



## Sorption of polar herbicides and herbicide metabolites by biochar-amended soil



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### HIGHLIGHTS

- No effect of biochar on the sorption of three out of four tested compounds.
- Sorption of a chloridazon metabolite enhanced due to higher organic matter content.
- No significant effect of the biochar amendment on desorption.
- Biochar has limited potential to mitigate the leaching of polar pollutants in soil.

### ARTICLE INFO

#### Article history:

Received 14 November 2013

Received in revised form 7 February 2014

Accepted 8 February 2014

Available online 12 March 2014

#### Keywords:

Biochar  
Pesticides  
Sorption  
Leaching  
Soil amendment  
Metabolites

### ABSTRACT

Biochar-amended soil has been proven to possess superior sorption capacities for several environmental pollutants compared with pure soil. However, the role of biochar in the immobilization of polar pesticides and their metabolites has hardly been tested. The aim of this study was therefore to investigate the effect of a soil amendment with biochar on the sorption of selected polar herbicides and herbicide metabolites ( $\log K_{ow}$  0.3–<2). To simulate worst-case sorption, a sandy soil (1.7% organic matter) was amended with 1.5% biochar (fresh or composted) to determine sorption/desorption isotherms of the test compounds. One herbicide (imazamox) and three herbicide metabolites (methyl-desphenyl-chloridazon, metazachlor oxalic acid, metazachlor sulfonic acid) were tested, i.e. three anionic and one neutral polar compound. The results showed that the presence of biochar increased the sorption capacity of the soil only in the case of the uncharged compound methyl-desphenyl-chloridazon, for which the average distribution coefficients in biochar-amended soils were higher than in pure soil by a factor of 2.1–2.5. However, this effect rather seemed to reflect the increased soil organic carbon content after the addition of biochar than a preferred sorption of methyl-desphenyl-chloridazon to biochar. In the case of the three anionic compounds imazamox, metazachlor oxalic acid and metazachlor sulfonic acid, biochar amendment did not increase the sorption capacity of the soil for these compounds, presumably as a result of its negative net charge. Similarly, desorption experiments did not show any significant effect of the biochar amendment on desorption. This suggests that the potential of using biochar to mitigate the leaching of the tested polar pesticides or metabolites is limited.

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### 1. Introduction

Following the agricultural use of pesticides, mobile active ingredients or their metabolites pose a potential risk of groundwater pollution. Pesticides or their degradation products are among the most intensively monitored and relevant chemicals found in European groundwater (Loos et al., 2010). Due to their higher water solubility, polar contaminants may represent an elevated risk of leaching, which, however, also depends on their dissipation

behavior in soil. As the leaching of pesticides is strongly influenced by their sorption and desorption behavior in soil, increasing the sorption of pesticides to soil components by e.g. soil amendments will lead to a decreased leaching potential (Guo et al., 1993). In this regard, biochar in soil was recently shown to act as a “supersorbent” for environmental contaminants (as reviewed by Kookana et al., 2011), thus giving rise to the question whether a biochar addition to soil might contribute to mitigate groundwater contamination with polar pesticides.

Biochar is defined as a “carbon-rich solid material produced by heating biomass in an oxygen-limited environment” (Joseph et al., 2010). Several studies reported that biochars from the burning of

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wood, wheat and rice residues are 400–2500 times more effective than pure soil in sorbing pesticides (Yang and Sheng, 2003; Yang et al., 2006; Xu et al., 2008). Consequently, a soil amendment with biochar remarkably enhanced the sorption of non-polar and moderately polar pesticides (e.g. diuron, simazine, atrazine), even when biochar was added in amounts as low as  $\leq 1\%$  of soil mass (Yang and Sheng, 2003; Loganathan et al., 2009; Kookana, 2010). The high sorption capacity of biochar for various organic contaminants is typically ascribed to its aromaticity and elevated specific surface area (SSA) (Kookana, 2010), which primarily causes the adsorption of pollutants (Accardi-Dey and Gschwend, 2003). Furthermore, the entrapment of organic compounds in micropores or pore deformation mechanisms may cause desorption hysteresis in biochars (Brada et al., 2003; Loganathan et al., 2009; Zhang et al., 2010). However, sorption mechanisms mostly depend on the properties of biochar, which are strongly influenced by the pyrolysis conditions, and most notably by the charring temperature (Keiluweit et al., 2010). High pyrolytic temperatures ( $>500\text{ }^\circ\text{C}$ ) produced well carbonized materials with high SSA and few functional groups, while lower pyrolytic temperatures ( $<400\text{ }^\circ\text{C}$ ) produced only partially carbonized biochars with reduced SSA and higher surface functionality (Chun et al., 2004). The sorption properties of the chars differed accordingly, surface adsorption being the dominant sorption mechanism in the highly aromatic biochars while partitioning into the remaining amorphous carbon and specific interactions with remaining functional groups could additionally be found in the low-temperature biochars (Chun et al., 2004). This implies that biochar may sorb compounds of different polarity and planarity (Chun et al., 2004; Cornelissen et al., 2005; Chen et al., 2008). It therefore seems appropriate to mitigate the leaching of various pesticides in soil. To test this assumption, we chose pesticides or pesticide metabolites of polar nature (see Table 1 for their physico-chemical properties) that may be susceptible to enhanced leaching into groundwater under vulnerable conditions and tested the effects of biochar addition on their sorption to soil.

