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INSPIRATION bulletin

CL:AIRE's INSPIRATION bulletins describe practical aspects of research which have direct application to the management of contaminated soil or groundwater in an agricultural context. This bulletin describes how the properties of biochar can influence its performance for the restoration of metal-polluted soil.

Bio-restoration of metal-contaminated soil using biochar to enhance the productivity of marginal land

1. Introduction

Some metals and semimetals commonly denoted as "heavy metals" are environmental pollutants of particular concern due to their widespread occurrence and potential toxic effects on living organisms (Amari *et al.*, 2017). Although the term heavy metal refers to the atomic density of the elements, which is rarely a biologically significant property, in the literature it has been used extensively to refer to metals that have been associated with contamination and potential toxicity or ecotoxicity (Duffus, 2002). Nowadays, most heavy metals are released to the environment by industrial and mining activities (Su *et al.*, 2014). In elevated concentrations some metals may cause negative effects such as a reduced agricultural productivity, phytotoxicity and bioaccumulation in crops (Bandara *et al.*, 2017). They do not biodegrade and persist in the environment (Moreno *et al.*, 2011), representing a complex challenge as they can affect soil, water and groundwater quality through pollutant run off and leaching (Zalidis *et al.*, 2002).

Biochar application in soils is currently being studied as an environmentally friendly option for the restoration of heavy metal-polluted sites. Biochar is a black carbon produced from the pyrolysis of residual biomass. It typically possesses high specific surface area and is rich in oxygenated functional groups (Tang *et al.*, 2013). Because of these properties, biochar can bind with heavy metals present in soils (Park *et al.*, 2011), immobilising them by sorption and/or metal precipitation processes and reducing metal toxicity which may then enable land to be restored to productive use (Qadeer *et al.*, 2017). The use of biochar is gaining attention as it can bring other benefits. These include acting as a carbon sink for carbon sequestration purposes and also improving some soil characteristics required for plant growth, such as water holding capacity, regulating pH of acidic soils, improving aggregation capacity and increasing nutrient availability and retention in soils (Laghari *et al.*, 2016; Li *et al.*, 2017).

The application of biochar as an alternative for the restoration of heavy metal-polluted soils is promising. Nevertheless, more understanding is required to overcome some of the present uncertainties related to the wide variety of biochars available and the unique character of each one contrasted with the lack of a technical criterion for its selection and application in the restoration of heavy-metal polluted soil. Thus, this study describes how the mechanistic properties of biochar influence its performance for the restoration of heavy metal-polluted soil. It aims to provide guidance for biochar selection and use in soil restoration processes.

2. Methodology

2.1 Biochar selection and characterisation

The appropriate selection of biochar materials is a key step in a successful restoration process, as each biochar has unique properties that determine its potential as an adsorbent and soil amendment. These properties are determined by two factors: i) the nature of the feedstock materials, and ii) the pyrolysis conditions (Janus *et al.*, 2015).

Considering these features, the properties and characteristics of five biochars produced by the UK Biochar Research Centre were evaluated in the present study. The feedstocks from which these biochars were produced represent the major terrestrial biomass types (woody and herbaceous) and cover a wide range of physico-chemical properties (Mašek *et al.*, 2018). These materials were characterised for their cation exchange capacity (CEC), specific surface area (SSA) and pH (Table 1), as critical determinants of biochar performance. Surface morphology was studied by scanning electron microscopy (SEM), as depicted in Figure 1.

Table 1: Characteristics of selected biochars

Biochar	Feedstock	Production temperature °C	Organic carbon [molar ratio]	CEC cmol.kg^{-1}	pH	SSA [m^2.g^{-1}]
WSP550	Wheat straw	550	0.08	29.86	9.94	26.4
MSP550	Miscanthus straw	550	0.09	29.82	9.77	33.6
OSR700	Oil seed rape straw	700	0.09	30.72	10.41	25.2
SWP550	Softwood pellets	550	0.09	14.17	7.91	26.4
OSR550	Oil seed rape straw pellets	550	0.1	30.27	9.78	7.3

