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Changes in sorption and bioavailability of herbicides in soil amended with fresh and aged biochar

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ABSTRACT

Knowledge of long-term pesticide behavior in biochar (BC) amended soil is still contradictory. In this work, we compared the sorption of three highly persistent and ionizable pesticides [two anionic (imazamox and picloram) and one weak base (terbuthylazine)] on both fresh and field-aged BC as well as on a soil amended with these biochars. The aging process was performed by burying the biochar at 10 cm in a silt loam soil [Upper Midwest USA (Wisconsin)] for six months. Field aged BC removed the three pesticides from solution to a higher extent (> 85%) than the fresh BC (< 16%). This removal was attributed to water-soluble components on the biochar. Laboratory incubation experiments demonstrated that dissipation in soil and biochar mixtures were both a function of pesticide and biochar type. The amounts of soil extractable (i.e, bioavailable) pesticide were inversely related to the extent of sorption. Similar dissipation and sorption of imazamox was observed in unamended and BC-amended soils. Terbuthylazine dissipated similarly in all treatments, but sorption increased with incubation time in the aged BC-amended soil. Conversely, picloram dissipated to a higher extent in aged BC-amended soil when compared to unamended or fresh BC-amended soil. This work demonstrates temporal variability of biochar sorption capacities due to soil exposure, which alters the efficacy and bioavailability of soil applied pesticides.

1. Introduction

Biochar (BC) is defined as a solid material produced by the thermal decomposition of biomass under limited supply of oxygen. It is more biologically inert as compared to other forms of carbon, due to its highly condensed aromatic structure (Rechberger et al., 2017; Spokas et al., 2014). This material has attracted attention in the field of environmental and agricultural science, because it simultaneously improves soil quality (e.g., nutrient availability, water holding capacity) and acts as agent for mitigating climate change due to its carbon sequestration ability (Lehmann and Joseph, 2015). However, BC is not a homogenous product, showing varying complexity and heterogeneous chemical and physical properties, which are dictated by the feedstock and pyrolysis conditions. This has led to an increasing effort by the scientific community to standardize BC production in order to maximize its benefits as soil amendment (Lehmann and Joseph, 2015; Sohi, 2010; Spokas et al., 2012). However, properties of BC also change with time in soils during weathering or aging processes (Martin et al., 2012; Pignatello et al., 2015). The implications of these modifications are still not yet fully understood (Mia et al., 2017a; Trigo et al., 2014).

Biochar has attracted attention primarily due to its sorption capacity (Cabrera-Mesa and Spokas, 2010; Yavari et al., 2015). The affinity of BC for organic compounds is hypothesized to be determined by its surface area, structural porosity, and surface chemistry. Freshly-applied biochar to soil has been widely documented to affect the fate of pesticides and it has been proposed as a tool to mitigate contamination problems derived from pesticide use. Typically, BC increases the sorption of pesticides in soils (Cabrera-Mesa and Spokas, 2010; Yavari et al., 2015), but their availability is intimately governed by desorption processes. Sorption has been shown to decrease biodegradation and leaching of pesticides (Cabrera-Mesa and Spokas, 2010; Lehmann et al., 2011; Sopeña et al., 2012), but may also reduce pesticide efficacy (Gámiz et al., 2017a; Yavari et al., 2015).

Once in the soil, BC undergoes a range of biogeochemical processes, in which biochar is believed to react with soil constituents, such as dissolved organic and inorganic matter, gases, nutrients, metals, microorganisms, fauna, and plant roots, all of which will affect BC physical stability (i.e., fragmentation in soils) (Joseph et al., 2010; Spokas et al., 2014), and alter its surface chemistry (Mia et al., 2017a). Thus, BC can be impacted by biotic and/or abiotic reactions (Joseph et al.,

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2010; Pignatello et al., 2015), modifying its chemical functionality by forming new surface moieties (−OH, −C═O, and −COOH) which change the polarity, acid-basic properties and cationic and anionic exchange capacity properties (Kookana, 2010). In addition, the pore structure and particle size of aged biochar can be altered by their interaction with clay minerals or dissolved organic carbon, which either stabilizes or coats its surface, thus changing the way biochar will interact with the soil environment. These modifications involve changes of differing time scales, which transform BC sorption capacity correspondingly (Gámiz et al., 2017b; Joseph et al., 2010; Mia et al., 2017b). This is particularly critical for biochar, since mechanisms involving the chemical functionality of this material: H-bonding, cation bridging, covalent bonding, hydrophobic and π-π EDA interactions or pore-filling determine its overall sorption capacity (Joseph et al., 2010; Kookana, 2010).

To further complicate matters, studies of pesticide sorption on biochar are inconclusive. Initially, hypotheses focused on the fact that the sorption capacity for BC would decrease with time, due to physical blockage of pores by the adsorbed natural organic matter on the aged BC surfaces. Furthermore, this would also reduce the number of sorption sites available on the BC, as has been observed for the antimicrobial sulfamethazine (Teixido et al., 2013). Martin et al. (2012) also observed reduced MCPA and diuron sorption on aged biochar, indicating the importance of the reduced sorption sites as well as potential chemical alteration on BC's surfaces. Additionally, changes in dissolved organic carbon content (DOC) can attenuate sorption of pesticides and other organic compounds (Luo et al., 2017; Yang and Sheng, 2003). Others have observed greater sorption for indaziflam on aged BC because of the corresponding increases in SSA and porosity, but limited sorption in the case of terbuthylazine and MCPA (Trigo et al., 2014). Ren et al. (2018) found that atrazine was sorbed differently on aged BC, depending on the temperature of pyrolysis at which the biochar was made. Thus, atrazine was sorbed to a greater extent on aged BC produced at 300 °C than on aged biochar prepared at 700 °C. These observations illustrate the complexity of the weathering process, hampering our ability to predict the behavior of pesticides on aged biochar, and consequently their bioavailability. Less is known about the impact on bioavailability of pesticide in aged BC-amended soil with time. Trigo et al. (2016) found lower extractable amounts of metolachlor in aged biochar and sorption increased with longer batch equilibration times.

