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## Biochar mediated alterations in herbicide breakdown and leaching in soil

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#### A R T I C L E I N F O

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#### ABSTRACT

Biochar application to soil has been proposed as a mechanism for improving soil quality and the long term sequestration of carbon. The implications of biochar on pesticide behavior, particularly in the longer term, however, remains poorly understood. Here we evaluated the influence of biochar type, time after incorporation into soil, dose rate and particle size on the sorption, biodegradation and leaching of the herbicide simazine. We show that typical agronomic application rates of biochar  $(10-100 \text{ t ha}^{-1})$  led to alterations in soil water herbicide concentrations, availability, transport and spatial heterogeneity. Overall, biochar suppressed simazine biodegradation and reduced simazine leaching. These responses were induced by a rapid and strong sorption of simazine to the biochar which limits its availability to microbial communities. Spatial imaging of <sup>14</sup>C-labeled simazine revealed concentrated hotpsots of herbicide co-localized with biochar in the soil profile. The rate of simazine mineralization, amount of sorption and leaching was inversely correlated with biochar particle size. Biochar aged in the field for 2 years had the same effect as fresh biochar on the sorption and mineralization of simazine, suggesting that the effects of biochar on herbicide behavior may be long lasting. We conclude that biochar application to soil will reduce the dissipation of foliar applied pesticides decreasing the risk of environmental contamination and human exposure via transfer in the food chain, but may affect the efficacy of soilapplied herbicides.

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#### 1. Introduction

The continued loss of soil organic matter (SOM) represents a major environmental and political issue in many regions of the world (Bellamy et al., 2005). This loss is typically associated with a decline in soil quality, decreased agronomic potential and a loss in ecosystem service provision. Of critical importance is the role that SOM losses have to play in exacerbating global climate change. Consequently, natural or anthropogenically engineered solutions are required to preserve and enhance existing organic and inorganic carbon (C) stocks in soil (Lehmann, 2007; Manning, 2008). In many regions of the world, however, this necessitates that solutions are also socially acceptable (i.e. they maintain economic returns and food security while respecting social and cultural values; Shepherd, 2009; Whitman and Lehmann, 2009). Although the need for land use change is well recognized internationally as a mechanism to preserve and enhance SOM stocks (e.g. afforestation, re-flooding, destocking; Paustian et al., 1997), there appears to be little political will to implement effective strategies to bring about change in most nations (Lazarus, 2009; Lee, 2009). This implies that climate change mitigation strategies are more likely to be adopted if they are compatible with current land use. One potential opportunity to meet the needs for enhanced soil C storage without a dramatic alteration in management is the application of biochar to agricultural soils (Sohi et al., 2010).

Biochar is the C rich product produced during the pyrolysis of common organic residues such as wood, animal wastes, crop residues, municipal waste and biosolids (Lehmann and Joseph, 2009). Once incorporated into the soil it has been shown to be highly chemically stable thus providing the potential to store C in the landscape for hundreds of years as well as potentially providing other tangible benefits such as increased soil nutrient and water retention (Lal, 2008; Sohi et al., 2010). Further, if combined with bioenergy production, biochar production offers further carbon-negative benefits for mitigating against climate change (Sanchez et al., 2009). However, the use of biochar is not without its critics. From a negative perspective, the biomass used to produce biochar could be used instead to offset petroleum-derived greenhouse gas emissions by complete combustion and energy production (Shepherd, 2009). Further, concerns have been raised about potential negative aspects of biochar on soil quality (e.g. on microbial function, nutrient immobilization, acceleration of native SOM loss) and whether it





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could ever be removed from the soil profile once added. Overall. in low fertility soils (e.g. in highly weathered tropical soils such as those found in Latin America, sub-Saharan Africa and Northern Australia) the application of biochar appears to have a positive benefit on soil quality and productivity (Lehmann and Joseph, 2009). This is largely attributed to its ability to bind nutrient cations, alongside its ability to ameliorate acidity, bind toxic metals (e.g. Al<sup>3+</sup>) and enhance soil structure. In countries with high fertility soils (e.g. young post-glacial soils such as those in Europe and North America) it is likely that few of these direct benefits will be seen and thus the adoption of biochar technologies is being treated cautiously until a holistic risk assessment can be undertaken. One particular aspect that has drawn interest is the behavior of xenobiotics in soil. Biochars produced from a range of feedstocks are known to readily bind organic pollutants and heavy metals and have great potential for remediating contaminated sites (Chen and Chen, 2009; Cao et al., 2009). In an agricultural context, however, biochar addition to soil is likely to significantly influence pesticide behavior. For example, sorption may decrease the efficacy of soil-applied agrochemicals via influencing their bioavailability and susceptibility to leaching (Yang and Sheng, 2003; Loganathan et al., 2009).

