Environmental Pollution 181 (2013) 44–50

Contents lists available at SciVerse ScienceDirect

Environmental Pollution

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

# Influence of biochar on isoproturon partitioning and bioaccessibility in soil

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ARTICLE INFO

*Article history:*
Received 14 March 2013
Received in revised form
23 May 2013
Accepted 24 May 2013

*Keywords:*
Biochar
Herbicide
Isoproturon
Bioaccessibility
Partition coefficient

ABSTRACT

The influence of biochar (5%) on the loss, partitioning and bioaccessibility of $^{14}$C-isoproturon ($^{14}$C-IPU) was evaluated. Results indicated that biochar had a dramatic effect upon $^{14}$C-IPU partitioning: $^{14}$C-IPU extractability (0.01 M $CaCl_2$) in biochar-amended treatments was reduced to <2% while, $^{14}$C-IPU extractability in biochar free treatments decreased with ageing from 90% to 40%. A partitioning model was constructed to derive an effective partition coefficient for biochar:water ($K_{BW}$ of $7.82 \times 10^4$ L kg$^{-1}$). This was two orders of magnitude greater than the apparent $K_{foc}$ value of the soil organic carbon:water (631 L kg$^{-1}$). $^{14}$C-radiorespirometry assays indicated high competence of microorganisms to mineralise $^{14}$C-IPU in the absence of biochar (40.3 ± 0.9%). Where biochar was present $^{14}$C-IPU mineralisation never exceeded 2%. These results indicate reduced herbicide bioaccessibility. Increasing IPU application to ×10 its recommended dose was ineffective at redressing IPU sequestration and its low bioaccessibility.


## 1. Introduction

Biochar is defined as the carbon-rich product obtained when biomass is heated in an oxygen limited environment (Blackwell et al., 2009). Biochar is composed primarily of recalcitrant carbon structures (Sombroek et al., 2003). The recalcitrant properties of biochar carbon prevent its decomposition and as a consequence the addition of biochar to soil results in long-term carbon storage (McGill, 1996; Sohi et al., 2009). In addition to these carbon sequestration benefits, biochar amendment to soil has also been reported to bring benefits in terms of both soil physical and biological attributes, with a number of authors reporting enhanced plant growth following biochar amendment to soil (Lehmann et al., 2003; Lehmann and Rondon, 2006; Collison et al., 2009; Glaser et al., 2009). Soil improvements have been linked to two key factors, namely i) soil fertility (through nutrient provision, influence on nutrient cycling and changes to soil cation exchange capacity) (Chan and Xu, 2009; Sohi et al., 2009; Verheijen et al., 2009) and, ii) influences on soil water dynamics (Villarreal et al., 2010).

While these reports highlight the agronomic benefits of biochar and, thereby, support its application to agricultural land, the sorptive capacity of biochar for soil-applied herbicides may undermine these benefits if this trait reduces herbicide efficacy. The extensive sorptive capacity of biochar was recently been reported by Yu et al. (2009). This capacity has been related to a number of mechanisms, including: i) greater abundance of association sites being present in biochar-amended soil, ii) greater affinity between herbicides and the matrix resulting in stronger association and sorption–desorption hysteresis, and, iii) greater opportunity for herbicide entrapment within the more porous biochar-matrix. While organic chemical interactions with biochar or other 'black carbon' materials has received considerable attention (Jonker and Koelmans, 2002; Thorsen et al., 2004; Jonker et al., 2005; Smernick, 2009; Yu et al., 2009) there have been relatively few studies on herbicide interaction in soil-biochar mixtures. In addition, existing studies are focused mainly on the influence of biochar abundance rather than on pesticide behaviour and bioaccessibility (Yang and Sheng, 2003; Quilliam et al., 2012; Sopeña et al., 2012). Recently, Sopeña et al. (2012) reported that biochar appeared to reduce herbicide (IPU) bioaccessibility in soils with reductions increasing with increasing biochar concentrations.

The research reported herein considers the temporal implications of biochar presence (5%) on the herbicide isoproturon (IPU) applied to soil at a recommended application rate of 1 mg kg$^{-1}$ soil and up to ten-times this recommended application rate. This research draws together evidence regarding biochar influence on: i) herbicide dissipation (loss); ii) herbicide partitioning, and iii) herbicide bioaccessibility. A simple partitioning model was constructed to describe the interactions between the soil matrix, added

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http://dx.doi.org/10.1016/j.envpol.2013.05.042

biochar and the soil solution. The research builds upon that of Sopeña et al. (2012) in that it considers the influence of herbicide concentration upon its fate in biochar amended soil. While Sopeña et al. (2012) indicated biochar presence to reduce the mineralisation of $^{14}$C-isoproturon, the results reported herein show how biochar influences IPU-microorganism interactions and the subsequent development of their catabolic competence to mineralise IPU in biochar amended soil.

