



Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass

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ARTICLE INFO

Article history:

Received 9 December 2010

Received in revised form 4 April 2011

Accepted 5 April 2011

Available online 9 April 2011

Keywords:

Heavy metals

Compost

Biochar

Ryegrass

Pore water

Remediation

ABSTRACT

Green waste compost and biochar amendments were assessed for their assistance in regulating the mobility of copper (Cu) and lead (Pb) and the resultant uptake of these metals into vegetation. The amendments were mixed with a heavily Cu and Pb contaminated soil (600 and 21,000 mg kg⁻¹, respectively) from a former copper mine in Cheshire (UK), on a volume basis both singly and in combination in greenhouse pot trials. Ryegrass (*Lolium perenne* L. var. Cadix) was grown for the following 4 months during which biomass, metals in soil pore water and plant uptake were measured in three consecutive harvests. Very high Pb concentrations in pore water from untreated soil (>80 mg l⁻¹) were reduced furthest by compost amendment (<5 mg l⁻¹) whereas biochar was the more effective treatment at reducing pore water Cu concentrations. Duly, ryegrass shoot Cu levels were reduced and large, significant reductions in shoot Pb levels were observed after biochar and compost amendments, respectively during successive harvests. However, because green waste compost singly and in combination with biochar vividly enhanced biomass yields, harvestable amounts of Pb were only significantly reduced by the compost amendment which had reduced shoot Pb levels furthest. The low biomass of ryegrass with biochar amendment meant that this was the only amendment which did not significantly increase harvestable amounts of Cu. Therefore the two amendments have opposing metal specific suitability for treating this contaminated soil regarding whether it is a maximum reduction in plant tissue metal concentration or a maximum reduction in harvestable amount of metal that is required.

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1. Introduction

Anthropogenic activities have produced numerous sites with extensive areas of contamination in proximity to residential and recreational areas. In the case of heavy metals, their lack of degradation in the environment ensures a statutory requirement to remediate polluted sites to reduce exposure risk to humans and the environment many years after emission from the pollutant source has ceased [1]. Historically, remediation techniques have involved various degrees of excavating contaminated soil to landfill, a practice now generally considered environmentally disruptive and economically unfeasible [2,3]. Modern remediation approaches increasingly focus on *in situ* environmentally friendly techniques, such as assisted natural attenuation and phytostabilisation often primed by the addition of soil amendments [4–7].

Stabilisation of inorganic contaminants by processes of adsorption, binding or co-precipitation with the additive amendments [4] has been widely researched in the last decade [8–10]. Of the numerous amendments used for *in situ* stabilisation of contaminants, organic materials such as biosolids, manures and composts, rich in organic matter, have proved successful at reducing the mobility of contaminants in multi-metal polluted soils [3,6,11–13]. In the UK the production of green waste compost (GWC) has increased dramatically resulting in nationwide establishment of composting facilities making quality GWC widely available. Many frequently encountered inorganic contaminants such as Cu, Pb, Zn and Cd show varying degrees of affinity for organic matter [7,14,15], encouraging the study of experimental application of GWC to contaminated soils. Furthermore, increasing interest in integrating remediation and the provision of ecosystem services, such as carbon sequestration in soils, has provided an attractive land management option for contaminated sites [16] using materials rich in carbon.

Biochar (biologically derived charcoal) is produced by pyrolysis of biomass under low oxygen conditions, and may be another suitable soil ameliorant due to already demonstrated soil conditioning

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properties. For example; enhanced cation exchange capacity, binding of nutrients and prevention of subsequent nutrient run-off, reduced nitrogen leaching, improved soil water retention capacity, neutralising soil acidity and providing conditions suitable for micro-organisms [17]. Furthermore, by incorporating biochar into soil, reducing carbon stocks could be replenished [18] and long term storage of carbon could be increased [19,20]. More recently, it was demonstrated that biochar was effective at reducing concentrations of Cd and Zn in soil pore water, reducing phytotoxicity to *Lolium perenne* L. but tended to mobilise some elements such as As and Cu due to increases in pH and DOC, alluding to element specific effects of adding char to soils [21], which warrant further investigation.

The main objectives of the present study were to (i) determine the efficacy of compost and biochar amendments both singly and in combination for modifying the solubility and uptake of Cu and Pb from a highly polluted former mining site soil to perennial ryegrass and hence (ii) evaluating the prospects for revegetation of this soil and the attendant risks to the transfer of metals.

