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The effects of woodchip- and straw-derived biochars on the persistence of the herbicide 4-chloro-2-methylphenoxyacetic acid (MCPA) in soils

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ABSTRACT

Sorption and degradation are the primary processes controlling the efficacy and runoff contamination risk of agrochemicals. This study assessed the influence of two biochars, made from woodchips and straw at a pyrolysis temperature of 725 °C and applied to a loamy sand and a sandy soil in the concentration of 5.3 g 100 g^{-1} sandy soil and 4.1 g 100 g^{-1} loamy sand soil, or 53 t ha^{-1} for both soil types, on degradation of the herbicide 4-chloro-2-methylphenoxyacetic acid (MCPA). Soils were spiked with 50 mg MCPA kg^{-1} soil. In the sandy soil, significantly more MCPA remained after 100 days if amended with straw-derived biochar in comparison to wood-derived biochar. Both biochars types significantly increased urease activity ($p < 0.05$) after 37 days in the loamy sand soil, but these differences disappeared after 100 days. A root and shoot elongation test demonstrated that the soils containing straw-derived biochar and spiked with MCPA, showed the highest phytotoxicity. Both biochars were found to retard MCPA degradation in loamy sand and sandy soils. This effect could not be explained only by sorption processes due to comparatively low developed micro/mesoporous structure of both biochars shown by BET surface analysis. However, an enhanced MCPA persistence and soil toxicity in sandy soil amended with straw biochar was observed and further studies are needed to reveal the responsible mechanisms.

1. Introduction

Biochar is being recognized as a valuable soil amendment that has a potential to improve soil fertility and sequester carbon (Lehmann and Joseph, 2009; Ackerman, 2000; Elad et al., 2010; Kwapinski et al., 2010; Kookana et al., 2011; Barrow, 2012).

The effects of biochar application to agricultural soils depend on the feedstock used for biochar production, pyrolysis temperature, application rates and soil type (Lin et al., 2012; Atkinson et al., 2010; Schimmelpfennig and Glaser, 2012). Soil fertility is mostly improved after biochar additions (Rondon et al., 2007; Blackwell et al., 2009). The greatest positive effect was observed in acidic, free-draining soils (Verheijen et al., 2010). Negative or no effects of biochar on plant productivity were also observed (Blackwell et al., 2010; Gaskin et al., 2010).

The highly porous structure and a large surface area of most biochars, play an important role in the soil processes. In particular, weed control in biochar-amended soils may prove more difficult, as herbicides may be less effective when adsorbed by the biochar (Kookana et al., 2011; Nag et al., 2011). Sorption and degradation are the primary processes controlling the efficacy and runoff contamination risk of agrochemicals. Chemical, photochemical, or biological processes are responsible for the degradation of pesticide molecules (Thorstensen and Lode, 2001).

The phenoxyalkanoic acid herbicide 4-chloro-2-methylphenoxyacetic acid (MCPA) is a systemic, hormone-type selective herbicide readily absorbed by leaves and roots and used for the control of annual and perennial weeds in cereals, grassland, and turf

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(WHO, 2003). More than 2000 t are used in the Western European countries per year (Bojanowska-Czajka et al., 2007). It is very mobile in soils and has the potential to contaminate groundwater (Hiller et al., 2006). MCPA is one of the most widespread pesticides in terms of frequency of detection in rivers, lakes and groundwater (Comoretto et al., 2007). Leaching of MCPA into groundwater has been positively correlated with the total soil organic carbon content and negatively correlated with the soil pH (Yu et al., 2011; Cabrera et al., 2011; Hiller et al., 2012). Generally, MCPA sorption decreases in the presence of phosphate ions and low-molecular-weight organic acids (Hiller et al., 2012).

Different mechanisms for MCPA degradation in soil and wastewaters were described recently. An addition of Fe^{2+} to the MCPA-containing wastewater sufficiently increased MCPA decomposition, with formation of CO_2, H_2O and chloride via by-products such as 4-chloro-2-methylphenol (CMP), formic acid and acetic acid (Iijima et al., 2009). Addition of biochar to soils has a pronounced effect on degradation, desorption, leaching and uptake of MCPA by plants with the consequent reduction of adverse impacts of pesticide residues on the environment (Tatarkova et al., 2013).

