



Does biochar application alter heavy metal dynamics in agricultural soil?



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ABSTRACT

Biochar incorporation into soil has been advocated as a potential large scale solution to offset global greenhouse gas emissions. However, the application of biochar to agricultural land must have few if any negative economic and environmental consequences if farmers are to readily adopt biochar as soil amendment. Biochar use as an organic amendment has been recently rising due to its positive effect on soil fertility, but there is still limited information available about longer-term effects, especially with regard to the effects on soil pollutant content and distribution. In a field-scale trial we investigated the effect of single doses of biochar (25 and 50 t ha⁻¹) and repeat-applications (two years later) of biochar (25 + 25 and 50 + 50 t ha⁻¹) on heavy metal (As, Cu, Zn, Cd, Ni) content and distribution in soil, together with metal concentrations in plants (barley, beans) over repeated cropping cycles. Here we demonstrate that biochar produced from forest residues is of a low risk due to its inherently low metal content and the lack of observed negative effects on crop or soil quality. Although biochar did cause small changes in metal fractionation in soil, it did not alter total metal concentrations in soil or plants. We conclude that the application of wood-derived biochar does not increase the concentrations of metals in this soil, even after repeated applications, and could be safely used for agriculture

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1. Introduction

Organic soil amendments (e.g. compost, biosolids, manure) are widely used to promote crop growth in agriculture due to their positive effect on soil nutrient content and a range of soil biophysical and chemical properties (Jones and Healey, 2010). In addition to stimulating soil microbial activity, soil amendments help conserve water holding capacity, promote nutrient cycling, suppress plant diseases and replenish soil organic matter (SOM) reserves. However, although the maintenance of adequate SOM is a major factor for agroecosystem fertility, poor agricultural management practices have severely reduced SOM contents in many agricultural lands, leading to reduced crop yields, chronic declines in soil quality and an increased risk of erosion and desertification (Tejada et al., 2001). Therefore, there is an urgent need to restore SOM to agricultural soils, and the addition of organic amendments should be

an important component of all agricultural management regimes. However, due to the progressive biodegradation of organic materials added to soil, their positive effects are typically short-lived and to realise the long-term benefits of SOM there needs to be continual replenishment.

Biochar is produced from the pyrolysis of organic materials, e.g. crop and wood residues, animal manures and a range of industrial wastes such as paper sludges and biosolids (Jones and Healey, 2010; Sohi et al., 2010; Lehmann, 2007), and when buried in soil can act as a long term soil carbon (C) store, i.e. remaining for hundreds of years (Sohi et al., 2010; Atkinson et al., 2010). Recent studies have also highlighted the ability of biochar to supply a range of agronomic benefits, e.g. increased nutrient cycling, improved fertility and health (Sohi et al., 2010; Atkinson et al., 2010; Lehmann et al., 2006) and environmental benefits, e.g. production of bioenergy, climate change mitigation and adsorption of heavy metals (Atkinson et al., 2010; Lehmann et al., 2006; Cao et al., 2009; Kookana et al., 2011), making it a potentially valuable and sustainable tool to improve soil quality. Burial of biochar in soil has therefore been proposed as a potential mechanism to not only enhance soil fertility but also to lock up biogenic C by offsetting C emissions associated with

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the burning of fossil fuels (Lehmann et al., 2006; Kookana et al., 2011; Streubel et al., 2011) and to remediate polluted soils (Cao et al., 2009).

The potential effectiveness of biochar for soil remediation relies upon its ability to retain both organic and inorganic contaminants. For example, biochar can reduce metal solubility by raising the pH, and through retention on cation exchange sites (Namgay et al., 2010; Beesley and Marmiroli, 2011; Uchimiya et al., 2011a,b; Houben et al., 2013). Biochar can also increase the sorption of pesticides (Yang and Sheng, 2003), which can limit their leaching and breakdown; although this can increase their persistence in soil (Jones et al., 2011a).

The feedstock and production process can also affect the composition of both organic (e.g. dioxins, polycyclic aromatic hydrocarbons) and inorganic (e.g. heavy metal(loid)s) contaminants in the biochar, and its addition to soil could result in soil contamination (Quilliam et al., 2013). A thorough analysis of the feedstock intended for biochar production is therefore needed prior to application to avoid increasing the pollutant load of the soil or the availability or mobility of indigenous contaminants (Pérez-de-Mora et al., 2006; Madrid et al., 2007; Lucchini et al., in press). However, there is currently a lack of field-scale experiments providing data about the pollutant content of biochar and the subsequent bioavailability to both crops and soil organisms. This lack of data prevents policymakers from making informed decisions about the risks of amending soil with biochar, together with associated agronomic management decisions and climate change mitigation strategies. Therefore, the aim of this study was to investigate the influence of variable rates of biochar addition on soil heavy metal concentrations and associated plant uptake in a field-scale biochar trial within a vegetable-cereal crop rotation system. We hypothesised that higher biochar addition rates would be more effective at reducing metal availability and plant uptake due to increases in soil pH and cation exchange capacity (CEC) and the increased immobilisation of metal contaminants. In addition, we evaluated whether field-aged and fresh biochar had different effects on metal distribution within the soil-plant system.