2. Materials and methods

2.1. Study site and soil collection

Surface samples of soil (0–10 cm) were collected in a randomised formation, from a barren area of 20 m² within mature woodland at a former copper mine site (Alderley Edge, Cheshire, UK; 53°17'43"N, 2°13'03"W). In the laboratory the soils were bulked and homogenised to give one representative sample of approximately 40 kg. This soil was air-dried (22 °C) for 1 week before being sieved to a particle size of <11.2 mm to remove larger debris and coarse materials. Composted green waste (GWC) (supplied by White Moss Horticulture Ltd., Kirkby, Liverpool, UK) was mixed by hand with soil at 30% (v/v). Biochar derived from British Oak, Ash, Sycamore and Birch (supplied by Bodfari Charcoal, Denbigh, North Wales, UK) was mixed at 20% (v/v), and a combination of GWC and biochar were mixed at proportions of 30% and 20% (v/v), respectively. These rates were used to replicate an application of up to 5–10 cm of organic amendment added to the surface of contaminated soils. The amended soils were thoroughly homogenised and distilled water was applied until soil reached 70% water holding capacity (WHC) after which they were allowed to equilibrate in plastic bags for four weeks at 15 °C. Sub-samples were taken from each treatment after equilibration, air-dried as described previously and sieved to a particle size of <2 mm diameter. These sub-samples were analysed to determine pH, available P, organic matter, water soluble (extractable) nitrogen and water soluble (extractable) carbon and pseudo-total elements as follows.

2.2. Soil physico-chemical analysis

The pH of amended soils and compost was determined using a 10 g sample mixed with 25 ml of deionised water, which was stirred and left for 30 min at room temperature (22 °C). The suspension was tested using a Jenway 3051 pH meter. Organic matter content was determined by the loss on ignition (LOI) method. Water soluble organic C (WSC) and water soluble total nitrogen (WSN) were obtained by aggressive aqueous extraction using a 1:10 soil to de-ionised water suspension (2.5 g soil:25 ml water), which was shaken for 3 h and centrifuged at 3000 rpm for 10 min [22], then filtered using Whatman 42 filter paper. The filtered supernatant was analysed using a TOC-VE Shimadzu analyser (Shimadzu, Tokyo, Japan).

Available P was determined colourimetrically using the molybdenum blue method after extraction with 0.5 M NaHCO₃ (1:10, w/v) for 30 min [23]. Pseudo-total Cu and Pb concentrations (mg kg⁻¹) were determined for the amended soils using 0.2 g of sample digested with 10 ml of Analar grade 14 M HNO₃ in a Mars Xpress (CEM, NC, USA) microwave digester for 10 min at 185 °C followed by 10 min at 125 °C. Soil digests were analysed by flame atomic absorption spectroscopy (AAS; Perkin-Elmer AA100, MA, USA).

2.3. Plant and pore water investigations

Equilibrated amended soil was transferred to triplicate plastic pots (2 l), each placed on a saucer (Fig. 1) to prevent loss of leachate from the system, and sown with 2 g of ryegrass seed (*L. perenne* L. var. Cadix) in August 2008. Additionally identical triplicate pots of only green waste compost (green waste compost reference; GWCR) were included as a control. The ryegrass was grown in a temperature-controlled greenhouse 18 °C, watered daily with distilled water (approximately 150–200 ml, as required) and subsequently harvested at 3 successive intervals (Oct, Nov and Dec 2008). Ryegrass biomass was harvested by cutting 1 cm above the soil surface in each pot. Shoots were washed in deionised water, gently blotted with tissue, weighed and then oven-dried at 45 °C for 24 h. Oven-dried samples were re-weighed, then ground in a Cyclotec 1093 electric mill. Aliquots of the ground material were weighed (0.2 g) into digestion vessels, 10 ml of 14 M Analar grade HNO₃ was added, and samples were extracted using microwave digestion (as previously described). Plant digests were analysed for metal concentration by ICP-MS (XSERIES 2 ICP-MS, Thermo Scientific, MA, USA).

Four weeks after ryegrass had germinated one 'Rhizon' soil pore water sampler (Eijkkelkamp Agrisearch Equipment, The Netherlands) was inserted into the soil in each replicate pot through a pre-drilled hole in the pots at an angle of approximately 45°, and the holes were sealed with silicone to prevent water leakage (Fig. 1). Vacuum tubes (13 ml) were attached via a luer-lock system and hypodermic needles to extract pore water when required. The Rhizon samplers were initially left in the soil for 4 weeks to equilibrate, and then sampled every 4 weeks resulting in 3 successive sampling collections. Unlike the extraction used for WSC and WSN, rhizon samplers are a passive, non-destructive sampling technique. Pore water samples were analysed for pH (using the equipment described above), dissolved organic carbon (DOC) and dissolved total nitrogen (DTN) by a TOC-VE Shimadzu analyser (Shimadzu, Tokyo, Japan), and for metal concentrations by ICP-MS. For plant samples and pore water, ICP-MS was preferred to AAS, because of its lower detection limits. All of the above analyses were carried out in triplicate.

