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The changes in biochar properties and sorption capacities after being cultured with wheat for 3 months

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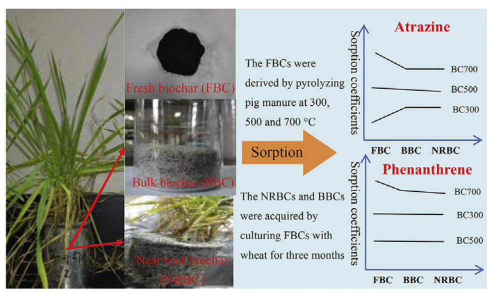
HIGHLIGHTS

- Wheat root aging changed properties of biochars with high ash content.
- The changes depended on biochar type and the distance from the roots.
- Root-aging reduced sorption on high-temperature biochar due to pore-blockage.
- Root-aging enhanced sorption on low-temperature biochar.
- The changes in sorption differed due to different sorption mechanisms.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochars that were produced from pig manure at three different temperatures were amended to sand and cropped with wheat to examine the effect of wheat roots on biochar properties and its sorption capacity. After being aged with wheat roots for three months, the biochar samples showed significant changes in their physicochemical properties, which depended on biochar types and their distances from the roots. In general, the ash content and micropores decreased and the polarity increased after root aging. The changes in the biochar properties in turn affected biochar sorption capacities. The sorption of atrazine and phenanthrene by the biochar that was produced at 300 °C (BC300) both increased by different extents after aging, significantly decreased for BC700, and there were little changes for BC500. The complex changes were due to the different dominant sorption mechanisms for different biochars and different chemicals. For BC700, hydrophobic partition and pore-filling were the main processes, especially for phenanthrene, whereas for BC300, polar interactions dominated.

1. Introduction

Biochar is a carbon-rich solid product of biomass materials such as wood, manure, and leaves when the raw material is heated in a closed container with limited air (Manya, 2012). The origin of biochar application can be dated to *Terra Preta de Indio* in the Amazon region, where dark earth was created through the use of slash-and-char technique (Marris, 2006). However, biochar had not received widespread attention until the article "Putting the carbon back: Black is the new green" was published in Nature in 2006 (Marris, 2006). Now, biochar is emerging as a novel combined means of sequestering carbon, improving soil fertility and remediating contaminated soil (Beesley et al., 2011; Manya, 2012), and these applications have driven a recent surge in biochar studies.

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The great sorption capacities for various contaminants is the feature that biochar is used as a novel material for pollution remediation. A prerequisite for biochar remediation technology is that the high sorption capacity is maintained over a long period of time, especially when in close contact with soil or on exposure to changing environmental conditions (Zimmerman, 2010). In soils, due to its strong affinity for organic matter and inorganic mineral ions, biochar is likely to undergo a series of biogeochemical reactions and physical processes that will result in the alteration of its properties with time (Kwon and Pignatello, 2005; Cheng et al., 2008; Farrell et al., 2013). It has been reported that the sorption capacity for organic compounds decreases significantly by an aged soil-biochar mixture compared to the fresh mixture (Martin et al., 2012). However, another study noted that aging had little effect on the sorption of biochar (Jones et al., 2011). In most of the studies, artificial aging methods were used to examine the effects of simulation aging processes on biochar properties, such as microbial degradation, physical freeze–thaw cycles, oxidative chemical treatment and incubating in amended soil mixtures (Zimmerman, 2010; Liu et al., 2013; Qian and Chen, 2014).

Plant roots extensively exist in soil especially in farmland, where biochar is suggested to apply. Biochar constituents have been reported to be able to be absorbed by plant roots and stimulate root growth (Prendergast-Miller et al., 2014). Besides, the porous structure of biochar provides a suitable habitat for many microorganisms by protecting them from predation and desiccation and by providing many of their diverse carbon, energy and mineral nutrient needs (Thies and Rillig, 2009). It is well documented that plant roots release many organic exudates, including low molecular weight organic compounds, polymer degrading enzymes, saccharides and amino acids (Ling et al., 2009; Toyama et al., 2011; Lefevre et al., 2013; Tan et al., 2013). These exudates could not only enhance the activities of microorganisms but also could be adsorbed by biochars, which may affect the properties and sorption capacities of biochars. However, studies about the impact of root system on biochar properties are rather scarce.

