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Research article

Biochar and compost amendments enhance copper immobilisation and support plant growth in contaminated soils

Sarah Jones [a], R. Paul Bardos [a,*], Petra S. Kidd [b], Michel Mench [c,d], Frans de Leij [e], Tony Hutchings [e], Andrew Cundy [f], Chris Joyce [f], Gerhard Soja [g], Wolfgang Friesl-Hanl [g], Rolf Herzig [h], Pierre Menger [i]

[a] r3 Environmental Technology UK Ltd, H9 TOB1, University of Reading Whiteknights Campus, Reading, UK
[b] Instituto de Investigaciones Agrobiológicas de Galicia (IIAG), Consejo Superior de Investigaciones Científicas (CSIC), Santiago de Compostela, 15706, Spain
[c] UMR BIOGECO INRA 1202, Ecologie des Communautés, Université de Bordeaux, Bât. B2, allée Geoffroy St-Hilaire, CS50023, F-33615, Pessac cedex, France
[d] INRA, UMR BIOGECO INRA 1202, 69 Route d'Arcachon, 33610, Cestas, France
[e] C-Cure Solutions Ltd, Forest Research, Wrecclesham, Farnham, Surrey, UK
[f] Environment and Technology, University of Brighton, Lewes Road, Brighton, BN2 4GJ, UK
[g] AIT Austrian Institute of Technology GmbH, Konrad Lorenz-Str. 24, 3430, Tulln, Austria
[h] Phytotech Foundation & AGB, Quartiergasse 12, CH3013, Berne, Switzerland
[i] Tecnalia Research & Innovation, Parque Tecnológico de Bizkaia, E-48160, Derio - Bizkaia, Spain

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ABSTRACT

Contamination of soil with trace elements, such as Cu, is an important risk management issue. A pot experiment was conducted to determine the effects of three biochars and compost on plant growth and the immobilisation of Cu in a contaminated soil from a site formerly used for wood preservation. To assess Cu mobility, amended soils were analysed using leaching tests pre- and post-incubation, and post-growth. Amended and unamended soils were planted with sunflower, and the resulting plant material was assessed for yield and Cu concentration. All amendments significantly reduced leachable Cu compared to the unamended soil, however, the greatest reductions in leachable Cu were associated with the higher biochar application rate. The greatest improvements in plant yields were obtained with the higher application rate of biochar in combination with compost. The results suggest joint biochar and compost amendment reduces Cu mobility and can support biomass production on Cu-contaminated soils.

1. Introduction

Trace element (TE) contamination of soils is a challenging risk management issue. TEs do not degrade over time and are therefore persistent in the environment (Megharaj et al., 2011), and conventional methods for their remediation (e.g. dig and dump) are often costly (Bolan et al., 2014) and non-sustainable. An interesting low input approach to *in situ* remediation of TE contaminated soils may be the use of amendments such as biochar and compost.

Biochar is the carbon-rich end product of biomass pyrolysis. It has diverse potential environmental applications. Amongst other uses, biochar may be used in carbon sequestration, bioenergy production and agricultural waste recycling (Ahmad et al., 2014). Biochar may also be an immobilisation agent for TE in contaminated soil (Venegas et al., 2015; Houben et al., 2013; Khan et al., 2013; Beesley and Marmiroli, 2011; Park et al., 2011; Sizmur et al., 2011). Biochar's ability to sorb contaminants has been attributed to an increase in oxygen-containing surface functional groups (carboxyl, hydroxyl and phenolic) with biochar addition to soil (Tong et al., 2011; Uchimiya et al., 2011). Biochar is also highly durable (Gurwick et al., 2013) which could result to a long term immobilisation effect. Whilst biochars have been shown to reduce

* Corresponding author. r3 Environmental Technology Ltd, H9 TOB1, University of Reading, Earley Gate, Reading, RG6 6AT, UK. Tel. +44 118 378 8164; fax: +44 118 3290476.

E-mail addresses: sarah@r3environmental.co.uk (S. Jones), paul@r3environmental.co.uk (R.P. Bardos), pkidd@iiag.csic.es (P.S. Kidd), mench@bordeaux.inra.fr (M. Mench), frans@ccuresolutions.com (F. de Leij), tony@ccuresolutions.com (T. Hutchings), A.cundy@brighton.ac.uk (A. Cundy), Gerhard.soja@ait.ac.at (G. Soja), Wolfgang.friesl@ait.ac.at (W. Friesl-Hanl), rolf.herzig.agb@bleuwin.ch (R. Herzig), pierre.menger@tecnalia.com (P. Menger).

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the bioavailability of TE in soils, further study of this process is required in a range of contaminated soils in order to fully understand both its potential and its limitations.

Compost amendment has also been used in the remediation of contaminated soil. Compost addition can reduce the exchangeable fraction in soil for a number of TE, due to increased cation exchange capacity (CEC) and the strong affinity of metals for organic complexation sites (Bes and Mench, 2008; Fleming et al., 2013). Alvarenga et al. (2009) showed that composts derived from green waste and municipal solid waste reduced mobile concentrations of copper (Cu), lead (Pb) and zinc (Zn) as a consequence of altered soil chemical characteristics, including increased pH and organic matter (OM) content.

Biochar and compost incorporation into soil for remediation purposes also provides soil fertility improvements (including nutrient provision, enhanced CEC, improved soil structure and water retention, and pH control). These wider benefits may also be very useful for brownfield sites, which commonly have poor soil quality (Mallik and Karim, 2008; Nixon et al., 2001). Additionally, higher plant yields obtained with organic amendment addition may support increased biomass production on brownfields, and therefore enhanced phytoremediation (Beesley et al., 2011).