Earlier studies on the degradation of MCPA and other herbicides (e.g., 2,4-dichlorophenoxyacetic acid) used aquatic plants in wetland systems (Matamoros et al., 2012) and microorganisms isolated from contaminated soil (e.g., *Pseudomonas spp*., *Ochrobactrum sp*., *Serratia marcescens* and *Penicillium sp*., *Comamonas sp*., *Acinetobacter sp*., and *Klebsiella oxytoca*) (Onbasili and Aslim, 2011; Lü et al., 2008; Silva et al., 2007; Marrón-Montiel et al., 2006). The results of those studies indicated a high potential for microbial degradation of the aforementioned herbicides; however, microbial activity largely depends on soil properties, climatic conditions, and agrochemical management schemes. Therefore, the impact of biochar amendments on the sorption and environmental fate of herbicides in agricultural soils needs further investigation under local specific conditions.

The aim of this study was to assess the influence of woodchip- and straw-derived biochars prepared by pyrolysis at a temperature of 725 °C on the persistence of MCPA in soils. During a 100-day laboratory experiment, loamy sand and sandy soils, collected from a 5 to 20 cm depth, were amended with the two types of biochar and spiked with MCPA. The concentrations of MCPA and its degradation product CMP were evaluated, as a function of time. In addition, the microbial activity and phytotoxicities of the soils were measured.

2. Materials and methods

2.1. Materials

The feedstock for wood biochar consisted of shattered wooden boxes (10%) and disposable wooden pallets (90%). The straw biochar was made from pelletized wheat straw. Both biochars were produced at a maximum pyrolysis temperature of 725 °C with a residence time of 1 h, at continuous flow with constant heating. The generated producer-gas had a temperature of 460 °C. The bulk densities of the woodchip- and straw-derived biochars were 0.16 g cm^{-3} and 0.39 g cm^{-3}, respectively. Loamy sand soil was collected from 5 to 20 cm depth on agricultural land that had been fallow for the last 10 years. Sandy soil was collected near the agricultural land. The soil was thoroughly mixed and passed through a 4 mm sieve. Visible roots or plant parts were removed. The particle size distribution was 1.9% clay, 8.9% silt and 89.2% sand for the loamy sand and 0% clay, 0.8% silt and 99.2% sand for the sandy soil.

The soil density of the loamy sand was 1.0 g cm^{-3} and 1.3 g cm^{-3} for the sandy soil. Biochars were applied at a rate of 160 g per pot (5 l-pots with 3 L soil), corresponding to 5.3 g 100 g^{-1} sandy soil and 4.1 g 100 g^{-1} loamy sand soil, or 53 t ha^{-1} for both soil types.

2.2. Experimental design

The pots were prepared in triplicate and placed randomly under a tent located outdoors. Commercially available MCPA (Nufarm, 750 g L^{-1}, dimethylamine salt) was used to spike the soils at the dose of 50 mg kg^{-1}. For each soil, three pots were left unspiked and were referred to as L and S treatments for the loamy sand and sandy soil, respectively. After 7 days, soil from each pot was mixed thoroughly and 160 g of biochar was added. The acronyms of the spiked treatments were H (no biochar), HW (biochar from woodchip) and HSt (biochar from straw), to which L or S preceded to indicate the type of soil. A nutrient amendment with the following composition was prepared: 6.0 g L^{-1} $Na_2HPO_4 \times 12H_2O$, 3.0 g L^{-1} KH_2PO_4, 0.5 g L^{-1} NaCl, 0.3 g L^{-1} $(NH_4)_2SO_4$, 2.0 g L^{-1} yeast extract, and 5.0 g L^{-1} molasses. Sugar beet molasses (40% sucrose) contributed to the final concentration with 0.2 g L^{-1} total nitrogen, 0.5 g L^{-1} carbon, and 0.11 g L^{-1} sulfur. Each pot received 50 mL of the nutrient amendment in order to stimulate soil microorganisms capable of promoting biodegradation. The duration of the experiment was 100 days, from 27 June 2012 to 6 October 2012. The pots were left outdoor under a cover and soil moisture was maintained at 50–60% of water holding capacity (WHC). Soil mixing and sampling was performed three times during experiment: on day 1, day 37, and day 100. The collected samples were frozen immediately and stored until analysis.