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Inspiration

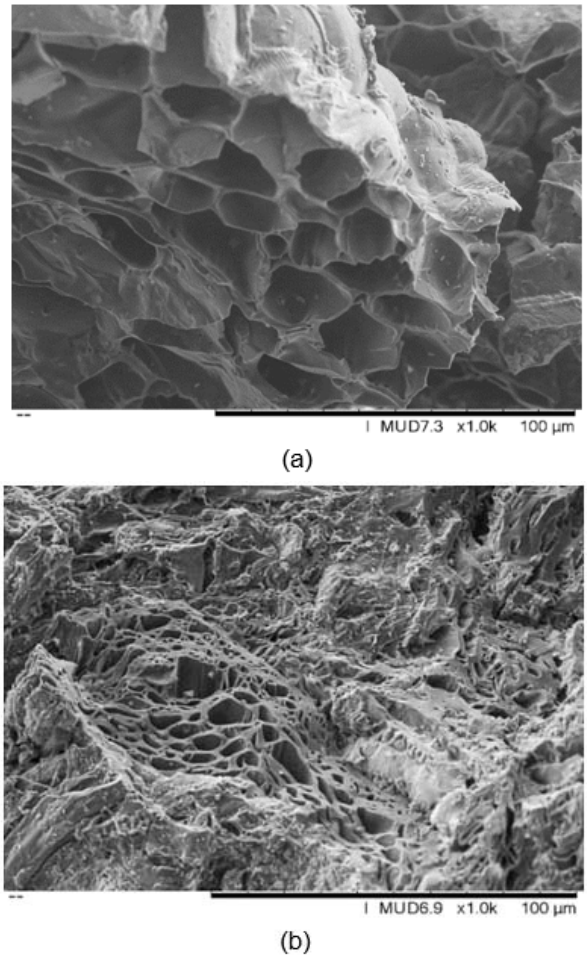

Figure 1: SEM image of biochar a) OSR550 and b) SWP550.

2.2 Biochar and soil restoration/remediation

The addition of biochar to contaminated soil generally decreases the amount of metals that are easily accessible or bioavailable to living organisms (Park *et al.*, 2011). A decrease in the bioavailable fraction of metals accompanied by an increase in the more recalcitrant (non-bioavailable) metal fraction in soil has been reported after biochar addition (Beesley *et al.*, 2010; Puga *et al.*, 2016). As a proof-of-concept the role of biochar in decreasing bioavailable heavy metal fractions was assessed with a soil sample amended with biochar using a sequential extraction procedure. This procedure estimates the proportion and relative distribution of metals between different operationally defined soil fractions [exchangeable, carbonate-bound, Fe-Mn oxide-bound, organic matter-bound and residual]. A description of the reagents used for the extraction of each fraction and the time required at each stage is provided in Table 2. It is generally considered that metals bound to the exchangeable and carbonate fractions are potentially bioavailable and consequently toxic, while the metals stored in the other reservoirs are relatively stable under normal soil conditions (Filgueiras *et al.*, 2002). The soil used originated from a steel works and the chemical analysis indicated the following approximate total concentration of metals: Cd (0.5 $mg.kg^{-1}$); Pb (55 $mg.kg^{-1}$) and Zn (266 $mg.kg^{-1}$). The soil was amended with biochar SWP550 at different application rates (0, 1, 1.5 and 3% w/w) and incubated for four weeks in a laboratory experiment.

2.3 Studies of metal immobilisation mechanisms by biochar

Adsorption experiments were performed using a batch equilibration technique in order to study the mechanisms responsible for immobilisation of heavy metals by the selected biochars (Table 1). Stock solutions of Zn (II), Cd (II), and Pb (II) were prepared (Bogusz *et al.*, 2015) and a synthetic soil pore water solution based on the average ion composition of UK soil solution (Sparks, 2003) was used as the background medium for all the adsorption experiments. To study the effect of contact time on metal adsorption (kinetics), 100 mg of biochar was mixed with 20 ml of 1 $mg.l^{-1}$ solution of each metal and samples were taken at intervals of 1, 2, 4, 8, 10, 18, 24, 48, 76 and 92 hours. To study the effect of pH on metal adsorption capacity the initial pH of the synthetic soil solution was adjusted in the range pH 4 to 10 using either NaOH 0.1 M or HCl 0.1 M. To study the effect of adsorbent dose on metal sorption and the determination of the optimal dose, different biochar to liquid ratios were tested, ranging from 0.25 to 5 $g.l^{-1}$. All extracts were filtered through a 0.45 µm nylon membrane and stabilised by the addition of 1% of concentrated HNO_3 trace analysis grade. Samples were stored at ± 4°C until analysis of metal concentrations by Inductively Coupled Plasma Mass Spectrophotometry (ICP-MS).

