



## Pesticide leaching from two Swedish topsoils of contrasting texture amended with biochar



Mats Larsbo<sup>a,\*</sup>, Elisabeth Löfstrand<sup>a,1</sup>, David van Alphen de Veer<sup>b</sup>, Barbro Ulén<sup>a</sup>

<sup>a</sup> Department of Soil and Environment, Swedish University of Agricultural Sciences (SLU), P.O. Box 7014, 75007 Uppsala, Sweden

<sup>b</sup> Swedish Rural Economy and Agricultural Societies, P.O. Box 402, 75106 Uppsala, Sweden

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### ABSTRACT

The use of biochar as a soil amendment has recently increased because of its potential for long-term soil carbon sequestration and its potential for improving soil fertility. The objective of this study was to quantify the effects of biochar soil incorporation on pesticide adsorption and leaching for two Swedish topsoils, one clay soil and one loam soil. We used the non-reactive tracer bromide and the pesticides sulfosulfuron, isoproturon, imidacloprid, propyzamid and pyraclostrobin, substances with different mobility in soil. Adsorption was studied in batch experiments and leaching was studied in experiments using soil columns (20 cm high, 20 cm diameter) where 0.01 kg kg<sup>-1</sup> dw biochar powder originating from wheat residues had been mixed into the top 10 cm. After solute application the columns were exposed to simulated rain three times with a weekly interval and concentrations were measured in the effluent water. The biochar treatment resulted in significantly larger adsorption distribution coefficients ( $K_d$ ) for the moderately mobile pesticides isoproturon and imidacloprid for the clay soil and for imidacloprid only for the loam soil. Relative leaching of the pesticides ranged from 0.0035% of the applied mass for pyraclostrobin (average  $K_d$  = 360 cm<sup>3</sup> g<sup>-1</sup>) to 5.9% for sulfosulfuron (average  $K_d$  = 5.6 cm<sup>3</sup> g<sup>-1</sup>). There were no significant effects of the biochar amendment on pesticide concentrations in column effluents for the loam soil. For the clay soil concentrations were significantly reduced for isoproturon, imidacloprid and propyzamid while they were significantly increased for the non-mobile fungicide pyraclostrobin suggesting that the transport was facilitated by material originating from the biochar amendment.

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### 1. Introduction

Organic matter plays an important role for the retention of pesticides in soil. It is, therefore, not surprising that organic soil amendments like manure, compost and biosolids used primarily to increase agricultural productivity also have effects on pesticide sorption and leaching (Briceño et al., 2007; Guo et al., 1993; Larsbo et al., 2008; Major et al., 2009). Black carbon (BC),

often referred to as biochar or charcoal when produced under controlled conditions, has during the last decades received increasing interest as a soil amendment because of its potential for long-term soil carbon sequestration, thereby reducing the amount of carbon dioxide released to the atmosphere (Lehmann, 2007) and for its potential to improve soil fertility (Glaser et al., 2002).

Because of the large sorption capacity of BC, incorporation in soil also has effects on the adsorption and leaching of organic pollutants such as pesticides. Cabrera et al. (2011) studied sorption of the mobile herbicides fluometuron and MCPA in a sandy loam soil with low total organic carbon (TOC) content (TOC < 5 g kg<sup>-1</sup> dw) amended with six different biochars. They showed that sorption strength was increased for five of the

Abbreviations: BC, black carbon; DOC, dissolved organic carbon; dw, dry weight; SSA, specific surface area; TOC, total organic carbon.

\* Corresponding author. Tel.: +46 18 671238.

E-mail address: [Mats.Larsbo@slu.se](mailto:Mats.Larsbo@slu.se) (M. Larsbo).

<sup>1</sup> Now at: Swedish Rural Economy and Agricultural Societies, P.O. Box 124, 53222 Skara, Sweden.

included biochars and decreased for one. Yang and Sheng (2003) showed that sorption of the slightly mobile herbicide diuron was positively correlated to the amount of ashes from wheat and rice in soil-ash mixtures for a silt loam soil. Sheng et al. (2005) reported that wheat char ( $0.01 \text{ kg kg}^{-1} \text{ dw}$ ) mixed with the same silt loam soil contributed to more than 70% of the sorption of the moderately mobile herbicides ametryne, bromoxynil and diuron. Wang et al. (2010) reported a 63 times more effective sorption of the moderately mobile herbicide terbutylazine in a volcanic ash soil amended with biochar produced from sawdust. Si et al. (2011) and Tian et al. (2010) found that the adsorption of the moderately mobile herbicide isoproturon in three loamy soils amended with charcoal was positively correlated to the amount of charcoal added and to the specific surface area (SSA) of the charcoals (Tian et al., 2010). Spokas et al. (2009) concluded from experiments on a silt loam soil mixed with a biochar produced from sawdust that the biochar amendment increased sorption of the moderately mobile herbicides atrazine and alachlor.

The increased sorption capacity of soils amended with BC suggests that incorporation in agricultural soils should have beneficial effects on the leaching of pesticides to groundwater and surface waters. Consequently, it was shown by Si et al. (2011) that the leaching of isoproturon from repacked columns was decreased by charcoal amendments for three loamy soils. Cabrera et al. (2011) concluded from repacked soil column experiments that the mobility of fluometuron and MCPA may either increase or decrease depending on the properties of the BC amendments. In their study the leaching of both pesticides decreased when biochars with high SSA ( $\text{SSA} = 46$  and  $16 \text{ m}^2 \text{ g}^{-1}$ ) was used as amendments to a sandy loam soil.

