



Pyrochars and hydrochars differently alter the sorption of the herbicide isoproturon in an agricultural soil



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HIGHLIGHTS

- Chars with high carbonization degree (high C stability) have high sorption capacity.
- Impact of raw materials on sorption capacity depends on carbonization conditions.
- High bioaccessibility in hydrochar amended soil irrespective of the raw material.
- Hydrochars react as H-bond acceptor, pyrochars through hydrophobic and H-bonding.
- The micro-porosity determines the amount of non-extractable residues.

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ABSTRACT

Carbonaceous material from pyrolysis (pyrochars) and hydrothermal carbonization (hydrochars) are applied to soil to improve soil fertility and carbon sequestration. As a positive side effect, the mobility of pesticides and the risk of groundwater contamination can be minimized. However, the impact of various raw materials on the sorption capacity of different pyrochars and hydrochars is poorly understood. Thus, sorption experiments were performed with ¹⁴C-labeled isoproturon (IPU, 0.75 kg ha⁻¹) in a loamy sand soil amended with either pyrochar or hydrochar (0.5% and 5% dry weight, respectively). Carbonaceous materials were produced from three different raw materials: corn digestate, miscanthus, woodchips of willow and poplar. After 72 h of incubation, a sequential extraction procedure was conducted to quantify *in situ* IPU bioavailability, total amount of extractable IPU, and non-extractable pesticide residues (NER).

Added char amount, carbonization type, and raw materials had statistically significant effects on the sorption of IPU. The amount of *in situ* available IPU was reduced by a factor of 10–2283 in treatments with pyrochar and by a factor of 3–13 in hydrochar treatments. The surface area of the charred material was the most predictive variable of IPU sorption to char amended soil. Some physical and chemical char properties tend to correlate with pore water-, methanol- or non-extractable IPU amounts. Due to a low micro-porosity and ash content, high water extractable carbon contents and O-functional groups of hydrochars, the proportion of NER in hydrochar amended soils was considerably lower than in soil amended with pyrochars.

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1. Introduction

Groundwater contamination by leaching of pesticides from agricultural soils is a severe problem in modern food production worldwide (Lehr et al., 1996). The phenyl urea herbicide isoproturon [3-(4-isopropylphenyl)-1,1-dimethyl-urea; IPU] is intensively used in European cereal production (Umweltbundesamt, 2006). The pesticide has a high water-solubility (70 mg L⁻¹), which frequently

results in surface- and groundwater concentrations exceeding the maximum tolerable concentration of the European directive for drinking water ($\geq 0.1 \mu\text{g L}^{-1}$) (Umweltbundesamt, 2006).

The mobility of pesticides in soils depends highly on the sorption potential of soil organic matter (OM) (Ertli et al., 2004). Therefore, the development of approaches to minimize the mobility of critical pesticides is a promising step towards sustainable groundwater protection. In recent years, the addition of carbon (C)-rich solids from the incomplete combustion of biomass via pyrolysis (termed pyrochars or biochars; Wiedner et al., 2013) to agricultural soils has gained considerable interest in order to improve soil C

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sequestration and crop yield by better retention of nutrients and water (Glaser et al., 2002; Kammann et al., 2012). As a positive, desirable side effect, these materials have been shown to increase the sorption potential of soils for several pesticides (Yang et al., 2006; Yu et al., 2009; Martin et al., 2012). The high sorption potential of pyrochars is the result of their physico-chemical properties, e.g., a large specific surface area (SSA), and micro-porosity, as well as a high aromaticity coupled to the presence of oxygen-containing functional groups (Chun et al., 2004; Cao and Harris, 2010; Liu and Zhang, 2011). These properties may entail different sorption mechanisms of variable strength (Sobek et al., 2009; Tian et al., 2010). Furthermore, sorption of organic chemicals in pyrochar amended soils may be enhanced indirectly, e.g., by increasing the cation exchange capacity and reduction of the dissolved organic C content (Gomez-Eyles et al., 2011). Nonetheless, it remains poorly understood to which extent the sorption potential of pyrochars is affected by the type of raw material used (Chen et al., 2008; Uchimiya et al., 2010; Zhang et al., 2011).

Promising experimental results regarding the impact of pyrochar amendment on C sequestration and nutrient retention encouraged the scientific community to seek for less energy-intensive processes yielding carbonization products with similar capabilities (Titirici et al., 2007; Steinbeiss et al., 2009; Cao et al., 2011). During hydrothermal carbonization (HTC), residues of OM are converted into C-rich solids, called hydrochars, at relatively low temperatures (180–250 °C) and under high pressure (about 2 MPa) in the presence of water. In contrast to pyrolysis, this process does not require an energy-intensive pre-drying step (Mumme et al., 2011). While high-temperature pyrochars are considered the most promising additives for agricultural soils concerning climate change mitigation due to their high microbial resistance (Kammann et al., 2012), HTC products have been reported to have beneficial effects on the plant available water capacity in sandy soils (Abel et al., 2013). Their effects on selected soil functions will likely differ as result of their varying physico-chemical properties arising from the specific production conditions (Libra et al., 2010). For example, the SSA of pyrochars varies considerably and reaches values up to 1000 m² g⁻¹ (Qiu et al., 2009; Uchimiya et al., 2011). For hydrochars, average SSA values of 8 m² g⁻¹ have been reported (Schimmelpfennig and Glaser, 2012). The molar H/C and O/C ratios, which describe the carbonization degree of chars and char-like material, are generally lower for pyrochars than for hydrochars (Gajić et al., 2012). However, the sorption potential of hydrochars for organic agrochemicals in soil has been rarely investigated (Sun et al., 2012).