In addition, a greenhouse incubation experiment was conducted using sandy loamy soil artificially contaminated with Cd, Pb and Zn and a mixture of these metals in a series of soil pots was conducted. Laboratory-spiked samples often exhibit greater toxicity than contaminated field samples with similar metal concentrations (Schwertfeger and Hendershot, 2013). For this reason, the spike/leach procedure to prepare samples for trace metal ecotoxicity soil testing recommended by Schwertfeger and Hendershot (2013) was adapted to this study in order to create more environmentally-relevant concentrations. The soil was spiked progressively over five days with $ZnCl_2$, $Pb(NO_3)_2$ and $Cd(NO_3)_2$ solutions. The soil was then left to stabilise for 2 months outdoors (January-February 2018) to allow natural leaching. The pH and electric conductivity were measured periodically to ensure salt effect to be overcome (Schwertfeger and Hendershot, 2013). Once the soil was ready, different biochar application rates were tested: 1%, 3% and 5% (w/w). *Arabidopsis thaliana* col-0 var seeds were added to the experimental pots to evaluate the effect of biochar on plant growth.

Table 2: Extractants used in sequential extraction and nominal phases.

Fraction	Phase	Reagent	Shaking time
1	Exchangeable	1M $MgCl_2$ at pH 7	1 hour at 20ºC
2	Bound to carbonates	1M NaOAC at pH 5	5 hours at 20ºC
3	Bound to Fe and Mn oxides	0.04 M $NH_2OH.HCl$ in 25% (v/v) HOAC pH 2	5 hours at 95ºC
4	Bound to organic matter	0.02M HNO_3 in 30% H_2O_2	4 hours at 85ºC
5	Residual	Aqua regia (3:1 HCl:HNO_3)	2.5 hours at 140ºC

Arabidopsis thaliana is widely used as a model organism in plant biology as it has a rapid life cycle and its genome is well characterised. The pots were incubated over 8 weeks at 60% water holding capacity and controlled conditions [23ºC, with a photo light period of 12 hours]. Plant development was monitored continuously using a plant screening system composed of a RGB (red, green and blue) camera and chlorophyll fluorescence camera Fluorcam 7.0 (Photon Systems Instruments). These images provided information of growth rate and plant health state by monitoring the functioning of photosystem II (Fv/Fm) and an estimation of the above ground biomass area.

3. Results

The sequential extraction of the soil from the steel works revealed that the addition of biochar SWP550 decreased the amount of exchangeable and carbonate-bound Cd (potential bioavailable fractions) and Fe-Mn oxide-bound fraction, compared with the un-amended soil. This decrease was accompanied by an increase in the metals bound to the residual fraction at 1 and 3% w/w biochar application rate (Figure 2). In the case of Pb and Ni no effect was observed. This experiment demonstrated the selective immobilisation of metals by biochar and its effect at different application rates. In addition, the sequential extraction method was shown to be a useful approach for evaluating the change in heavy metal distribution between soil fractions after biochar addition.