In this study, we investigated the effects of three biochars and compost on plant growth and Cu mobility in a contaminated soil from a former wood preservation site. Leaching tests were performed on amended soils to determine Cu mobility, and plant (pot) trials were undertaken to assess impacts on plant growth and plant metal concentrations. Sunflower was selected as the trial plant as it has high adaptability and aesthetic appeal, and is widely used as a biofuel substrate (Zhao et al., 2014; Mench et al., 2010; Amon et al., 2007; Gerçel, 2002). The IBL04 sunflower mother clone was chosen for its relatively high metal tolerance (Herzig et al., 2014; Nehnevajova et al., 2007, 2009) and has previously been cultivated in the field in amended soils at the Gironde site (Kolbas et al., 2014).

2. Materials and methods

2.1. Study site and soil sampling

Cu contaminated soil was obtained from a former wood preservation site in the Gironde County Saint Médard d'Eyrans, France (N 44º 43.353, W 000º30.938) (Bes et al., 2010). Soil was sampled randomly and collected in February 2014 with an unpainted stainless steel spade from the P7 sub-site (0–25 cm depth) which has previously been investigated by Bes and Mench (2008), Mench and Bes (2009), and Bes et al. (2010). Soil material (5 subsamples totalling 100 kg) was manually homogenised and sieved to 4 mm. The P7 soil (WRB classification: Eutric gleysol; pH_{water} 7; LOI 3%) is largely classified as a sandy loam. At the P7 sub-site, wood was dipped in creosote and Cu sulphate as preservative treatments. The P7 soil consequently has high levels of Cu and polycyclic aromatic hydrocarbon (PAH) contamination (see supplementary materials for detailed soil analysis of: PAHs, trace elements, hydrocarbons and BTEX - http://doi.pangaea.de/10.1594/PANGAEA.846932).

2.2. Amendments

Three biochars were tested: BC1, BC2 and BC3. BC1 (pH_{water} 10; LOI 49%) was a specialised biochar agent, *C-Cure Metal*, developed and patented for the remediation of metal contaminated substrates (C-Cure Solutions™ Ltd, Farnham, UK)[1](patent number: WO2009016381A2). BC2 (pH_{water} 10; LOI 42%) and BC3 (pH_{water} 10; LOI 40%) were produced by the AIT (Austrian Institute of Technology GmbH) in co-operation with Sonnenerde GmbH using chopped poplar wood previously harvested from the P7 sub-site. BC2 and BC3 were produced via pyrolysis at 525 °C in a Pyreg reactor (Pyreg GmbH, Dörth, Germany) with a residence time of approximately 15–20 min. BC2 was used unaltered. BC3 was mixed with 20% Fe_2O_3 purchased from VWR (VWR International GmbH, Darmstadt, Germany). Fe_2O_3 was trialled in an attempt to improve the number of sorption sites. Iron oxides have known sorption capabilities and have been applied as intended "sinks" for certain TE (Komárek et al., 2013; Cundy et al., 2008; Cornell and Schwertmann, 2003). Compost (pH_{water} 8; LOI 18%) made from green waste and sandy soils/sand was purchased in France and was stored at the Gironde site for one year under tarpaulin. Soil and amendments were transported to IIAG-CSIC,[2] Spain, where the leaching and plant trials were carried out.

Table 1
Sample ID showing amendments and rates.

Unamended	Compost (1%)	BC3 (3%) + C (1%)
BC1 (1%)	Compost (2%)	BC1 (1%) + C (2%)
BC2 (1%)	BC1 (1%) + C (1%)	BC2 (1%) + C (2%)
BC3 (1%)	BC2 (1%) + C (1%)	BC3 (1%) + C (2%)
BC1 (3%)	BC3 (1%) + C (1%)	BC1 (3%) + C (2%)
BC2 (3%)	BC1 (3%) + C (1%)	BC2 (3%) + C (2%)
BC3 (3%)	BC2 (3%) + C (1%)	BC3 (3%) + C (2%)

2.3. Experimental design

Each of the biochars was trialled as a single amendment at rates of 1% and 3% w/w. Green waste compost (C) was also trialled as a single amendment at application rates of 1% and 2% w/w. Additionally, each of the three biochars was trialled in combination with compost, at the aforementioned application rates. Soils were amended with a total of 20 amendments alongside unamended soil (see Table 1 below).

Prior to soil amendment, all biochars were air-dried for three days then ground to <2 mm. Compost was sieved to <2 mm before addition and application rates were amended to allow for moisture content. For incubation trials (see below), 150 g aliquots of soil were amended (20 amendments, plus unamended). For plant trials, soil was sieved to 4 mm and bulk amended in batches of 3 kg (20 amendments, plus unamended). To determine the effect of the soil amendments on Cu mobility and plant growth, leaching tests and plant trials were carried out. pH and Dissolved Organic Carbon (DOC) were measured in parallel to leaching tests.

2.4. Leaching tests

Leaching tests (adapted from Houba et al., 2000) were carried out to determine the effect of amendment application on Cu mobility in soil. Leaching tests were carried out at three "time points": "pre-incubation", "post-incubation" and "post-growth". "Pre-incubation" leaching tests were carried out 24 h after amendment by removing aliquots (2.5 g) of amended and unamended soil to 50 ml centrifuge tubes (4 replicate tubes per amendment) and mixing with 25 ml of 0.01 M $CaCl_2$. Samples were then placed on a shaker for 24 h prior to centrifugation at 3752 g for ten minutes (J2-MI, Beckman Coulter, Inc., Brea, CA, USA). Samples were extracted for 24 h as biochar producers C-CURE have found

[1] www.ccuresolutions.com.

[2] www.iiag.csic.es.