The aim of this study was to investigate the influence of two commercial wood-derived biochars on pesticide behavior in a highly weathered low fertility Australian soil and a high fertility UK soil. In addition, we aimed to suggest potential ways in which biochar can be applied to soil that might help overcome the potential negative effects associated with agricultural biochar application and pesticide use efficiency.

#### 2. Materials and methods

#### 2.1. Soil samples

Two agricultural soils currently receiving commercial biochar but differing in fertility were used (Table 1). Soil 1 (Typic Dystrochrept; referred to hereafter as the high fertility soil) was collected from the Ah horizon (0–15 cm) of a freely-draining, sheep-grazed grassland soil which receives regular fertilization (120 kg N, 60 kg K and 10 kg P y<sup>-1</sup>) and is located at Abergwyngregyn, Wales (53°14′N, 4°01′W; temperate climate regime). The soil supports an established sward consisting of *Lolium perenne* L., *Trifolium repens* L. and *Cynosurus cristatus* L. Soil 2 (Natric Haploxeralf; referred to hereafter as

#### Table 1

Characteristics of the two soils used in the experiments.

	High fertility soil	Low fertility soil	P value
Texture	Sandy clay	Loamy sand	
	loam		
Dry bulk density (g cm <sup>-3</sup> )	$\textbf{0.55} \pm \textbf{0.01}$	$1.35\pm0.02$	***
Moisture content (%)	$36\pm2$	$1.7\pm0.2$	***
Soil respiration	$\textbf{33.1} \pm \textbf{1.2}$	$\textbf{8.5}\pm\textbf{2.0}$	***
$(\mu mol CO_2 kg^{-1} h^{-1})$			
Soil microbial biomass-C	$\textbf{0.75} \pm \textbf{0.04}$	$\textbf{0.20}\pm\textbf{0.02}$	***
$(g kg^{-1})$			
рН	$\textbf{6.2} \pm \textbf{0.2}$	$\textbf{4.8} \pm \textbf{0.3}$	***
Electrical conductivity	$56\pm 6$	$30\pm10$	NS
$(\mu S \text{ cm}^{-1})$			
Total C (g kg <sup>-1</sup> )	$35\pm2$	$10\pm1$	***
Total N (g kg $^{-1}$ )	$\textbf{2.6} \pm \textbf{0.2}$	$0.5\pm0.1$	***
C-to-N ratio	$13\pm1$	$22\pm2$	*
Extractable NO <sub>3</sub> (mg N kg <sup>-1</sup> )	$9.3\pm3.6$	$\textbf{2.4} \pm \textbf{0.3}$	NS
Extractable NH <sub>4</sub> <sup>+</sup> (mg N kg <sup>-1</sup> )	$\textbf{0.7}\pm\textbf{0.1}$	$2.1\pm0.5$	*
Available P (mg P kg <sup>-1</sup> )	$22\pm2$	$5\pm1$	**

Values represent means  $\pm$  SEM (n = 3) for the 0–15 cm layer. All values are expressed on a dry weight basis. NS, \*, \*\* and \*\*\* indicate *t*-test results of P > 0.05, P < 0.05, P < 0.01 and P < 0.001 respectively.

the low fertility soil) was collected from the Aph horizon (0-15 cm) of a highly weathered fertilized (80 kg N, 30 kg K and 15 kg P  $y^{-1}$ ) freelydraining wheat field (Triticum aestivum L.) located in Meckering, Western Australia (31°40'N, 117°00'E; Mediterranean climate regime). At each site three independent samples of soil were collected from the field and stored at 4 °C (Jones and Willett, 2006). Soil pH and electrical conductivity (EC) were determined on fieldmoist soil (1:1 w/w soil-to-distilled water). Moisture content was determined by drying at 105 °C (24 h). Total C and N were determined using a CHN2000 analyzer (Leco Corp, St Joseph, MI). Exchangeable cations were extracted using 1 M NH<sub>4</sub>Cl (1:10 w/v) and the extracts analyzed using a Jenway Flame Photometer. Soil respiration (40 g, 20 °C) was determined using an SR1-IRGA soil respirometer (PP Systems Inc., Hitchin, UK) after wetting the soils to 70% of their water holding capacity. Available NO<sub>3</sub> and NH<sup>+</sup><sub>4</sub> were determined in 1 M KCl extracts (1:5 w/v) using a segmented-flow autoanalyzer (Skalar UK Ltd., York, UK).

