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Effect of aging in field soil on biochar's properties and its sorption capacity☆

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ABSTRACT

Due to its high sorption capacity for different kinds of contaminants, biochar is advocated as a novel remediation strategy for contaminated soils. However, it is not clear how long this extraordinary sorption capacity will be maintained after the biochar is applied to the soil. In this study, a commercial biochar was applied to an agricultural soil, and the sorption of atrazine and phenanthrene on biochar amended soils with different aging periods ranging from 0 to 2 y was investigated. The application of fresh biochar in soil led to an obvious enhancement of the sorption coefficients (K_d) of atrazine and phenanthrene (by 3.13 and 2.93 times at $C_e = 0.01\ S_w$, respectively) compared with the untreated soil. The surface area of biochar first increased and then decreased with aging time. Correspondingly, the sorption of atrazine and phenanthrene on the biochar amended soils first increased and then decreased markedly. Based on the changing trend of the K_d values with aging time, it could be predicted that the sorption capacity of biochar amended soils will decrease to the level of the untreated soil after 2.5 y.

1. Introduction

Biochar is a carbon-rich solid product obtained by pyrolyzing biomass materials such as leaves, manure and agricultural straws under limited oxygen (Beesley et al., 2011). Compared to raw materials, biochar has a higher carbon content, larger surface area and greater cation exchange capacity (Keiluweit et al., 2010; Lee et al., 2010). Previous studies revealed that biochar applied to soil can significantly enhance the sorption capacities of soils for contaminants with different properties and decrease their bioavailability to animals or plants in soils (Beesley et al., 2011; Cao et al., 2009; Chen and Yuan, 2011). This feature makes biochar a novel reagent for the remediation of contaminated soil (Beesley et al., 2011; Kong et al., 2014; Meyer et al., 2011), which has drawn widespread scientific interest.

However, a prerequisite for the successful biochar application in the remediation of contaminated soils is that its strong sorption capacity for contaminants maintains over a long period of time. After being applied in soil, biochar is likely to undergo a series of biogeochemical reactions, which ultimately lead to time-dependent alterations in its physicochemical properties (Martin et al., 2012). Soil organic matter, especially the most labile fraction-dissolved organic matter (DOM) has been reported to interact with biochar through different pathways. First, the adsorption of DOM may lead to the reduction in surface area of biochar due to the blockage of micropores and enhancement of surface polarity (Pignatello et al., 2006; Zhang et al., 2013). Second, the co-existence of DOM may stimulate the degradation of biochars, which has been shown to lead to increase of oxidized functional groups, thus resulting in increasing CEC (Keith et al., 2011; Liang et al., 2006; Ren et al., 2016). Moreover, it was found that soil mineral particles may incorporate onto the surface of biochar in the first few months after the application of biochar to field soil (Lin et al., 2012). Additionally, the activities of soil organisms may also affect biochar structure. Our previous study (Ren et al., 2016) revealed that the properties of biochars obtained from pig manure at 300 and 700 °C pyrolyzing temperatures clearly changed after being cultivated with wheat root for 90 d, where both root exudates and rhizosphere microorganisms exhibited important roles, in addition to the interactions with soil constituents.

The alteration in biochar structural properties will in turn influence the sorption capacities of biochar for contaminants. The

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aging effects of soil on biochar sorption capacities have been reported in previous studies (Chen and Yuan, 2011; Hale et al., 2011; Jones et al., 2011; Martin et al., 2012). For example, Martin et al. (2012) found that compared to biochar amended soil without aging (at 10 t ha^{-1}), the sorption of diuron and atrazine on biochar amended soil decreased markedly after being aged for 32 months. Conversely, another study revealed that the aging of biochar in soil for 2 y did not change the sorption capacity for simazine (Jones et al., 2011). The conflicting results may be attributed to multiple factors. In summary, there appears to be no consensus of whether and how the sorption capacity of biochar for organic pollutants changes with prolonged aging time of biochar in field soils.

In this study, a commercial biochar was applied to an agricultural soil, and the sorption of atrazine and phenanthrene on biochar amended soils with different aging periods ranging from 0 to 2 y was investigated. In consideration of different structural properties such as polarity and aromaticity, we chose atrazine and phenanthrene as typical organic contaminants in soil. The major objectives of this work were (i) to investigate the alteration in biochar properties with increased aging time in field soil and (ii) to explore the time that biochar can maintain its high sorption capacity in field soil.

2. Materials and methods

2.1. Chemicals

Analytical-grade reagents atrazine (97%) and phenanthrene (Phen, 98%) were used as received, and stock solutions were prepared separately in LC-grade methanol for sorption experiment. LC-grade atrazine and Phen were used as standards for HPLC analysis. More detailed information of chemicals used in this study is described in the Supporting Information (SI).