We hypothesized that the behavior of three highly persistent herbicides with different physico-chemical properties can vary according to biochar characteristics (fresh or aged), either limiting or increasing sorption and, in consequence their bioavailability in soil. Hence, the objectives of this work were: i) to characterize an aged biochar and to compare the sorption of three pesticides on fresh and aged biochars, and ii) to assess the bioavailability of three pesticides in unamended and amended soil with fresh and aged biochar and its relationship with sorption. Highly persistent herbicides, such imazamox, terbuthylazine and picloram were selected to avoid problems with rapid biodegradation, which hampers the interpretation of slow sorption kinetics (Gámiz et al., 2017a). Results of this work will guide biochar production according to soil and pesticide characteristics, which is a critical step in wide-spread use of BC as a soil amendment.

2. Materials and methods

2.1. Biochars, soil and herbicides

The fresh biochar (BC_{fresh}) was prepared from oak wood by slow pyrolysis in a Missouri-type concrete kiln at 550 °C (maximum pyrolysis temperature). Some of this biochar was initially placed into a mesh bag (Mesh Cord Bags, Vaultz®, Idea Stream Consumer Products LLC, Cleveland, OH; 1.5 mm openings) and buried in a silt loam soil located in Columbia County, Wisconsin (USA) for 6 months (April–October). The soil at the site had 14% sand, 71% silt, and 15% clay, 2.0% organic carbon (OC), cation exchange capacity (CEC) of 14 $cmol_c\ kg^{-1}$ and a pH of 7.0. After the aging period, pieces of biochar (BC_{aged}) were rinsed with large quantities of deionized water (10 L per 100 g of char), while the biochar was still in the mesh bag, to dislodge soil that was visibly present on the biochar surfaces. Following this rinsing, the biochar was removed from the mesh bag and oven dried at 105 °C. Both fresh and aged BC were ground to < 2 mm prior use, to aid in homogenization. The elemental composition of the biochar samples was analyzed using thermal combustion (LECO analyzer Model CHN 932). Specific surface area (S_{BET}) of the two BCs was measured by physisorption of CO_2 (ASAP; Model 2420). The pH was determined in a 1/2.5 (w/v) biochar:deionized water slurry. Dissolved organic carbon (DOC) was extracted from biochar suspensions prepared in 0.01 M of $CaCl_2$ (1:2, w/v) after shaking for 15 min, then the samples were centrifuged and the supernatant was removed to measure the DOC (Shimadzu TOC-5050A analyzer). The extracts of DOC were also characterized by fluorescence spectroscopy by recording the spectra from 300 to 480 nm under excitation at 254 nm (HITACHI F-2500 FL-Spectrophotometer). Zeta potential values were measured with a Zetasizer Nano ZS equipment (Malvern Instrument) in BCs suspensions of 1 $mg\ mL^{-1}$. Fourier transform infrared (FT-IR) spectra of 1% w/w samples in KBr pellets were recorded using a Jasco FT/IR 6300 spectrometer (Jasco Europe s.r.l.) to evaluate surface functional groups. The X-Ray Photoelectron Spectra (XPS) were gathered using a Leybold-Herens mod. LHS-10/20 instrument with a mono-chromated Al-Kα X-ray XPS with photon energy of 1486.61 eV, a power of 100 eV, and a 500-μm spot size.

A typical Mediterranean soil characterized by low organic carbon content was selected for the laboratory incubations. The soil was collected from an experimental farm of IRNAS (Coria del Río, Sevilla, Spain), by sampling the top 0–20 cm of soil, then mixed, air-dried and sieved (2 mm mesh) and finally stored at 4 °C. The soil was a sandy loam soil with 86% sand, 4% silt, and 11% clay, 5.9% of $CaCO_3$, organic carbon (OC) of 1.3%, CEC of 15 $cmol_c\ kg^{-1}$ and pH of 7.9.

Three ionizable herbicides were selected based on their specific structures as model molecules. Two anionic herbicides, picloram (pyridine moiety) and imazamox (imidazolinone) and the weak basic herbicide terbuthylazine (triazine). All three herbicides, supplied by Sigma-Aldrich, were analytical grade (> 97%). The main characteristics of the compounds are compiled in Table S1 and their structures are shown in Fig. 1.

2.2. Standard sorption experiments on biochar

The sorption of pesticides on the biochars was determined at a single initial concentration by the standard batch equilibration method. Triplicate 40 mg of BC samples were equilibrated separately in Pyrex® glass tubes with 8 mL of an aqueous solution of each herbicide with

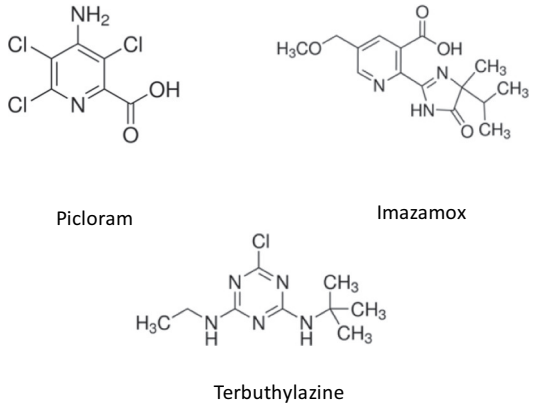

Fig. 1. Chemical structure of the three pesticides used in this work.