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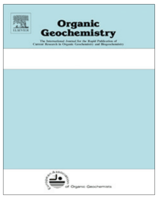

Sorption properties for black carbon (wood char) after long term exposure in soils

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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.

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