2.2. Biochar and soil

The biochar used in this work was purchased from Sanli New Energy Company in Shangqiu City, Henan Province, China. The commercial biochar was produced from wheat straw at the pyrolysis temperature of 500 °C for 4 h with a heating rate of 5–10 °C min^{-1}. The selected properties of this fresh biochar sample are provided in Table 1s in the SI. Fresh biochar was stored in a glass tube with PTFE sealing caps in a −20 °C freezer.

An agricultural field located in Jinnan district (Tianjin, China) was selected as the biochar field trial location. The field was primarily cropped with lettuces in greenhouses. Four greenhouses (8 m × 50 m each) were chosen as the trial plots for four different aging times, and for each of them 1/4 of the area was set as the control and the rest of the greenhouse was amended with the commercial biochar at a rate of 20 t ha^{-1} (equivalent to ca. 1% w/w based on incorporation to 20 cm depth) and was mixed well using farm machinery. In order to investigate the dynamic changes in the sorption capacity of biochar amended soil, we applied the commercial biochar to the four greenhouses at four different times from October 2014 to May 2016. These field plots were designed as agronomic trials and were planted with lettuces similar to before the trial without biochar application. More information about the trial plots and biochar application time is shown in the SI.

Soil sampling was conducted in October 2016, and biochar-soil samples of up to 2 y of aging time were obtained. In order to reduce the system error caused by the uneven mixing of the biochar in field soil, five cores from a 0–20 cm profile were sampled in each greenhouse with the diagonal sampling method and mixed well to form a single sample. Both the soil and biochar amended soil samples collected were air-dried and passed through a 2-mm sieve after being ground. Based on the biochar application time (aging time), the biochar amended soil samples were marked as BC-Soil 2# (0.5 y), BC-Soil 3# (1 y), BC-Soil 4# (1.3y) and BC-Soil 5# (2 y) and their corresponding control soils were labeled Soil 2#, Soil 3#, Soil 4# and Soil 5#, respectively. To conduct the sorption experiment, the original fresh biochar was mixed thoroughly with soil 5# at the same application rate of 20 t ha^{-1} and studied as biochar amended soil without aging (fresh amended biochar-soil sample), which was labeled BC-Soil 1#. The selective properties of the soil samples in each greenhouse are listed in Table 2s.

2.3. Characterization of the biochar samples

Visible biochar particles were recovered from a subsample of biochar amended soil samples with different aging times by hand with fine forceps to investigate changes in biochar properties with aging in soil. The fresh and aged biochar particles were analyzed for morphology, specific surface area and surface elemental composition. The morphology of fresh and aged biochars was observed with a scanning electron microscope with energy dispersive spectrometer (SEM-EDS) (Shimadzu SS-550, Shimadzu, Japan). Surface areas were obtained by N_2 gas adsorption-desorption using a surface area analyzer (ASAP, 2020/Tristar 3000, USA). The surface elemental compositions and carbon-based functionalities of all biochar samples were determined using an X-ray photoelectronic spectrometer (XPS) (ULVA-CPHI PHI 5000 VersaProbeII, Japan). The XPS core lever spectra were analyzed using the CasaXPS 2.3 software.

2.4. Sorption experiment

Sorption isotherms of atrazine and Phen on soil and biochar amended soil samples were obtained using a batch equilibration technique. Briefly, an appropriate amount of soils or biochar amended soils (1.0 g for atrazine and 0.01 g for Phen) was added to 40-mL glass tubes with PTFE sealing caps. Then, a background solution containing 0.05 M $CaCl_2$ to maintain a constant ionic strength and 200 mg L^{-1} of $HgCl_2$ to act as a bio-inhibitor was prepared and added into each tube. After 12 h of pre-equilibration, a set amount of the stock solution of atrazine or Phen was filled into each tube to total seven initial sorbate concentrations (1–30 mg L^{-1} for atrazine and 0.1–1 mg L^{-1} for Phen). The percentage of methanol in each tube was less than 0.1% v/v to minimize the co-solvent effect. The vials were shaken in a rotary shaker at room temperature (20 ± 0.5 °C) for 3 d (for atrazine) or 7 d (for Phen), which was sufficient to reach sorption equilibrium.

After the sorption equilibrium, all tubes were centrifuged at 2500 r min^{-1} for 15 min, and 2 mL of the supernatant was sampled to determinate the concentration of atrazine or Phen by a high-performance liquid chromatographer (HPLC, Agilent 1200). The control experiments showed that the average loss of the initially added atrazine or Phen was lower than 2%. Before the sorption experiment, the background level of atrazine or Phen in soil were determined, and both atrazine and Phen were not detectable (lower than 1 μg/kg). Therefore, the amount of atrazine or Phen adsorbed by sorbents was calculated by mass difference.

More detailed information about the analysis of atrazine or Phen by HPLC is described in the SI. All the sorption experiments were performed in duplicate.

2.5. Data analysis

The Freundlich model was used in this study to analyze the sorption data of atrazine and Phen. The equation is described as follows:

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