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Sorption, bioavailability and ecotoxic effects of hydrophobic organic compounds in biochar amended soils

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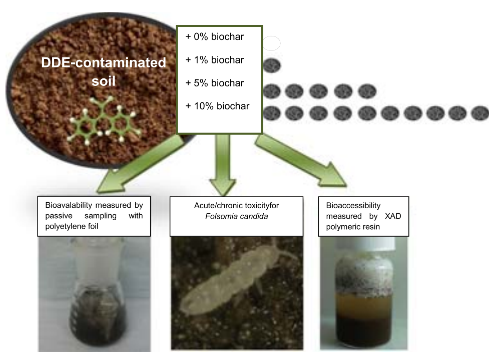
HIGHLIGHTS

- Biochars had similar sorption capacities to hydrophobic organic compounds.
- Competitive sorption to biochar in the presence of multiple contaminants was not observed.
- Sorption of compounds to biochar was not reduced in the presence of soil organic matter.
- Bioavailability and bioaccessibility decreased with increasing biochar dose.
- Biochars at 10% dose posed reproductive toxic effects to *Folsomia candida*.

GRAPHICAL ABSTRACT



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ABSTRACT

This work addresses the effect of biochar amendment to soil on contaminant sorption, bioavailability, and ecotoxicity. A distinction between positive primary amendment effects caused by reduced toxicity resulting from contaminant sorption, and negative secondary amendment effects of the biochars themselves was seen. Two biochars (one from high technology and one from low technology production processes) representing real world biochars were tested for the adsorption of pyrene, polychlorinated biphenyl (PCB) 52), and dichlorodiphenyldichloroethylene (*p,p′*-DDE). Sorption by both biochars was similar, both for compounds in single and mixed isotherms, in the presence and absence of soil. *p,p′*-DDE natively contaminated and spiked soils were amended with biochar (0, 1, 5, and 10%) and bioavailability, operationally defined bioaccessibility and ecotoxicity were assessed using polyethylene (PE), polymeric resin (XAD) and *Folsomia candida*, respectively. At the highest biochar dose (10%), bioavailability and bioaccessibility decreased by >37% and >41%, respectively, compared to unamended soils. Mortality of *F. candida* was not observed at any biochar dose, while reproductive effects were dose dependent. *F. candida* benefited from the reduction of *p,p′*-DDE bioavailability upon 1% and 5% biochar addition to contaminated soils while at 10% dose, these positive effects were nullified by biochar-induced toxicity. *p,p′*-DDE toxicity corrected for such secondary effects was predicted well by both PE uptake and XAD extraction.

1. Introduction

Soils contaminated by persistent, bioaccumulative and toxic pollutants present a substantial challenge for environmental risk

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management. Contamination of soil results both from current and previous intentional chemical use (e.g., pesticide application (Maliszewska-Kordybach et al., 2014; Qu et al., 2016)), as well as from unintentional pollutant release from various industrial and urban sources (Cetin, 2016). With this in mind, it is paramount to improve soil quality via the application of effective remediation strategies. The addition of biochar to soils has been touted as one method that could potentially assist in solving this issue (Ahmad et al., 2014; Beesley et al., 2011; Singh et al., 2015).

Biochar is the charred solid product resulting from the pyrolysis (Nartey and Zhao, 2014) of crop and plant residues (Singh et al., 2015) and animal wastes (Elzobair et al., 2016) under low oxygen environments (Sun et al., 2014). Biochar has a porous structure, charged surfaces, and an abundance of surface functional groups (carboxyl, hydroxyl, phenolic hydroxyl, and carbonyl groups) making it an efficient sorbent for both organic and inorganic contaminants and a promising tool for soil remediation (Chen and Yuan, 2011). Biochar has been shown to reduce the bioavailability of organic contaminants (Denyes et al., 2016; Hale et al., 2016), inorganic contaminants (Trakal et al., 2011; Xu et al., 2016), and both inorganic and organic contaminants simultaneously (Beesley et al., 2010; Cao et al., 2009; Gomez-Eyles et al., 2013) when added to contaminated soil. Parameters such as biochar feedstock, pyrolysis temperature and production method affect biochars physicochemical properties which in turn influence biochars sorption characteristics, and as demonstrated in a previous extensive review, these properties can vary extensively among biochars (Hale et al., 2016). In general, sorption increases with pyrolysis temperature as a result of increasing surface area, pore volume, aromaticity, and thermal stability (Kupryianchyk et al., 2016).

