (Pignatello et al., 2006; Hockaday et al., 2007). However, when we calculated the sorption capacity normalized to its surface area (unit mg/m^2), the historical BC exhibited a higher surface area-normalized sorption capacity than fresh BC (data not shown). This finding is somewhat counterintuitive because historical BC is more hydrophilic than fresh BC. The results may suggest that using N$_2$ as the probe gas for characterizing an environmental BC surface for such a comparison was not valid. For instance, Kwon and Pignatello (2005) showed that N$_2$ gas measurement at 77 K was blocked from reaching the internal pore spaces coated with non-BC material, whereas these internal pore spaces could be accessed by the sorbates at higher temperature. Nevertheless, coating of non-BC material can still attenuate sorption capacity because the sorbed non-BC material could occupy the sorption sites or act as competitive a sorbate for diuron and atrazine sorption (Yang and Sheng, 2003b; Kwon and Pignatello, 2005; Pignatello et al., 2006; Wang et al., 2008; Cheng and Lehmann, 2009).

In addition to the reduced sorption capacity of diuron and atrazine, historical BC exhibits a lower nonlinearity. This is likely the result of the oxidation or the surface coating of non-BC OM of BC. It is because both oxidation and surface coating processes particularly reduce sorption capacity at the lower equilibrium concentration and bend the sorption isotherm toward a more linear shape (e.g. Chun et al., 2004; Pignatello et al., 2006; Wang et al., 2008).

Although the long term exposure of BC reduces its ability for diuron and atrazine sorption, the sorption capacity, sorption nonlinearity and K_{OC} of BC-containing soils are still greater than those of adjacent soils. These results are in agreement with many studies demonstrating that the BC fraction of soils/sediments with a higher BC fraction possesses stronger sorption capacity and sorption nonlinearity than the non-BC fraction (e.g. Accardi-Dey
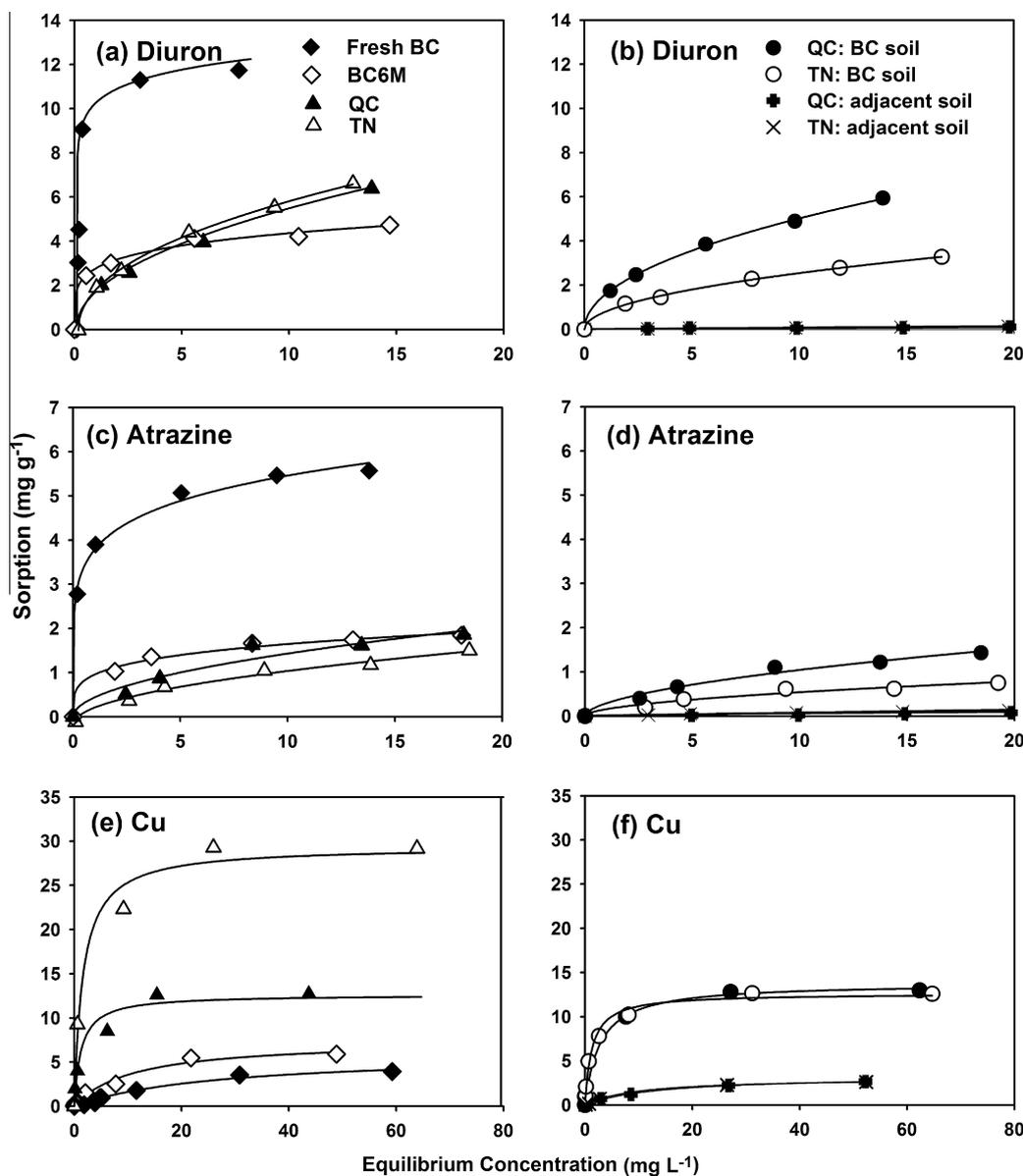
Fig. 4. Sorption isotherms for diuron, atrazine and Cu^{2+} on BCs (a, c and e) and soils (b, d, and f).