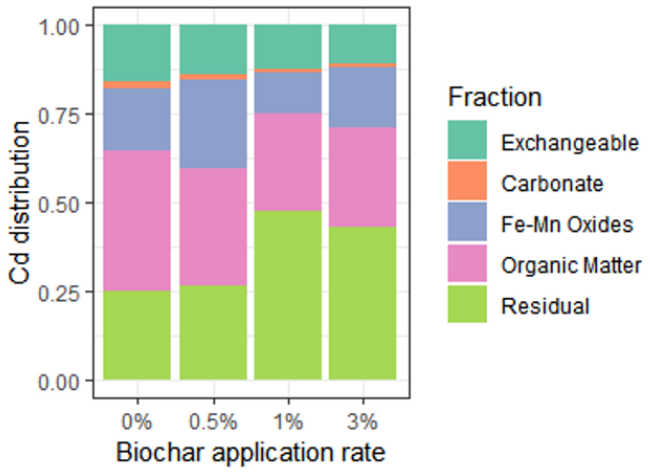

Figure 2: Cadmium (Cd) distribution in metal-contaminated soil amended with biochar SWP550 at 0.5, 1 and 3% (w/w).

The batch tests provided insight about the mechanisms responsible for metal immobilisation. For instance, the effect of contact time on metal sorption by biochar (kinetics) indicated that equilibrium is reached before 24 hours, as depicted in Figure 3a. The process can be described by a pseudo-second order model, characterised by fast sorption onto particle surfaces (chemisorption) followed by slow inner diffusion within the biochar matrix (physical sorption). The kinetic constant, k_2, estimated from the sorption isotherms showed that sorption occurred in the following order: Pb>Cd>Zn for all biochars. The study of pH effects demonstrated that biochars can immobilise Zn between pH 5 and 8, and Cd between pH 5 and 7, whereas the adsorption capacity of Pb is limited above pH 5 due to precipitation of metal (Pb) hydroxides (Figure 3b). In the kinetic study, there was a significant effect on sorption capacity determined by biochar type and the metal present in the medium at equilibrium

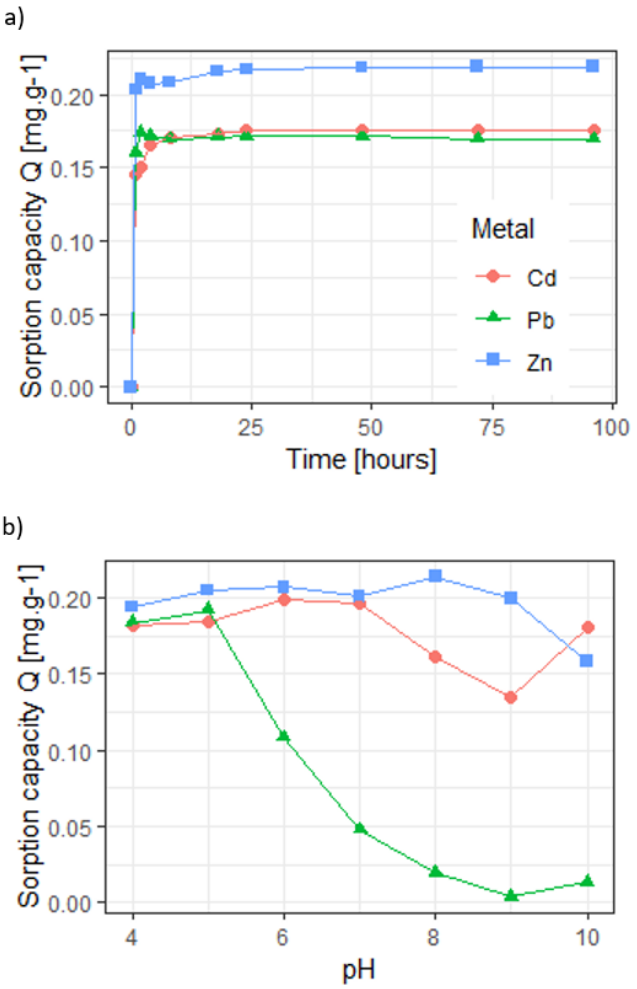

Figure 3: a) Effect of contact time for Zn, Cd and Pb sorption by biochar MSP550 over 96 hours. b) Effect of initial pH of the media solution on metal sorption capacity of biochar MSP550.

