



Stabilization of metal(loid)s in two contaminated agricultural soils: Comparing biochar to its non-pyrolysed source material



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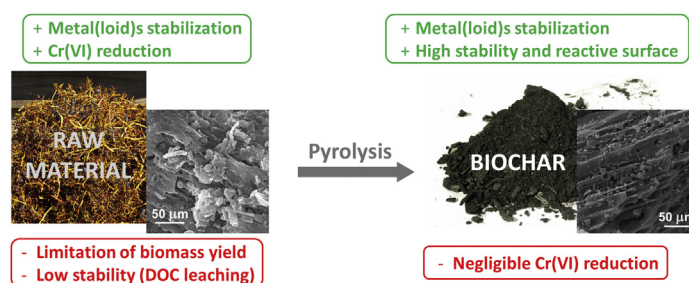
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HIGHLIGHTS

- Biochar and its source material stabilized various metal(loid)s in the soils.
- Original grape stalks can effectively reduce Cr(VI) to Cr(III).
- Biochar was the more stable material with high reactive surface.
- Source material generated higher DOC concentrations and acidic pH in the pore water.
- Source material significantly decreased ryegrass yield in comparison to biochar.

GRAPHICAL ABSTRACT



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ABSTRACT

Two metal(loid) contaminated agricultural soils were amended with grape stalk (wine production by-product)-derived biochar as well as its pre-pyrolysed origin material, to investigate their geochemical impacts on As, Cr, Cu and Zn. Detailed physico-chemical evaluation combined with a column leaching test determined the retention of metal(loid)s from soil solution by each amendments. A pot experiment measured metal(loid)s in soil pore water and their uptake to ryegrass when the amendments were mixed into soils at 1 and 5% (w/w).

Total Cr and Zn concentrations were reduced furthest in column leachates by the addition of raw material and biochar respectively, compared to the untreated soil; Cr(III) was the predominant specie initially due to rapid acidification of leachates and organic complexation resulting from raw material addition. Loadings of metal(loid)s to the amendments recovered from the post-leached columns were in the order Cu » Zn > Cr ≈ As.

In the pot test ryegrass Cr uptake was initiated by the addition of both amendments, compared to the untreated soil, whereas only biochar addition resulted in significant increases in Zn uptake, explained by its significant enhancement of ryegrass biomass yield, especially at 5% dosage; raw material addition significantly decreased biomass yields. Inconsistent relationships between pore water parameters and ryegrass uptake were common to both soils investigated.

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Therefore, whilst both amendments modified soil metal(loid) geochemistry, their effects differed fundamentally; in environmental risk management terms these results highlight the need to investigate the detailed geochemical response of contaminated soils to diverse organic amendment additions.

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1. Introduction

In recent years, a great deal of attention has been focused on the use of biochars as soil amendments, justified in part by their supposed longevity in soils and resistance to degradation. Experimental application of biochars to soils have been reported to increase water holding capacities (Thies and Rillig, 2009), C, N and P (Lehmann, 2007; Chan and Xu, 2009; Borchard et al., 2012), major cation availability (Major et al., 2010; Gartler et al., 2013), removal of metals and As from waste-waters (Mohan et al., 2007) and metals from soil leachates (Beesley et al., 2010; Beesley and Marmiroli, 2011; Fellet et al., 2011). Several mechanisms have been described by which biochars incorporated into metal(loid) contaminated soils can reduce their mobility and onward impacts to plant growth and health (when some of them are essential up to given concentration). These include direct mechanisms, such as sorption and precipitation, as well as indirect effects, such as pH changes and other physico-chemical modifications to soils (Beesley et al., 2015). However, such effects, especially those that modify soil biochemistry, are also achievable by the incorporation of the selected non-pyrolysed organic materials (organic amendments) directly into soils (i.e. composts, manures, sludges etc; Bernal et al., 2007; Sud et al., 2008). For example, the cation-exchange-capacity (CEC) of biochars is heavily influenced by pyrolysis temperatures and origin of the source material (Kim et al., 2016; Trakal et al., 2014); loss of organic functional groups from organic matter during pyrolysis can reduce CEC of the final material (Ippolito et al., 2015) with attendant consequences to N content, availability of nutrients in soils and metal(loid) mobility (Beesley et al., 2015), though several studies prove increased CEC of biochar amended soils (Igalavithana et al., 2016). Some advantageous soil modifications induced by biochars have been found to be short-term; amongst others, in a 3-year agricultural field trial initial alkalinity was neutralised and exchangeable cations diminished (Jones et al., 2012), suggesting leaching loss of the ash fractions upon environmental exposure.