and Gschwend, 2002; Yang and Sheng, 2003a; Xiao et al., 2004; Cornelissen et al., 2005b; Sobek et al., 2009). Our study further indicates that BC can retain part of this high sorption capacity and nonlinearity on a centennial scale. The high sorption capability of BC is generally due to its relatively rigid, planar and aromatic surface, whereas the non-BC material is less condensed and consists of more polyanionic macromolecules (Lu and Pingatello, 2004; Cornelissen et al., 2005b). The NMR spectra and elemental analysis in this study confirmed that the historical BC was condensed carbonaceous material consisting primarily of highly aromatic C. However, XPS (Cheng et al., 2008a) and NEXAFS spectra indicated that the surface of historical BC contains a greater portion of O-containing functional groups. This suggests that herbicides can be sorbed on the nonpolar aromatic patch of the BC surface or move into the aromatic sorption sites in the interior pores that are undetected with the surface-oriented XPS and NEXAFS techniques.

Unlike the sorption of diuron and atrazine, the sorption of Cu^{2+} by historical BC was substantially higher than that of fresh BC. This higher sorption capability of Cu^{2+} can be attributed to the

formation of surface O-containing functional groups that directly enhance the surface negative charge and provide more electrostatic attraction between the Cu^{2+} and the BC surface (Cheng et al., 2008a). These findings of greater Cu^{2+} sorption on historical BC are in agreement with studies using various oxidizing agents (e.g. chemical oxidants, O_3 and thermal oxidation) to enhance cation uptake (Toles et al., 1999; Demirbas et al., 2009). The long term natural oxidation of BC can produce a similar range of maximum Cu^{2+} sorption capacity with other biomass chars artificially oxidized by chemical reagents (Demirbas et al., 2009).

4.2. Bioassay of BC amended soils under diuron and Cu^{2+} applications

The results of the bioassay in herbicide experiments and the results of previous studies suggest that BC amendments in soils can effectively reduce herbicide efficiency (Yang et al., 2006; Yu et al., 2006; Nag et al., 2011; Jones et al., 2011; Graber et al., 2012; Martin et al., 2012). Similar to the sorption capacity of the herbicide, the newly produced BC is better at reducing herbicide efficiency than historical BC. Hence, the effect of herbicide effectiveness from

Table 2
Freundlich and Langmuir parameters for sorption isotherms of diuron, atrazine and Cu^{2+} on BC and soils.

Freundlich model	K_f	n	R^2	Q_e (mg/g) at 1 mg/l	K_{OC} (L/mg) at 1 mg/l	Q_e (mg/g) at 10 mg/l	K_{OC} (L/mg) at 10 mg/l
Diuron							
Fresh BC	8.52	0.19	0.90	8.52	9.38	13.32	1.47
BC6M	2.77	0.20	0.99	2.77	3.18	4.36	0.50
QC	2.02	0.47	1.00	2.02	2.79	5.89	0.82
TN	1.64	0.52	0.99	1.64	2.38	5.40	0.78
QC BC soils	1.60	0.50	1.00	1.60	3.96	5.02	1.24
TN BC soils	0.62	0.56	1.00	0.62	2.75	2.24	1.00
QC adjacent soils	0.01	0.88	0.98	0.01	0.31	0.08	0.24
TN adjacent soils	0.01	0.65	0.96	0.01	1.04	0.06	0.47
Atrazine							
Fresh BC	3.78	0.16	1.00	3.78	4.16	5.46	0.60
BC6M	0.95	0.24	0.99	0.95	1.10	1.65	0.19
QC	0.34	0.53	0.99	0.34	0.48	1.16	0.16
TN	0.44	0.51	0.95	0.44	0.63	1.43	0.21
QC BC soils	0.29	0.55	0.98	0.29	0.72	1.04	0.26
TN BC soils	0.16	0.54	0.96	0.16	0.69	0.54	0.24
QC adjacent soils	0.003	1.23	0.81	0.003	0.08	0.005	0.14
TN adjacent soils	0.001	1.37	0.99	0.001	0.09	0.003	0.22