A number of studies reviewed by e.g. Beesley et al. (2011), Xie et al. (2015) and Ogbonnaya and Semple (2016) that investigated the sorption capacity of biochars for a diverse range of hydrophobic organic compounds (HOCs) have been reported, where various end point tools have been used to assess the extent of contaminant immobilization. Sorption has most often been quantified as the biochar-water partitioning coefficient (K_D) obtained by determining the concentration of the target contaminant in the aqueous and the solid (biochar) phase at equilibrium (Hale et al., 2011; Chen et al., 2008; Tang et al., 2013). Sorption studies often employ passive samplers (PS) in order to accurately determine very low aqueous concentrations of hydrophobic and water insoluble compounds (Mayer et al., 2016). Passive samplers provide a measure of chemical activity (the potential for spontaneous physicochemical processes such as passive diffusion) by quantifying the freely dissolved aqueous concentration, C_{FREE} (Adams et al., 2007). Thus, C_{FREE} gives a measure of pollutant bioavailability and this is known to be closely related to toxicity to organisms (Denyes et al., 2016). In contrast, depletive extraction methods (such as XAD and Tenax desorption as well as the recently introduced use of sorbent traps (Mayer et al., 2016)) can be used in order to quantify the amount of contaminant that is, or can become, available within a given time span (Cui et al., 2013). This desorbable fraction gives a measure of pollutant bioaccessibility and represent the amount of pollutant that is accessible to organisms over a relevant time scale (Reichenberg and Mayer, 2006).

To maximize the positive effect of biochar addition to soil, mitigation of potential risks following contaminant immobilization via biochar amendment should occur simultaneously with an improvement of, or at least non-detrimental effect on, the ecological function of the soil. In comparison to the significant number of sorption studies, the effects of biochar amendments on soil biota have mainly focused on earthworms and reported mixed biological effects of biochar amendments (Centofanti et al., 2016; Elmer et al., 2015; Gu et al., 2016; Khorram et al., 2016; Malev et al., 2016; Malińska et al., 2016; Paz-Ferreiro et al., 2015; Shan et al., 2014; Tammeorg et al., 2014; Wang et al., 2016, 2014). Gomez-Eyles et al. (2011) observed a significantly higher weight loss in earthworms that were placed in hardwood biochar-amended PAH contaminated soil as compared to a unamended control. Within this study, the confounding effect of the presence of organic pollutants along with the biochar did not allow the authors to conclude whether the root cause of the negative effects was the biochar amendment or the pollutants themselves. Other soil-dwelling invertebrates often used in ecotoxicological studies, such as the springtail *Folsomia candida* (ISO, 1999) and potworm *Enchytreius crypticus* (ISO, 2004), have been used less often in biochar toxicity studies (Hale et al., 2013). where both increased and decreased toxicity to organisms following biochar amendment to contaminated soils (Kołtowski and Oleszczuk, 2016; Kołtowski et al., 2016) and non-contaminated soils (Domene et al., 2015; Marks et al., 2014) has been observed. For example, Marks et al. (2014) observed that biochars had no effect on the survival of *F. candida* (except for one biochar) when added to clean soil, but both stimulated and inhibited reproduction depending on biochar type, the latter effect due to biochar's alkaline nature. Domene et al. (2015) observed an inhibition of collembolan reproduction when certain biochars were added to clean soils at intermediate to high field equivalent application rates (>7%), despite low levels of total heavy metal and PAHs in the biochars themselves. In the field, mixed effects of biochar amendments have been noted. Conti et al. (2014) reported a significant reduction in microathropod density, with an increased diversity and evenness, 2 years after the amendment of 30 t/ha of a gasification biochar to a poplar plantation on an acidic soil. These mixed literature results and limited understanding of the causes and consequences of biochar amendments on soil microathropods reveals a knowledge gap to be addressed.

To this end, contaminant sorption and bioavailability, in addition to ecotoxic effects, of both HOCs and biochar itself are determined here for two biochars amendment to both contaminated and non-contaminated soils. Sorption of pyrene, *2,2′,5,5′*-tetrachlorobiphenyl (CB 52), and *p,p′*-DDE to two biochars in the presence and absence of soil, in addition to as single compounds and in a mixture, was quantified. These compounds were chosen as they have varying hydrophobicities and are representative persistent, toxic and widely occurring soil pollutants (Cetin, 2016; Maliszewska-Kordybach et al., 2014; Qu et al., 2016; Wawer et al., 2015). Spiked and historically contaminated soils were used in order to investigate the fate and ecotoxicity of the pollutants following biochar amendment. Sorption and bioavailability were assessed by polyethylene (PE) passive samplers and an XAD extraction method and ecotoxicity was determined following the ISO standardized *Folsomia candida* toxicity test (ISO, 1999). In an effort to develop a more comprehensive understanding of the potential remediation and ecotoxic effects of biochars on contaminants and on *F. candida*, contaminant bioavailability was measured as well as ecotoxicity experiments were performed using native biota in both contaminated and non-contaminated soils. This allows the possible positive (primary) and negative (secondary) effects of biochars to be considered separately.

2. Material and methods

2.1. Chemicals and materials

Details about all chemicals and materials can be found in the supporting information.

2.2. Biochar and soil characterization

Mixed wood shavings and rice husks biochars were used and represent real world biochars both with respect to feedstock availability and production conditions. Both feedstocks are available in large quantities and the wood biochar was produced under highly-controlled conditions at the pilot scale, while the rice husk biochar was prepared under less controlled conditions on a small scale. These differences could potentially lead to varying sorption characteristics as well toxicity and represent biochars that could typically be produced in developed and