## 2. Materials and methods

### 2.1. Chemicals

Benzene ring [UL-$^{14}$C] IPU (2.74 GBq mmol$^{-1}$) (3-(4-isopropylphenyl)-1,1-dimethyl urea) (Fig. S1); was purchased from Amersham Ltd., UK. To reflect herbicide application in the 'real' world $^{12}$C-IPU was applied as the formulation 'Arelon 500' provided by NUFARM Ltd., UK. Liquid scintillation fluids (Ultima Gold and Ulitma Gold XR) and sample oxidiser cocktails (Carbosorb and Permafluor) were provided by Perkin Elmer, UK. Calcium chloride AR and potassium hydroxide AR were provided by Merck, UK.

### 2.2. Soil

The upper 10 cm layer of an agricultural silty loam soil, collected from a farm in Edgfield, Norfolk (TG 113 355), was partially dried (residual moisture = 2.6%) and homogenised by screening through a 2-mm sieve. This soil was selected as it had not received any IPU in the preceding 3 years.

### 2.3. Biochar

Biochar was obtained from a quarter-scale (500 kW) gasifier (Refgas UK, Flintshire, UK), fuelled by waste softwood chips from a sawmill. The gasification zone of the plant operated at around 1000 °C, the pyrolysis section around 500 °C and the "drying zone" at 200 °C. Negative pressure (−25 mbar) was maintained in the reactor. Through-put time from the drying zone to the ash discharge section was 1 h.

### 2.4. Microcosms

Microcosms were established in sterile glass jars containing either soil (500 g) or a mixture of soil (500 g) and biochar (25 g). A 5% biochar incorporation reflects a realistic application of 100 t ha$^{-1}$ (Jones et al., 2011) (specifically 100 t ha$^{-1}$ would equates to 4.3% biochar assuming incorporation to 30 cm in a receiving soil with a bulk density of 1.5 g cm$^{-3}$; assuming biochar to have a carbon content of 70%). Each microcosm was spiked with $^{12}$C-IPU at 1, 2, 5 and 10 mg kg$^{-1}$; parallel treatments with or without $^{14}$C-IPU at 40 Bq g$^{-1}$ were produced. A $^{12}$C-IPU stock solution (1000 mg L$^{-1}$) was prepared in ethanol using Arelon 500 and subsequent dilutions were prepared in ethanol such that a given stock solution could be added at a rate of 1 mL per 100 g (dry weight) soil to achieve the desired IPU dose. Similarly, a $^{14}$C-IPU stock solution was prepared such that 200 μL per 100 g (dry weight) soil achieved the desired $^{14}$C-activity. Spiking and soil rehydration was carried out as described by Reid et al. (2005). Each microcosm treatment was established in quadruplicate. Microcosms were incubated in the dark between 10 °C and 16 °C. $^{12}$C/$^{14}$C-IPU treatments were used for assessment of residual $^{14}$C-IPU associated activity and extractable $^{14}$C-IPU associated activity while $^{12}$C-IPU treatments were used to assess catabolic competence. The lowest dose of IPU (1 mg kg$^{-1}$) was selected based upon the agricultural application rate for IPU of 1.5 kg ha$^{-1}$ with the assumption that IPU would be incorporated to a depth of 10 cm in a soil with a bulk density of 1.5 g cm$^{-3}$.

### 2.5. Determination of residual $^{14}$C-IPU following incubation

Residual $^{14}$C-IPU associated activity remaining in the soil following incubation periods of 1, 13, 34 and 62 days was determined by sample oxidation (day 1 being the day of spiking). Soil samples from the $^{14}$C/$^{12}$C-IPU treatments (1 g; $n = 4$) were placed into cellulose combustion cones and 100 μL of Combustaid™ was added. The samples were then combusted using a Packard 307 Sample Oxidiser over a burn time of 2.5 min. Liberated carbon dioxide was trapped using Carbosorb and eluted using Permafluor. Prior to any samples being processed combustion efficiency was established to be >97% with carryover <0.1%. Liquid scintillation counting (Perkin–Elmer Tri-Carb 2900TR liquid scintillation analyzer) was used to assess $^{14}$C-radioactivity in the eluted samples (count time 10 min).

### 2.6. Determination of $^{14}$C-IPU partitioning

An aqueous $CaCl_2$ extraction technique was used to determine easily extractable $^{14}$C-IPU associated activity. Mordaunt et al. (2005) justified the use of 0.01 M $CaCl_2$ as an extractant to simulate the readily available fraction of pesticides, including IPU. The extraction method of Mordaunt et al. (2005) was adapted as follows. Samples of $^{14}$C/$^{12}$C-IPU spiked soils (3 g, $n = 4$) were weighed into Teflon centrifuge tubes and 0.01 M $CaCl_2$ (30 mL) added. Tubes were then placed on their sides on a flatbed shaker and shaken for 18 h at 100 r.p.m (IKA Labortechnik KS501). Thereafter, samples were centrifuged (at 2000 r.p.m. for 20 min; Sigma laboratory centrifuge 4K15). A sample of supernatant (10 mL) was then removed and added to a liquid scintillation vial containing Ultima Gold XR (10 mL). Samples were stored in the dark for a minimum of 24 h before $^{14}$C-activity was determined by liquid scintillation counting (Perkin–Elmer Tri-Carb 2900TR liquid scintillation analyzer; count time 10 min). Soil containing no $^{14}$C-IPU was used to correct the activities observed for background radiation. The fractions of $^{14}$C-IPU associated activity easily extracted into $CaCl_2$ are reported relative to residual $^{14}$C-activity at time of extraction (not the originally spiked $^{14}$C-activity).