Langmuir model	q_{max}	b	R^2	Q_e at 10 mg/l	Q_e at 50 mg/l
Cu^{2+}					
Fresh BC	5.98	0.04	0.98	1.62	3.89
6 month BC	7.47	0.09	0.98	3.56	6.12
QC	12.91	0.60	0.98	11.08	12.50
TN	30.12	0.44	0.99	29.45	29.98
QC BC soils	13.79	0.36	0.98	10.81	13.07
TN BC soils	12.60	0.78	0.99	11.17	12.29
QC adjacent soils	3.32	0.07	1.00	1.40	2.61
TN adjacent soils	3.09	0.10	1.00	1.57	2.59

Table 3
Survival rating (%) of ryegrass seeds in soil with different diuron doses (0, 1.5 and 6 mg/kg) and BC amendments (0, 0.1% and 1%) 3 weeks after planting.

	Rate of diuron (mg/kg)		
	0	1.5	6
Control soil	100[a]	0	0
Soil + 0.1% fresh BC	100	83 ± 7[b]	0
Soil + 1% fresh BC	100	100	26 ± 13
Soil + 0.1% QC	100	19 ± 9	0
Soil + 1% QC	100	76 ± 12	0

[a] 100% survival of ryegrass seeds and 0 no survival.
[b] Survival rate ± SE (n = 3).

Table 4
Dry wt. (mg/pot) of ryegrass shoot biomass in soils with different Cu^{2+} dozes (0, 30, 150 and 350 mg/kg soil) and BC amendments (0% and 1%) 4 weeks after planting; ns, no significance among treatments).

	Dose of Cu^{2+} (mg/kg soil)			
	0	30	150	350
Control soil	65 ± 15[a]	56 ± 2	53 ± 4	34 ± 1
Soil + 1% fresh BC	57 ± 4	57 ± 3	56 ± 1	31 ± 3
Soil + 1% QC	60 ± 4	51 ± 6	48 ± 8	31 ± 3
	ns	ns	ns	ns

[a] Dry wt. ± SE (n = 3).

Unlike the results of herbicide application, no significant differences in ryegrass seed growth appeared for the control soil and the soils amended with 1% fresh BC and QC, respectively, for any Cu^{2+} application rate. The variation in sorption capacity results suggests that Cu^{2+} is only slightly sorbed by the surface functional groups of BC and is available for root uptake. Previous research has suggested that the sorption of Cu^{2+} on the BC surface is easily reversible (Rozada et al., 2008) and root exudates may also enhance the exchange of the sorbed Cu^{2+} and facilitate Cu^{2+} uptake (Mench and Martin, 1991). However, some studies report that BC amendments reduce Cu phytotoxicity (Buss et al., 2011; Park et al., 2011). This discrepancy is likely caused by these studies having applied alkaline BC (pH > 10), which immobilized the Cu^{2+} because of greater ligand sorption and precipitation induced by BC application (Cao et al., 2009; Buss et al., 2011). However, this mechanism cannot occur for QC amendment because of its intrinsically low pH.
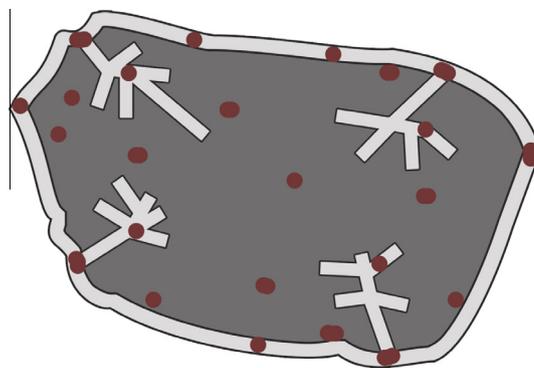
Fig. 5. Conceptual model of an environmental BC particle after long term exposure in soil. White represents the surface O-containing functional groups on the edge of a BC particle, gray the aromatic-rich core structure of BC and dark brown spots coatings of non-BC material. The sorption properties of BC particles are a complex interplay among these components.

BC amendments is likely to be alleviated over time, but minor effectiveness on reducing herbicide efficiency in the historical BC still exists and can persist longer than expected (Graber et al., 2011; Jones et al., 2011; Martin et al., 2012). In agricultural applications, BC may be amended periodically, and the aging process of BC in reducing herbicide inefficiency would become less important.