(TWO-WAY ANOVA: F 1167.13, $p < 0.05$; F 399.86 and $p < 0.05$ respectively). Biochars WSP550, MSP550, OSR550 and OSR700 had a higher adsorption capacity for Cd, Zn and Pb than SWP550 (Tukey multiple comparisons test, $p < 0.05$). The results suggest that the CEC is the primary property of biochar which influences sorption for Cd and Zn; in the case of Pb precipitation caused by changes in the pH was observed. These batch tests enabled the optimum conditions for adsorption of heavy metals to be determined for a better understanding of the mechanisms occurring in metal-contaminated soil.

The greenhouse incubation experiment indicated that biochar type and application rate have a significant effect on dry above ground biomass (TWO-WAY ANOVA: F 4.4544, $p < 0.05$; F: 4.1911, $p < 0.05$). Biochar application at 1% w/w has a potential protective influence for plants against heavy metal toxicity, while higher application rates showed no effect or inhibition of plant growth due to soil pH related shifts. Figure 4 illustrates the effect of application rate and different biochar types using the results from Zn spiked soil as an example. This experiment revealed the best application rate of each biochar, providing guidance for a future field experiment required to test these rates with a naturally-contaminated soil.

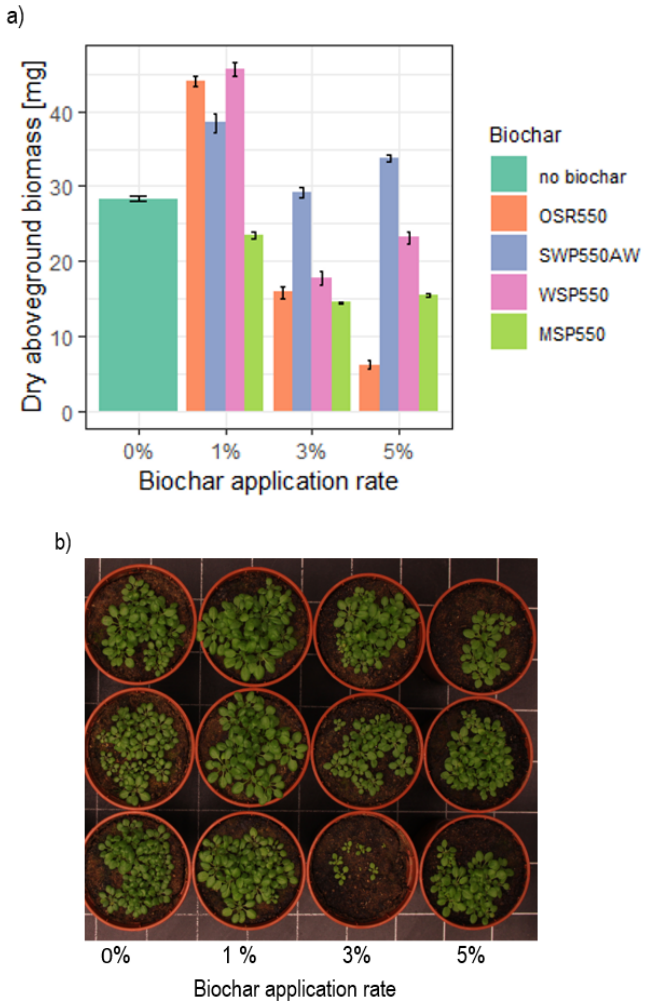

Figure 4: a) Dry above ground biomass from Zn artificially contaminated soil amended with different biochars at 0, 1, 3 and 5% w/w application rate; b) *Arabidopsis thaliana* plants growing on Zn artificially contaminated soil amended with biochar WSP550 at 0, 1, 3 and 5% w/w application rate in triplicate.

4. Conclusions

The present results indicate that biochar can potentially reduce the bioavailability of some heavy metals in metal-contaminated soil to support plant cultivation, as part of a restoration strategy for a site. Biochar has a different potential for metal immobilisation and effect on plant growth depending on the heavy metal and biochar application rate. Further experiments are underway to identify the drivers of the selective effect of biochar on heavy metal immobilisation. In addition, field trials will be conducted to monitor biochar performance under different environmental conditions and to assess its effect on microbial activity and the bioavailability of heavy metals after one year of biochar application.

Acknowledgments

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