#### 2.2. Biochar samples

Two hardwood-derived biochars were used in the experiments (Table 2). The first was a commercially available biochar (mechanically chipped trunks and large branches of Fraxinus excelsior L., Fagus sylvatica L. and Quercus robur L. pyrolysed at 450 °C for 48 h; BioRegional HomeGrown<sup>®</sup>; BioRegional Charcoal Company Ltd, Wallington, Surrey, UK) whilst the second was a commercial Eucalyptus marginatus Donn ex Sm. derived biochar (trunks and large branches pyrolysed at 600 °C for 24 h; Simcoa Ltd, Bunbury, Australia). The Australian biochar had a particle size <2 mm, whilst the UK-sourced biochar was used in two size grades (<2 mm or 2–10 mm diameter). Ash content was determined by heating at 750 °C (48 h: Matthiesen et al., 2005). Bulk density was calculated by determining the weight of biochar that could be packed into a 100 cm<sup>3</sup> cylinder. Particle size distribution was determined by dry sieving. Both pH and EC were determined in 1:5 (w/v) distilled water extracts. Replicate batches of biochar were used as supplied by the companies and stored dry in sealed plastic containers at 20 °C prior to use.

#### Table 2

Characteristics of the two commercial biochars used in the experiments.

	BioRegional biochar		Simcoa biochar	ANOVA
	>2 mm	<2 mm	<2 mm	
pН	$9.83\pm0.21^a$	$9.73\pm0.23^a$	$8.48\pm0.01^{b}$	**
$EC (\mu S cm^{-1})$	$1133\pm244^{ab}$	$1570\pm213^a$	$621\pm7^{b}$	*
Bulk density (g cm <sup>-3</sup> )	$0.20\pm0.01^a$	$0.35\pm0.02^{b}$	$0.45\pm0.01^c$	***
Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	ND	$39\pm4^a$	$4\pm1^{b}$	***
Moisture (%)	$3.5\pm0.7^{a}$	$6.4 \pm 0.7^{a}$	$11.6 \pm 1.5^{b}$	**
Ash content (%)	$1.8\pm0.4^{a}$	$9.2\pm0.2^{b}$	$\textbf{7.8} \pm \textbf{0.1}^{c}$	***
Total C (%)	$76\pm1^{a}$	$76\pm1^a$	$78\pm3^{a}$	NS
Total N (%)	$0.68\pm0.01^a$	$0.69\pm0.01^a$	$0.38\pm0.01^a$	***
Size fraction (% of total)				
7500–10000 μm	$\textbf{38.1} \pm \textbf{1.8}$	_	-	NA
5000–7500 μm	$\textbf{38.8} \pm \textbf{0.1}$	_	-	NA
2000–5000 µm	$\textbf{23.2} \pm \textbf{1.9}$	_	-	NA
500–2000 µm	-	$51.3\pm2.3^a$	$34.0 \pm 2.5^{b}$	*
250–500 µm	-	$14.8\pm0.3^a$	$16.6\pm0.5^a$	NS
125–250 µm	_	$14.3\pm1.3^a$	$15.8\pm0.8^a$	NS
<125 μm	_	$19.8\pm1.3^a$	$\textbf{33.8} \pm \textbf{1.3}^{b}$	*
DOC (mg C kg <sup><math>-1</math></sup> )	$108\pm 6^a$	$130\pm10^{b}$	ND	*
TSN (mg N kg <sup>-1</sup> )	$1.0\pm0.1^a$	$\textbf{0.6} \pm \textbf{0.4}^{a}$	ND	NS

Values represent means  $\pm$  SEM (n = 3). All values are expressed on a dry weight basis. NS, \*, \*\* and \*\*\* indicate ANOVA values of P > 0.05, P < 0.05, P < 0.01 and P < 0.001 respectively. NA indicates not applicable and ND not determined. Different superscript letters represent significant differences between biochar types at the P < 0.05 level. – indicates not present and ND indicates not determined. EC, electrical conductivity; DOC, dissolved organic carbon; TSN, total soluble N.

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