4.3. Structural model for BC particle and its environmental relevance

To clarify our results, a conceptual model for environmental BC that demonstrates its sorption characteristic is illustrated in Fig 5. An environmental BC particle can be depicted as three major components: (i) surface O-containing functional groups, (ii) sorbed non-BC material and (iii) an aromatic-rich core structure. Its sorption properties are the result of an interplay between these three components and the properties of sorbates.

4.3.1. Surface O-containing functional groups

Surface O-containing functional groups develop along the peripheral edge of the BC structure through both short term (Cheng et al., 2006) and long term natural oxidation (Cheng et al., 2008a). Unlike newly produced BC, the formation of surface O-containing functional groups causes environmental BC to become hydrophilic and less favorable for sorbing herbicides. In contrast, the negative charge of O-containing surface functional groups allows environmental BC to be more electrostatically attractive for cations, including heavy metal ions and cation nutrients (e.g. Ca, K and Mg).

4.3.2. Sorbed non-BC material

When BC is added to soils, it begins to interact with other soil components. The sorbed non-BC material may occupy sorption sites or act as a competitive sorbate that lowers the herbicide sorption capacity. In addition, the sorbed non-BC material can block the inner pore spaces of BC and decrease its surface area. This interaction between BC and minerals may also protect BC in soil against microbial decomposition (Brodowski et al., 2005).

4.3.3. Aromatic-rich core structure

Despite the formation of O-containing functional groups along the peripheral edge of the BC structure, the aromatic-rich core structure still predominates for the environmental BC particle. The aromatic-rich core structure distinguishes BC from non-BC material. This structure makes BC resistant to microbial decomposition (Baldock and Smernik, 2002). In pore interiors and microsites, aromatic functional groups retain high sorption ability toward pesticides or other hydrophobic compounds.

The proposed model is important for characterizing the BC structure and sorption properties in soils. This is especially true because no chemical pretreatment for BC samples was conducted. Analytical pretreatment by combustion at 375 °C or extraction to remove the non-BC fraction and physically isolate BC for further characterization are widely used, and these processes may alter the surface functionality of the residual fraction and change the overall sorption property (Chun et al., 2004; Xiao et al., 2004). In addition, the comparison between the fresh and historical BC in this study was based on BC samples with similar feedstock and charring conditions. This is significant because the sorption properties of BC differ with its source and charring conditions. The BC samples used were man-made from specific hardwood and also carefully tended by colliers to provide suitable charcoal for iron-making in a charcoal blast furnace.

This study examined the sorption properties of organic compounds on BCs using diuron and atrazine. Previous studies have shown that BC is a strong sorbent for a wide range of organic contaminants, including polycyclic aromatic hydrocarbons, polychlorinated biphenyls, dioxins, polybrominated diphenylethers and pesticides (Accardi-Dey and Gschwend, 2002; Cornelissen et al., 2004, 2005b; Koelmans et al., 2006; Sobek et al., 2009). Although the study did not test these compounds, similar effects can be anticipated because the changes of surface functionality and surface coating caused by the long term exposure of BC should be equally important (Moreno-Castilla, 2004). Similarly, the signifi-

cant increase in Cu^{2+} sorption capacity after long term exposure of BC should have the same effect for other cationic ions in the soil, including K, Ca and Mg. Increasing cation sorption is an important factor in retaining soil nutrients and thus plays an important role in soil fertility (Glaser et al., 2002; Liang et al., 2006; Cheng et al., 2008a).

Although BC amendments inactivate herbicide efficiency, they also have the positive outcome in reducing the risk of environmental contamination and human exposure to contaminants. For example, the amendment of contaminated sediments with BC has been proposed as a management method to immobilize organic contaminants and biological accumulation in benthic organisms (Koelmans et al., 2006). Along with its recalcitrance in environments, BC has a significant long term effect on the toxicity of contaminants and soil fertility.

5. Conclusions

The results indicate that the long term exposure of BC in soils has a significant effect on both physiochemical structure and sorption properties. The findings include: (i) the BC sorption of pesticides is diminished after long term exposure in soils, whereas the sorption of cations is enhanced; (ii) soils containing a high level of historical BC still exhibit a higher sorption capacity, sorption nonlinearity and K_{OC} to herbicides than adjacent control soils; and (iii) BC amendments reduce herbicide efficiency because newly produced BC substantially hindered herbicide efficiency, but historical BC still exerted an influence on reducing herbicide efficiency. These changes in BC sorption properties can be interpreted in terms of changes in BC structure. Thus, a conceptual model for environmental BC connected with its sorption properties is illustrated. The conceptual model depicts three major components of an environmental BC particle: (i) surface O-containing functional groups, (ii) attached non-BC material and (iii) an aromatic-rich core structure. The sorption properties of BC are a result of the interplay among these components. Along with its recalcitrance in environments, BC has a significant long term effect on the toxicity of contaminants and soil fertility.

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