Chloridazon is a pre- and post-emergence herbicide used for broad-leaved weed control in sugar beet crops (Tomlin, 2006). In soil, microbial degradation generates the two major metabolites desphenyl-chloridazon and methyl-desphenyl-chloridazon by

splitting off the phenyl-group and, if applicable, methylation (Tomlin, 2006). These metabolites are not herbicidally active (Fischer, 1962) and are classified in Germany as non-relevant metabolites (UBA, 2012) according to European regulations (EU, 2003), but they may be regarded as mobile and persistent in soil (EFSA, 2007). In this study, we tested the neutral chloridazon metabolite methyl-desphenyl-chloridazon.

Imazamox is used for post-emergence broad-leaved weed control in various crops (Tomlin, 2006). Imazamox is negatively charged under environmentally relevant pH values. It is considered mobile in soil (Tomlin, 2006) but has to our knowledge not yet been detected in groundwater in monitoring studies.

Metazachlor is a pre-emergence and early post-emergence pesticide for controlling annual grasses as well as broad-leaved weeds in rape, cabbage species and some specialty crops (Tomlin, 2006). The environmental fate of metazachlor in soil is characterized by a rapid microbial degradation (EFSA, 2008). The main metabolites metazachlor oxalic acid and metazachlor sulfonic acid, which were selected for this study, are classified in Germany as non-relevant metabolites (UBA, 2012) according to European regulations (EU, 2003), and are more persistent in soil than their parent compound (EFSA, 2008). Both metabolites are anionic under environmentally relevant pH values and show a weak sorption behavior in soil. They can therefore be classified as highly mobile in soil (EFSA, 2008).

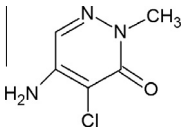
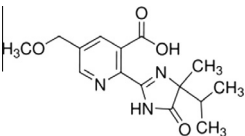
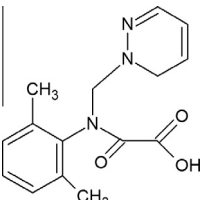
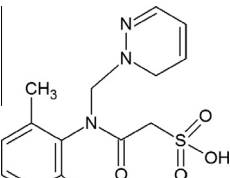
The objective of our study was to investigate the effect of a soil amendment with biochar on the sorption of these selected polar herbicides and herbicide metabolites. To simulate a worst-case scenario for herbicide sorption, a sandy soil with 1.7% of organic matter was chosen. The aging of biochar in the field was mimicked by using composted biochar and the tested herbicide concentrations were in the low  $\mu\text{g L}^{-1}$  range to simulate concentrations occurring under agricultural practice in soils.

## 2. Experimental

### 2.1. Materials used

Methanol and acetonitrile, both HPLC grade, and formic acid (purity 98%) were purchased from Merck (Merck KGaA, Darmstadt,

**Table 1**  
Structures and physicochemical properties of the herbicides and herbicidal metabolites studied (data source: Tomlin, 2006 unless otherwise stated).

	Methyl-desphenyl-chloridazon	Imazamox	Metazachlor oxalic acid	Metazachlor sulfonic acid
Structure				
Molecular formula	$\text{C}_5\text{H}_6\text{ClN}_3\text{O}$	$\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_4$	$\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_3$	$\text{C}_{14}\text{H}_{17}\text{N}_3\text{O}_4\text{S}$
Molecular weight ( $\text{g mol}^{-1}$ )	159.6	305.3	273.3	323.4
Melting point ( $^\circ\text{C}$ )	– <sup>a</sup>	165.5–167.2	–	–
Vapor pressure (25 $^\circ\text{C}$ , mPa)	–	$<0.0133$	–	–
Water solubility ( $\text{g L}^{-1}$ )	7.3 <sup>b,c</sup>	626 <sup>d</sup>	198 <sup>b,c</sup>	216 <sup>b,c</sup>
Log $K_{ow}$	0.33 <sup>b</sup>	0.73	$<2$ <sup>g</sup>	$<2$ <sup>g</sup>
$K_f/K_d$ ( $\text{mL g}^{-1}$ )	$K_f$ : 0.4–7.3 <sup>e</sup>	$K_d$ : 0.26–0.42 <sup>f</sup>	$K_d$ : 0.14–0.15 <sup>g</sup>	$K_d$ : 0.04–0.16 <sup>g</sup>
$\text{pK}_a$ (25 $^\circ\text{C}$ )	N/A <sup>h</sup>	2.3, 3.3, 10.8	3.3 <sup>b</sup>	1.6 <sup>b,i</sup>

<sup>a</sup> Data not available.

<sup>b</sup> Data provided by BASF.

<sup>c</sup> In deionized water.

<sup>d</sup> At pH 7 and 20  $^\circ\text{C}$ .

<sup>e</sup> EFSA (2007).

<sup>f</sup> Sakaliene et al. (2007).

<sup>g</sup> EFSA (2008).

<sup>h</sup> Not applicable.

<sup>i</sup> Calculated with ACD Labs.

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