2. Material and methods

2.1. Field experimental set up

The field trial was established in 2009 at Abergwyngregyn, Wales (53°14'N, 4°01'W) in a Eutric Cambisol with a sandy clay loam texture. The replicated ($n=4$) trial plots (6 m × 3 m) were laid out in a randomized block design in an existing flat agricultural field that had been used for cereal, vegetable and livestock production over the last 30 years. The site was ploughed and a commercially available wood-derived (*Fraxinus excelsior* L., *Fagus sylvatica* L., *Quercus robur* L.) biochar (pyrolysed at 450 °C, 48 h) spread on the surface at rates of either 0 (control), 25 or 50 t ha⁻¹. The biochar was then harrowed into the topsoil (0–20 cm Ah horizon) to ensure mixing. Further physiochemical details of the biochar, crop and soil management are provided in previous papers (Jones et al., 2012; Quilliam et al., 2012).

In June 2011, each of the plots was further split into two 3 × 3 m sub-plots and biochar of the same origin was then added to half of the sub-plots at rates of 0, 25 or 50 t ha⁻¹ to achieve a double loading of biochar i.e., 0 (control), 25, 50, 25 + 25 and 50 + 50 t ha⁻¹. Subsequently, all plots were sown (45 seeds m⁻²) with field bean (*Vicia faba* L. cv. Green Arrow). Soil management and plant and soil analysis are provided in Quilliam et al., 2012. In February 2012, spring barley (*Hordeum vulgare* L.) was sown, with no further fertilizer additions.

2.2. Soil and biochar analysis

In February 2012, four replicate soil samples (0–20 cm) were taken from each plot and within 1 h of collection soil samples were sieved to pass 5 mm and used for chemical analysis within 24 h. Measurements of basal soil respiration at quasi-steady state were made on 30 g of field-moist soil for 24 h at 20 °C using an automated multichannel SR1 infrared gas analyser soil respirometer (PP Systems, Hitchin, UK) 24 h after collection from the field. Water content was determined by drying at 105 °C (24 h) and EC and pH were determined with standard electrodes on field-moist soil (1:1 v/w soil-to-distilled water). Available NO₃⁻ and NH₄⁺ were determined in 0.5 M K₂SO₄ extracts (1:5 w/v) using the colorimetric methods Miranda et al. (2001) and Mulvaney (1996), respectively. CEC and available nutrients (B, Ca, K, Mg, Na, P, S) were measured at an ISO9001 and ISO17025 accredited laboratory (Lancrop Laboratories, Yara UK Ltd., York, UK). The concentration of arsenic and heavy metals (Cu, Ni, Pb, Zn) in oven-dried soil (105 °C, 24 h) samples and fresh biochar were determined by a 700 series ICP-OES (Varian Inc., Palo Alto, CA) after digestion in concentrated HNO₃ (USEPA, 1995a) and filtration through a nylon 0.45 μm syringe filter. To allow comparison of metal concentrations in different years, arsenic and metal concentrations were also measured at the end of September 2011.

Sequential extractions of As and heavy metals in soil (Shiowatana et al., 2001; Beesley et al., 2010) were carried out on the soil collected in February 2012. Briefly, for the first step (water soluble fraction), 1 g of dry soil or biochar was mixed with 30 ml of distilled water, shaken for 16 h (200 rev min⁻¹), centrifuged (3000 rev min⁻¹, 15 min) and filtered (Whatman No. 42). For the second step (surface adsorbed fraction), samples were re-suspended in 30 ml of 0.5 M NaHCO₃ and shaken, centrifuged and filtered as described above. For the third step (Fe and Al-associated fraction), the residue from the previous step was re-suspended in 30 ml of 0.1 M NaOH and treated as above. For the fourth step (carbonate bound fraction) the residue from the third step was re-suspended in 30 ml of 1 M HCl and treated as above. Finally, the residual pellet was dried at 37 °C for 48 h and digested in concentrated HNO₃ to measure residual As and metal contents (USEPA, 1995a).

2.3. Plant analysis

Bean and barley green leaf samples were collected (ca. 100 g FW) in September 2011 (flowering and pod formation) and May 2012 (stem elongation), respectively. Leaves were subsequently dried (80 °C, 48 h), ground (<1 mm), digested in concentrated HNO₃ (USEPA, 1995b), filtered (0.45 μm) and total As and metal concentrations measured by ICP-OES as described above. In August 2012, mature barley plants were harvested and crop height, tiller number and dry seed yield (dried 80 °C, 24 h) measured.

2.4. Statistical analysis

All experiments were performed in quadruplicate. After checking for normality and homogeneity of variances, differences in treatments were compared by one-way ANOVA and Tukey HSD (for soil properties) or Duncan post hoc tests (for heavy metals) (SPSS v.14, SPSS Inc., Chicago, IL).

3. Results

3.1. Changes in soil characteristics after biochar addition

There was no significant difference in basal soil respiration between the unamended soil and the soil that had contained

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