Most studies concerning sorption of pesticides examined the adsorption distribution coefficient (K_d) from standard batch experiments in solution (Yang and Sheng, 2003; Sobek et al., 2009; Yu et al., 2011; Martin et al., 2012), and thus under conditions that hardly resemble soil environmental conditions. Alternatively, Folberth et al. (2009) used an approach that mimics *in situ* pesticide availability in soils and allows pesticide quantification in the soil pore water following centrifugation of soil samples. Using a field equivalent soil water potential and bulk density during incubation, they introduced the *in situ* mass distribution quotient (iMDQ), which is calculated as the quotient of the adsorbed and dissolved pesticide concentrations. Thus, the iMDQ reflects more natural conditions because it takes the soil to pore water ratio into account and has been proven to adequately describe the bioavailability of IPU in soils (Folberth et al., 2009).

The main objective of this study was to comparatively investigate the pesticide sorption capacity of pyrochar vs. hydrochar amended soil using the iMDQ approach. We hypothesized that (i) the IPU sorption capacity in soil amended with pyrochar is higher compared to soil amended with hydrochar and (ii) different sorption mechanisms account for the differences in sorption behavior.

To test this, soil was incubated for 3 d with pyrochars carbonized at 750 °C and hydrochars carbonized at 200 °C and 250 °C, and the underlying sorption mechanisms were derived from applying a sequential extraction procedure involving extraction with water and methanol, followed by combustion of the extracted samples. Finally, we (iii) expected that the IPU sorption within each material group varies with the raw material used. Therefore, different raw materials (corn digestate, miscanthus, woodchips of willow and poplar) were used as precursor materials in the production of pyro- and hydrochars.

2. Material and methods

2.1. Soil material

Soil material was taken from 5 to 25 cm depth of a Cambisol at the organic farming section of the research station Scheyern in southern Germany (11°26'21" E and 48°29'51" N, 477 m a.s.l.). The soil was air-dried and sieved to ≤2 mm. The soil is a loamy sand with 68% sand, 15% silt, and 17% clay. Selected soil properties are given in Table 1. The air-dry soil was stored at -20 °C. Prior to laboratory experiments it was equilibrated at a soil water content of 10% (w/w) for 2 d at 4 °C and a further day at 20 °C.

2.2. Pyrochars and hydrochars

Pyrochars (pyro750) were produced from pyrolysis at the standard operating temperature of the Pyreg technology of 750 °C for 45 min (Pyreg GmbH, Dörth, Germany). Hydrochars (hydro200 and hydro250) were generated from HTC at 200 or 250 °C and 2 MPa for 6 hours (SmartCarbon AG, Jettingen, Germany). Raw materials in each case were corn digestate, miscanthus, and woodchips (willow and poplar), respectively. After cooling overnight, hydrochars were separated from the liquid phases with a 105-µm gauze filter. The pyrochars and hydrochars were oven-dried at 105 °C and sieved to <1 mm. Selected properties of the raw and carbonized materials are given in Table 1. The C and N contents were determined via dry combustion (LECO TruSpec, St. Joseph, USA). Total C is considered to equal organic C as no differences between C concentrations of unwashed and HCl-washed (4 M HCl) samples were observed (Scheibler method; Gajić et al., 2012). Water-extractable organic carbon (WEOC) contents of the solid materials were quantified after extraction with deionized water (1:10, w/v) and 0.45 µm-filtration by thermal oxidation with a TOC analyzer (DIMATOC2000, DIMATEC Essen, Germany). Hydrogen and oxygen contents of pyrochars, hydrochars, and the raw materials were determined with an elementary analyzer (Vario EL3, Elementar, Hanau, Germany). The pH of the solids was measured in 0.01 M CaCl₂ (1:10, w/v). The specific surface area (SSA), total pore volume (PV; pores <~200 nm), and average pore size (PS) were derived from 40-point N₂ gas adsorption isotherms recorded at 77 K with an Autosorb analyzer (Quantachrome Corp., USA). The SSA was calculated using the Brunauer–Emmett–Teller equation based on seven adsorption points in the relative pressure range of 0.05–0.3 P/P₀ (Brunauer et al., 1938). Total PV was determined at a relative pressure of 0.995 P/P₀ and the average PS was calculated as $r_p = 2V_{liq}/SSA$, where V_{liq} is the volume of liquid N₂ contained in the pores.

Fourier-transform infrared (FTIR) measurements for quantification of oxygen-containing surface functional groups were performed with a Tensor 27 (Bruker Optics, Billerica, USA) using the KBr technique (Ellerbrock et al., 2005). Briefly, 1 mg oven-dry solid sample was mixed with 200 mg KBr. For each spectrum 128 scans were collected with a resolution of 4 cm⁻¹. For quantitative comparison, normalization to the maximum absorbance of one and base

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