During the test period, the average maximum and minimum temperatures were as follows: 21 °C and 10 °C in June, 22 °C and 12 °C in July, 21 °C and 12 °C in August, 17 °C and 8 °C in September, and 14 °C and 6 °C in October. The temperature ranged from 6 °C to 31 °C throughout the 100-day period.

2.3. Analytical methods

The concentrations of MCPA and CMP in soil were measured according to the modified method described by Pozo et al. (2001). The samples were prepared by extracting 5 g soil with 10 mL of water and 10 mL acetonitrile for 10 min. A salt mixture prepared from 4.0 g of magnesium sulfate, 1.0 g sodium chloride, 1.0 g trisodium citrate dihydrate, and 0.5 g disodium hydrogen citrate sesquihydrate was added, and the sample was shaken vigorously for 1 min. The samples were then centrifuged and 100 μL of the acetonitrile layer was collected, mixed with 100 μL water, and injected into the HPLC–ESI–MS/MS.

The liquid chromatography (LC) analyses were conducted with a Waters Alliance 2690 series LC system (Waters Corp., Milford, MA, USA). An adequate chromatographic separation was achieved using a Synergy Hydro-RP column (150 mm × 2.00 mm; 4 μm particle size; 80 A pore size) (Phenomenex, Torrance, CA, USA) at 40 °C with a 50 μL injection volume. The mobile phase flow rate was 0.3 mL min^{-1} and the composition of mobile phase was 0.1% acetic acid in water as solvent A and acetonitrile as solvent B. The elution was performed with 60% solvent A and 40% solvent B. The sample run time was 10 min: the retention time for MCPA was 4.1 min, and the retention time for CMP was 5.8 min.

A Micromass Quattro LC mass spectrometer (Waters Corp.) equipped with an electrospray ionization source in the negative ion mode was used under the following operating conditions: capillary voltage, 3.5 kV; cone voltage, 30 V for MCPA and 36 V for CMP; source temperature, 100 °C; desolvation temperature, 350 °C; desolvation gas flow, 600 L/h nitrogen; cone gas flow, 45 L/h nitrogen; and argon collision gas pressure of 3×10^{-3} mbar. The multiple reaction monitoring (MRM) for MCPA was 199 > 141 and 201 > 143 with a 23 V collision energy and for CMP it was 141 > 105 and 143 > 105 with a 17 V collision energy.

Dry weight of the soil samples was determined by drying at 105 °C until constant weight. The ash content was determined by ISO 5984:2002/Cor 1: 2005, and the total nitrogen content was determined by ISO 5983-2:2005 using Auto Kjeldahl Unit K-370. Total carbon and sulfur were measured with an automatic C/S ELTRA analyzer (ELTRA GmbH, Haan, Germany). The pH values and redox potentials were measured in 1 M KCl (10 g of soil in 50 mL of solution) with a Hanna pH213 pH meter (HANNA Instruments, Woonsocket, RI, USA). The electrical conductivity of soil suspensions (10 g in 50 mL of deionized water) and biochar suspensions (0.45 g in 50 mL deionized water) was measured by a SensoDirect Con 110 conductivity meter (Tintometer, UK). The organic carbon content (C_{org}) of soils was determined with potassium dichromate, according to the method of Walkley and Black (1934). The soil microbial respiration rate was measured in a 100 mL incubation vessel containing 50 g of wet soil, previously sieved through a 3 mm sieve. Prior to conducting the respiration tests, the soil samples were wetted to 60% of WHC and pre-incubated at the ambient temperature for 2 h in order to restore mesophilic microbial activity. Each sample was thoroughly mixed after pre-incubation and 2.5 mL of 1% glucose was added to each sample. The carbon dioxide produced during the 6 h incubation period was collected in a glass vial with 5 mL of 0.05 M NaOH. Incubation included a blank of a sealed vessel with a NaOH trap, but no soil. After the 6 h incubation, measurements of CO_2 dissolved in NaOH were performed by titration of the NaOH solutions with a 0.05 M aqueous HCl solution.

2.4. Porous structure

Porous structure of biochars was evaluated from N_2 sorption/desorption. Isotherms were obtained using Sorptometer KELVIN 1042 (COSTECH Instruments). Degassing temperature was 250 °C; adsorption gas: nitrogen; carrier gas: helium. Brunauer–Emmet–Teller (BET) were used for calculation of specific surface (Bansal and Goyal, 2005).