Chemosphere 88 (2012) 77–83

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Assessing the chemical and biological accessibility of the herbicide isoproturon in soil amended with biochar

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ARTICLE INFO

Article history:
Received 14 November 2011
Received in revised form 16 February 2012
Accepted 17 February 2012
Available online 31 March 2012

Keywords:
Pesticide bioavailability/bioaccessibility
Sorption/desorption
Biochar
Isoproturon
Agricultural soil

ABSTRACT

There is considerable current interest in using biochar (BC) as a soil amendment to sequester carbon to mitigate climate change. However, the implications of adding BC to agricultural soil for the environmental fate of pesticides remain unclear. In particular, the effect of biochars on desorption behavior of compounds is poorly understood. This study examined the influence of BC on pesticide chemical and biological accessibility using the herbicide isoproturon (IPU). Soils amended with 1% and 2% BC showed enhanced sorption, slower desorption, and reduced biodegradation of IPU. Addition of 0.1% BC had no effect on sorption, desorption or biodegradation of IPU. However, the mineralization of ^{14}C-IPU was reduced by all BC concentrations, reducing by 13.6%, 40.1% and 49.8% at BC concentrations of 0.1%, 1% and 2% respectively. Further, the ratio of the toxic metabolite 4-isopropyl-aniline to intact IPU was substantially reduced by higher BC concentrations. Hydroxypropyl-β-cyclodextrin (HPCD) extractions were used to estimate the IPU bioaccessibility in the BC-amended soil. Significant correlations were found between HPCD-extracted ^{14}C-IPU and the IPU desorbed (%) ($r^2 = 0.8518$, $p < 0.01$), and also the ^{14}C-IPU mineralized (%) ($r^2 = 0.733$; $p < 0.01$) for all BC-amended soils. This study clearly demonstrates how desorption in the presence of BC is intimately related to pesticide biodegradation by the indigenous soil microbiota. BC application to agricultural soils can affect the persistence of pesticides as well as the fate of their degradation products. This has important implications for the effectiveness of pesticides as well as the sequestration of contaminants in soils.

1. Introduction

Adsorption to commercially available activated charcoal can render organic pollutants in soils and sediments less available to organisms (Rhodes et al., 2008a), but is still considered expensive due to the use of non-renewable and relatively expensive starting material, such as coal (Hameed, 2009). This has led to growing interest in the production of these materials, using renewable and cheaper biomass sources through low cost transformation processes. Fast pyrolyzers thermally transform biomass crops and agricultural waste materials into bio-oil, syngas, and usually contains 80–90% stable aromatic carbon that is resistant to decomposition and mineralization, possibly for hundreds to thousands of years. Therefore, there is currently considerable interest in using pyrolysis to apply the resultant 'biochar' to soil to remove carbon from atmosphere for storage to mitigate against climate change (Sohi et al., 2010; Shackley et al., 2011). There is evidence that application of biochar as an amendment to agricultural soils increases bioavailable water, builds soil organic matter, enhances nutrient cycling, lowers bulk density, and can provide refugia for beneficial soil microorganisms, such us bacteria and mycorrhizal fungi (Laird, 2008; Atkinson et al., 2010). Some physicochemical properties of biochar, such as large surface area, high microporosity, the presence of polyaromatic-C structures and heterogeneous surface properties may not only help to explain these agricultural benefits, but may also result in the sequestration of organic pollutants (Sohi et al., 2010; Kookana et al., 2011).

Biochar and other carbonaceous sorbents (commonly termed as black carbon) have been observed to be very effective in sorption of organic contaminants and heavy metals (James et al., 2005; Chai et al., 2007; Chen and Chen, 2009; Uchimiya et al., 2010), for which

Abbreviations: BC, biochar; HPCD, hydroxypropyl-β-cyclodextrin; IPU, isoproturon; MDIPU, monodesmethyl-isoproturon; 4-IA, 4-isopropylaniline.

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http://dx.doi.org/10.1016/j.chemosphere.2012.02.066

these material are very promising for remediation of contaminants. From an agronomic point of view, although the application of biochar to agricultural soils could influence the effectiveness, the fate and ecotoxicological impact of the pesticides in the environment, the available information is not enough to ensure a safe and sustainable use of biochar (Kookana, 2010; Kookana et al., 2011). Some recent research has investigated the impact of biochar on chemical sorption/desorption processes, biodegradation by selected microorganisms and soil persistence of some pesticides (e.g. Yang et al., 2006; Cao et al., 2009; Yu et al., 2009, 2010). However, the implications of adding biochar (BC) to agricultural soils for pesticide bioaccessibility remain unclear, despite the major implications it could have for the environmental fate of pesticides, including the rate and pathways of biodegradation processes, the formation of bound residues and ultimately leaching to groundwater and the effectiveness of the pesticide against its target group.

Pesticide bioaccessibility and bioavailability in soil are directly linked to desorption processes, as the compound needs to be released back into the soil solution to exert its intended effect. However, the effect of biochars on desorption behavior of compounds, and the relationship between desorption and bioaccessibility is poorly understood (Kookana, 2010). A number of different techniques have been used to predict the bioaccessible fraction of soil-associated pollutants (Reid and Jones, 2000). For example, a non-exhaustive aqueous technique, involving hydroxypropyl-β-cyclodextrin (HPCD) (Reid et al., 2000), has been used successfully to predict the mineralizable or bioaccessible fraction of hydrophobic organic contaminants, using either a catabolic inoculum or indigenous soil microbiota in diverse soils and sediments (Doick et al., 2005; Rhodes et al., 2008b). This technique has not previously been used, however, to predict the effect of biochar on the biodegradation of more hydrophilic compounds such as pesticides.