### 2.7. Determination of IPU catabolic competence

$^{14}$C-radiorespirometry was used to determine the catabolic competence of microbes to degrade IPU (Reid et al., 2005; Posen et al., 2006). Catabolic competence is defined as the relative ability of the microorganisms in a given treatment type to mineralise $^{14}$C-IPU to $^{14}CO_2$ (the level of competence being reported as extent (%) of mineralisation). Samples of $^{12}$C-only IPU spiked soil (10 g, $n = 5$) were added to sterile Schott bottles (250 mL) containing sterile distilled water (30 mL) and a spike of $^{14}$C-IPU added (250 Bq in 100 μL of ethanol). A vial containing 1 M KOH (1 mL) was suspended from the top of the Teflon lined respirometer lid to capture $^{14}CO_2$ produced by microbial mineralization of the freshly added $^{14}$C-IPU spike. The flasks were shaken (100 r.p.m.; IKA Labortechnik KS501) and the vials replaced following respirometer assay times of: 12 h, 1 d, 2 d, 4 d, 6 d, 8 d, 10 d, 12 d, 17 d, and 22 d. Once vials were removed, Ultima Gold scintillation fluid (5 mL) was added, the samples shaken and stored in the dark for a minimum of 24 h before $^{14}$C-radioactivity was determined by liquid scintillation counting (Perkin–Elmer Tri-Carb 2900TR liquid scintillation analyzer; count time 10 min). All results were corrected for background radiation using $CO_2$ traps obtained from respirometers that were not spiked with $^{14}$C-IPU.

### 2.8. Estimating apparent partition coefficient for biochar and soil organic carbon

A simple partitioning model was constructed in order to derive estimates for $^{14}$C-IPU associated activity partition coefficients between soil organic carbon and water and between biochar and water. A four phase system consisting of soil solids, biochar, air and water was considered. System dimensions and physical and chemical parameters used are presented in the Supporting Information. In the soil solids, the chemical was assumed to sorb only to soil organic carbon and to biochar.

The total $^{14}$C-IPU associated activity, $A_T$, was assumed to be the sum of the $^{14}$C-IPU associated activity in the organic carbon phase ($A_C$), in water ($A_W$), in air ($A_A$) and, if present, in biochar ($A_B$):

$$A_T = A_C + A_W + A_A + A_B = m_C \cdot C_{OC} + V_W \cdot C_W + V_A \cdot C_A + m_{BC} \cdot C_{BC} \quad (1)$$

where $m_C$ is the mass of organic carbon present in the system (kg), $C_{OC}$ is the $^{14}$C-IPU activity per unit mass of organic carbon (Bq kg$^{-1}$), $V_W$ is the volume of water in the system (L), $C_W$ is the $^{14}$C-IPU activity per unit volume of water (Bq L$^{-1}$), $V_A$ is the volume of air in the system (L), $C_A$ is the $^{14}$C-IPU activity per unit volume of air (Bq L$^{-1}$), $m_{BC}$ is the mass of biochar carbon in the system (kg) and $C_{BC}$ is the $^{14}$C-IPU activity per unit mass of biochar carbon (Bq kg$^{-1}$), assuming that the chemical only sorbs to carbon.

The equilibrium partition coefficients for air:water ($K_{AW}$); organic carbon:water ($K_{OC}$); and biochar : water ($K_{BW}$) are defined as follows:

$$K_{AW} = \frac{C_A}{C_W} \quad (2)$$

$$K_{OC} = \frac{C_{OC}}{C_W} \quad (3)$$

$$K_{BW} = \frac{C_{BC}}{C_W} \quad (4)$$

The partition coefficients were then used to rearrange Eq. (1) to yield:

$$A_T = m_C \cdot K_{OC} \cdot C_W + V_W \cdot C_W + V_A \cdot K_{AW} \cdot C_W + m_{BC} \cdot K_{BW} \cdot C_W \quad (5)$$

As it is widely accepted that IPU sorption in soils is most appropriately described using the Freundlich equation (Singh et al., 2001; Chao et al., 2010), in which the relationship between the sorbed phase ($C_S$) and the dissolved phase ($C_W$) is defined as:

$$C_S = K_f \cdot C_W^{1/n} \quad (6)$$

or, in terms of sorption to carbon, as:

$$C_{OC} = K_{foc} \cdot C_W^{1/n} \quad (7)$$