A recent review of the effects of biochars on soil acidity has also highlighted the general neutralising effect of biochars incorporated into acid soils, which is related to carbonates, silicates and alkaline oxides present in the ash fraction (Dai et al., 2017). Research has shown that this mineral (ash) fraction of biochar, amongst the organic matrix, is important in the precipitation of some metals (i.e. Pb) into more insoluble forms with carbonates, phosphates etc. (Sizmur et al., 2016), as well as the provision of macro-nutrients. However, longer-term trials using biochars have shown inconsistent effects on soil acidity, with much of the pH increase associated with biochar application being temporary; for example, in a 3-year field trial on agricultural soil in UK by Jones et al. (2012). Given existing concerns surrounding the prohibitively high costs associated with the production and transportation of some biochars (Dai et al., 2017), and limitations on their effectiveness, it is pertinent to compare the experimental performance of biochars versus their non-pyrolysed source materials to determine whether it is necessary at all to apply biochars to achieve satisfactory results in terms of risk-relevant metal(loid) behaviour.

Therefore the aim of this study was to 1) determine the short

term mobility and uptake of As, Cr, Cu and Zn after the treatment of two metal(loid) contaminated agricultural soils with raw biomass material versus its resultant biochar. Thereafter 2) assess the longer term leaching and fractionation of metal(loid)s and the sorptive capabilities of the treatment materials in a column leaching test, to identify any limitations induced by either material that would hinder their further deployment in trials on the tested soils.

2. Material and methods

2.1. Soil preparation

Two agricultural soils that had been previously contaminated with metal(loid) rich materials were used in the following experiments.

Soil A (labelled as 'CA'): was obtained from an upland farming estate in north-east Scotland (UK) stocked with cattle, sheep and deer. Soils on the farm are freely drained humus iron podzols ('Entic podzol' under WRB classification system) developed on old red sandstone (Glentworth and Muir, 1963). Soil was collected using a small spade, with equal volumes of soil gathered from 3 profile faces excavated to 50 cm depth, mixed and bulked together. Soil collection took place on part of the farm designated for experimental work being lightly grazed seasonally (sandy loam texture, organic carbon (OC) contents of ~7% and nitrogen (N) contents of ~0.6%). In 2011 a 70kw biomass boiler was installed at the farm, to provide heat for the farm buildings. Metal(loid) rich ash from this boiler was obtained after mixed chromated copper arsenate (CCA) treated waste wood burning during a short period in early 2014; ash contained maximum total metal(loid) concentrations of 10,000 mg kg⁻¹ (see Mollon et al., 2016). Subsequently ash was mixed with soil (approx. 2% ash by mass; labelled as 'SA') creating a metal(loid) contaminated soil (see Table 1) which is effectively limed due to high amounts of Ca in the ash, and subsequent pH increase.

Soil B (labelled as 'CB'): was obtained from a lowland farming estate in central Scotland (UK) stocked with cattle and sheep. Soils on the farm are poorly drained gleys ('Eutric Stagnosol' under WRB classification system) of the Rowanhill and Caprington series. Several controlled experimental applications of Zn-rich sewage sludge during the period 1994–1997 resulted in soils with high Zn concentrations (see Gibbs et al., 2006; labelled as 'SB'); sludge applied to these soils contained maximum total Zn concentrations of ~5000 mg kg⁻¹ (data not shown). The soil was collected using the same procedure as in the case of soil A, from part of the farm designated for experimental work, being plots having historically received controlled Zn-rich sludge applications (sandy clay loam texture, organic carbon (OC) contents of ~5% and nitrogen (N) contents of ~0.5%).

2.2. Amendment preparation and characterisation

The production methodology for the grape stalk-derived biochar used in this study are described elsewhere by Trakal et al. (2014). This material was selected because it showed the best sorption of tested metals in aqueous solutions in the cited study.

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