The objective of this study was to quantify the effects of biochar soil incorporation on the potential leaching of five pesticides with different sorption characteristics from two Swedish topsoils with contrasting soil texture. This was accomplished by conducting column leaching experiments under unsaturated conditions. Pesticide leaching is discussed in relation to pesticide adsorption strength measured in laboratory batch experiments and to the leaching of the non-reactive tracer bromide.

## 2. Materials and methods

### 2.1. Soils and sampling

Soils from two sites in eastern Sweden were included in the study: Säby ( $59^\circ 50' \text{N}$ ;  $17^\circ 42' \text{E}$ ) six km south east of Uppsala and Bornsjön ( $59^\circ 40' \text{N}$ ;  $17^\circ 40' \text{E}$ ) about 25 km southwest of Stockholm. The soils at Säby and Bornsjön are a loam (21% clay, 47% silt, 32% sand; Larsbo et al., 2009) and a heavy clay (58% clay, 40% silt, 3% sand; Andersson et al., 2013), respectively, both formed from post-glacial lake sediments. The field at Säby has been conventionally cultivated since 1997. At the time of sampling the stubble from the wheat crop was remaining in the field. The Bornsjön site was sown with grass in 2007 three years before sampling. The grass has since then been cut once or twice a year and left on the field.

Eight undisturbed soil columns (20 cm high, 20 cm diameter) were sampled in October 2010 at each site for the leaching experiments. The columns were taken from the

topsoil using a tractor-mounted hydraulic system which gently pressed plastic pipes into the soil. The plastic pipes containing the soil columns were then dug out by hand. At the same date soil samples were taken just beside the columns for pesticide adsorption batch experiments and for TOC analysis. All samples were stored at  $+2^\circ \text{C}$  until the start of the experiments.

### 2.2. Chemicals

We used the herbicides sulfosulfuron, isoproturon and propyzamid, the insecticide imidacloprid, the fungicide pyraclostrobin and the non-reactive tracer bromide. Pesticide properties according to the Pesticide Properties Database (PPDB, 2012) are given in Table 1. The pesticides represent a range of adsorption distribution coefficients and values of solubility in water, properties that are important for pesticide mobility in soils. All five pesticides are authorised for use within the EU. Analytical standard sulfosulfuron, isoproturon, imidacloprid, propyzamid and pyraclostrobin were purchased from Sigma-Aldrich, Steinheim, Switzerland. Potassium bromide (KBr; purity 99.5%) was purchased from Merck KGaA, Darmstadt, Germany.

We used biochar pellets (Bioagropellets™) from a Swedish commercial producer (Ecoera, Göteborg, Sweden). The pellets were produced by pyrolysis at  $500^\circ \text{C}$  from a mixture of seed coat, chaff and residues from wheat. The SSA of the biochar measured by nitrogen surface sorption according to the BET method (Brunauer et al., 1938) was  $2.0 \text{ m}^2 \text{ g}^{-1}$  (Lars Hylander, Uppsala University, Sweden, personal communication) and pH measured in distilled water at a 5:1 water–biochar ratio was 8.9 (Parvage et al., 2012). The chemical composition of the biochar is given in Table 2. We used a mortar to grind the biochar pellets to a fine powder before soil incorporation in order to enable mixing.

### 2.3. Adsorption batch experiments

Pesticide adsorption to soil and soil–biochar mixtures was analysed in batch experiments for one concentration only. Three replicate soil samples from the top 10 cm of each soil were carefully homogenized to an aggregate size of about 20 mm maximum diameter. About 200 g of soil from each sample was mixed with biochar powder to a nominal concentration of  $0.01 \text{ kg kg}^{-1} \text{ dw}$ . All five pesticides were dissolved in 35 ml of 0.01 M  $\text{CaCl}_2$  to give initial concentrations of  $5 \mu\text{g g}^{-1} \text{ dw}$  for isoproturon and propyzamid,  $0.20 \mu\text{g g}^{-1}$  for sulfosulfuron,  $1.5 \mu\text{g g}^{-1}$  for imidacloprid and  $2.5 \mu\text{g g}^{-1}$  for propyzamid. These concentrations were chosen to be representative for the conditions during the equilibration phase of the column experiments (see below) assuming that the pesticides were distributed in the top 1 cm of the soil at the start of the first simulated rain event.

Eight g dw of untreated soil (control) or soil–biochar mixture was shaken with 35 ml of the pesticide solution for 24 h at  $20^\circ \text{C}$  in 50 ml plastic tubes. Thereafter, the slurries were centrifuged for 30 min at 3000 rpm. Pesticide concentrations were measured in the supernatants and in the original pesticide mixture. Adsorption distribution coefficients,  $K_d$  ( $\text{cm}^3 \text{ g}^{-1}$ ), were calculated from these measurements according to  $C_s = K_d C_i$ , where  $C_s$  is the equilibrium concentration in adsorbed phase ( $\mu\text{g g}^{-1}$ ) and  $C_i$  ( $\mu\text{g cm}^3$ ) is

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