The aim of the present work was to examine the influence of biochar on pesticide chemical and biological accessibility using the herbicide isoproturon (IPU). For this purpose, agriculturally relevant concentrations of biochar were added to soil and samples were collected over time to investigate (i) the dissipation and mineralization of the herbicide; (ii) the formation and dynamics of the main IPU degradation products in soil; (iii) the sorption–desorption of IPU to test the sorbent capacity of BC, and (iv) the extractability of ^{14}C-IPU by using HPCD, as a tool to predict the bioaccessible fraction of IPU in BC amended soil.

2. Material and methods

2.1. Chemicals

Isoproturon (IPU) [3-(4-isopropylphenyl)-1,1-dimethylurea), monodesmethyl-isoproturon (MDIPU) [3-4(isoproppylphenyl-1-methylurea)] and 4-isopropyl-aniline (4-IA) were purchased from Greyhound Chromatography and Allied Chemicals (Merseyside, UK). [Ring-U-14C] IPU (>99% purity) was supplied by Bayer Corp (Leverkusen, Germany). Hydroxypropyl-β-cyclodextrin (HPCD) (97% purity) was purchased from Acros Organics (Loughborough, UK).

2.2. Biochar and soil

Soil for the biochar–herbicide incubation experiment was collected from Long Close field at the Wellesbourne campus of Warwick University, UK. This sandy loam arable soil has 14% clay, 74% sand and 12% silt (Whitfield, 1974). Soil was sampled from a depth of 0–20 cm, and passed through a 3 mm sieve. Before use soil was stored at 4 °C in the dark for 7 d. Isoproturon has been regularly applied to the field over the preceding 25 years. The soil pH was 6.85 and carbon and nitrogen content 1.29% and 0.14%, respectively.

Biochar in the form of wood charcoal was used. The biochar was manufactured in Brazil from red gum wood (*Eucalyptus dunni*) in a traditional brick kiln, at a temperature of approximately 500 °C. The biochar displayed the following characteristics: pH 7.8 in water, moisture content 3.73%, calorific value 16.6 MJ kg^{-1} and fixed carbon 42.1% (Cross and Sohi, 2011). The predominant particle size range was 2.5–4 mm, with only 0.48% mass comprising particles smaller than 53 μm.

2.3. Soil amendment and incubation

Prior to application, BC was sieved to below 3 mm. The soil was amended with BC at 0%, 0.1%, 1% and 2% on a dry weight basis. A concentration of 2% was equivalent to approximately 30 t C ha^{-1} in 23 cm topsoil, or an approximate doubling of soil carbon content in typical UK long-term arable soil. An aqueous solution of IPU and ^{14}C ring labelled analogue (^{14}C-IPU) (Amersham Ltd., UK) was added at a rate providing a soil concentration of 6 mg kg^{-1} and an activity of 100 Bq g^{-1}, while adjusting the soil water holding capacity to 35%. Control soil samples (without herbicide) were also incubated.

After mixing thoroughly by hand, soil was divided into equal aliquots of 100 g dry weight equivalent, and placed in screw-top glass bottles (250 mL) and incubated in darkness at 15 °C. Soil moisture content was maintained throughout by the addition of sterile distilled water as necessary. After 0, 8, 16, 32 and 64 d three replicate bottles for each treatment were destructively sampled. From each bottle, ^{14}C-IPU residues in soil and the $^{14}CO_2$ released was quantified to determine the pesticide mineralization, dissipation and bioaccessibility in each treatment.

2.4. Extractable IPU residues in soil

The bioaccessible IPU fraction was determined at each harvest time using the method described by Reid et al. (2000). HPCD solution (25 mL, 50 mM) was added to 1.25 g of soil placed in a glass conical flask (50 mL). The samples were incubated in darkness on an orbital shaker (100 rpm) at 15 °C. After 22 h, they were centrifuged for 5 min at 16 300*g*.

To determine how the herbicide persistence in soil is affected by BC addition, methanol extractions were performed according to the method previously described by Bending et al. (2006). The ^{14}C-IPU in the supernatant was quantified by scintillation counting, while the loss of parent compound as well as the presence and quantification of its major metabolites (Juhler et al., 2001) monodesmethyl (MDIPU) and 4-isopropylaniline (4-IA) were measured by high-performance liquid chromatography (HPLC) according to the method described below.

The total ^{14}C-Isoproturon associated activity in soils was determined by sample oxidation at each sampling point. Portions of the soil samples (1 g; $n = 3$) were combusted (Packard 307 Sample Oxidiser) as described by Reid et al. (2000).

2.5. Carbon mineralization

$^{14}CO_2$ was captured during soil incubation using 1 M NaOH (1 mL), as described by Reid et al. (2001). Traps were replaced every 3 d for the first 3 weeks, and then weekly for the rest of the experiment. Following removal from bottles 10 mL Ecoscint was added, a liquid scintillation cocktail (National Diagnostics Ltd., UK), and ^{14}C content determined by scintillation counting (Tri-Carb 2800TR, Perkin Elmer, Shelton, USA). The ^{14}C-activity measured in the $^{14}CO_2$ traps was calculated as the percentage of