In this work, we examined the effects of being cultured with wheat roots on the physical and chemical properties of biochars. The sorptions of atrazine and phenanthrene on fresh biochars and biochars that had been cropped with wheat (designated as “wheat root aged biochars”) were studied. Atrazine and phenanthrene were chosen as model contaminants due to their different polarities, electron polarizabilities, and aromaticities. The specific objectives of this research were (1) to determine whether and how plant root aging modify biochar properties and (2) to compare the sorption of specific organic pollutants on fresh and root aged biochars to better understand biochar environmental implications over time as soil amendments.

2. Materials and methods

2.1. Chemicals

Atrazine (97%) was obtained from the Rainbow Chemical Company (Shanghai, China), and phenanthrene (Phen, 98%) was obtained from J&K Scientific (Beijing, China). Stock solutions of atrazine and Phen were separately prepared in HPLC-grade methanol. The analytical grade standards of atrazine and Phen that were used as standards for the HPLC analysis were purchased from Accustandard (Connecticut, USA). The other chemicals that were used in this study were analytical grade.

2.2. Production of fresh biochar samples

Briefly, the biochar was produced by pyrolyzing air-dried pig manure under O_2 limited condition at 300, 500 and 700 °C, respectively for 4 h. After pyrolysis, the biochar samples were allowed to cool to room temperature and then ground. The biochar of particle size between 0.0385 and 0.45 mm (sieved by 200 and 40 mesh) was used. The biochar samples were stored in a desiccator before use. The biochars were designated as BC300, BC500, and BC700, based on their respective pyrolyzing temperatures.

2.3. Aging biochars with wheat roots

Wheat was chosen as the test crop to study the influence of being cropped with plant roots on the properties of biochars because it is a common crop in China. After germination, 10 wheat seeds were transferred to a pot that contained 500 g of a mixture of quartz sand and biochar that served as growth substrate. The quartz sand (0.45–1 mm) was pretreated with dilute hydrochloric acid (1:1) for 24 h, washed thoroughly with tap water and rinsed with distilled water, and then air-dried at room temperature. The mixture of biochar and quartz sand was prepared by thoroughly mixing the washed quartz with the accurately weighed biochar on a rotary shaker for 7 d. The percentage ratio of biochar in the mixture was 3% by weight (i.e. 15 g biochar) in accordance with the mediate agronomic addition rate (Jones et al., 2011). The plant pots were placed in a growth cabinet with a relative humidity of 75% under a cycle of 16 h/25 °C during the day and 8 h/20 °C at night. All of the pots were watered with 10 mL of modified Hoagland's nutrient solution (Supplementary Material, SM) every two days to support plant growth (Yoshitomi and Shann, 2001).

After 90 d of culture, a destructive harvest was performed to end the aging process of biochar by wheat roots. The growth substrate in the pots was divided into three sections according to its distance from roots (Fig. 1s), 1) the bulk samples at the top and bottom of individual pot that did not contact plant roots; 2) the near-root samples that settled within the root zone and hence may have been influenced by root exudates; and 3) the rhizosphere sample that remained attached to the roots after gentle shaking. The three sections of the growth substrate samples were air dried and the biochar particles were separately recovered from the quartz sand by hand with a magnet. The biochars showed ferromagnetism, as revealed by the magnetic hysteresis loop (Fig. 3s), with FBC700 showing higher ferromagnetism than those of FBC500 and FBC300 (Details are described in the SM, Fig. 3s). The biochars obtained were designated as bulk biochar (BBC), and near-root biochar (NRBC) and rhizosphere biochar (RBC), respectively, which were collectively called as wheat root aged biochars. In summary, twelve biochar samples were obtained, including three fresh biochars (denoted as FBC), i.e., FBC300, FBC500, and FBC700, and the wheat root aged biochars, BBC, NRBC and RBC, from the three FBCs.

2.4. Characterization of the biochar samples

The bulk and surface elemental compositions and the surface areas of the twelve biochar samples were analyzed by the methods described in our previous study (Zhang et al., 2013). Dissolved organic carbon (DOC) of each biochar sample was measured with an Analytikjenamulti N/C 3100 analyzer (Analytik Jena AG, Germany). Magnetic properties of the biochars were measured using a superconducting quantum interference device (SQUID) magnetometer (PPMS-9, Quantum Design, USA) at room temperature.

2.5. Sorption experiment

As stated in Section 2.3, the RBC was defined as the biochar that remained attached to the roots after gentle shaking, and hence, the amount of the RBC samples was very small (only 3–5 g) and was