2.4. Data and statistical analysis

Assessment of soil–plant metal transfer was based on the ratio of Pb and Cu concentration in ryegrass shoots to the Pb and Cu pseudo-total concentration in the substrate (transfer co-efficient) and to the Pb and Cu concentration in the pore water (bioconcentration factor). A one-way ANOVA followed by a Tukey's test was performed to analyse significant differences between means in each month/harvest for Pb, Cu, DOC, DTN and pH in pore water (PW), and Pb and Cu concentration and harvestable amount in plants. Linear regression analysis (backward method) was used between metal concentrations in pore water and other parameters in pore water (pH, DOC, DTN) and soil (OM, available phosphorous, pseudo-total metal concentrations). All statistical analyses were carried out using SPSS v.14.



Fig. 1. Experimental set-up showing rhizon samplers collecting pore water and differences in ryegrass growth between soil and treatments 7 weeks after germination, from left to right; green waste compost reference, untreated soil, soil plus green waste compost, soil plus biochar, soil plus green waste compost and biochar. Note that only one of the triplicates of each treatment is shown.

3. Results

3.1. Effects of amendments on soil characteristics

Untreated soil used in this study had high levels of Cu ($\sim 600 \text{ mg kg}^{-1}$) and very high Pb levels (equivalent to $\sim 2\%$; Table 1). Compost amended soil showed significantly higher pH values compared to the untreated soil ($p < 0.05$; Table 1) whilst biochar had no great effect on this parameter. The greatest increases in alkalinity were observed for the combined compost and biochar treatment. Similarly organic matter content, WSC, WSN and available P increased furthest with combined application of amendments, although singly compost amendment also increased available P whereas biochar reduced this parameter considerably (Table 1). Combined application of compost and biochar also reduced soil pseudo-total Pb and Cu furthest (for Cu, $p < 0.05$) but it must be noted that these changes could be attributed, in part to the dilution of the original contaminated substrate by the organic amendments applied.

3.2. Pore water pH, DOC, DTN and metal concentrations

The pH of the pore water varied across treatments and collections, apart from in the untreated soil (Fig. 2 inset) and increased furthest during the last collection for all treatments by nearly 2 units compared to untreated soil. This represented an increasing alkalinity with time ($p < 0.05$). The DOC concentrations in the soil pore water, in common with pH, showed variation between collection periods, but with a consistent trend to decrease in the last collection (Fig. 2A). A similar effect occurred for DTN, although occurring in greatest magnitude between the first and second collections of pore water (Fig. 2B). In soil treated with compost and biochar combined, and compost singly, DOC was significantly higher ($p < 0.05$) than in untreated soil (Fig. 2A). Biochar applied singly did not result in significantly greater DOC concentrations when compared to the untreated soil.

Mean copper concentrations in the soil pore water were substantially reduced by the incorporation of all of the amendments, compared to untreated soil, but furthest by biochar (from

$\sim 1.2 \text{ mg l}^{-1}$ to $< 0.3 \text{ mg l}^{-1}$; Fig. 2C). The hierarchy in the effectiveness of the amendments for reducing Cu in pore water, compared to the untreated soil, was as follows; compost singly (57% reduction; $p < 0.001$) < compost and biochar combined (63% reduction; $p < 0.001$) < biochar singly (69% reduction; $p < 0.001$). Lead concentrations in the soil pore water were far greater than those of Cu ($> 80 \text{ mg l}^{-1}$ in untreated soil; Fig. 2D), reflecting the far greater pseudo-total (Table 1). The compost and biochar combined treatment and compost singly applied resulted in comparable reductions of lead in pore water compared to the untreated soil, of 96 and 97%, respectively. Biochar alone was not as effective for this metal, especially in the first sampling, but nonetheless significantly reduced pore water concentrations of Pb (Fig. 2D).

3.3. Plant biomass and uptake of metals

Ryegrass grown in the untreated soil displayed some chlorosis and low biomass production (Fig. 1 and Fig. 3 inset) which are common symptoms of copper and lead phytotoxicity [24–26]. Notwithstanding total biomass across the three harvests, which was greatest for the combined treatment, all of the amendments increased biomass furthest in the first harvest, after which there was a decrease, relative to the untreated soil in successive harvests (Fig. 3 inset).

Copper concentrations in ryegrass shoots of untreated soil were around 30 mg kg^{-1} in the first two harvests, but increased in the last harvest (Fig. 3A; $p < 0.05$). Lead concentrations in shoots were far greater than those of Cu, and increased from $< 500 \text{ mg kg}^{-1}$ to $> 1500 \text{ mg kg}^{-1}$ from harvest 1 to 3 (Fig. 3B). The incorporation of compost significantly reduced transfer of Pb from soil to plant in all harvests (Fig. 3B; $p < 0.05$), with attendant reductions in the concentration in ryegrass shoots, but had less effect on Cu. Ryegrass grown in the biochar amended soil showed the smallest reduction of Pb uptake, relative to untreated soil, compared to the other treatments but the greatest initial reduction in Cu compared to untreated soil. In harvests 2 and 3, whereas Cu uptake increased in biochar amended soils, it decreased in soils with combined amendment application (Fig. 3A), relative to the first harvest.

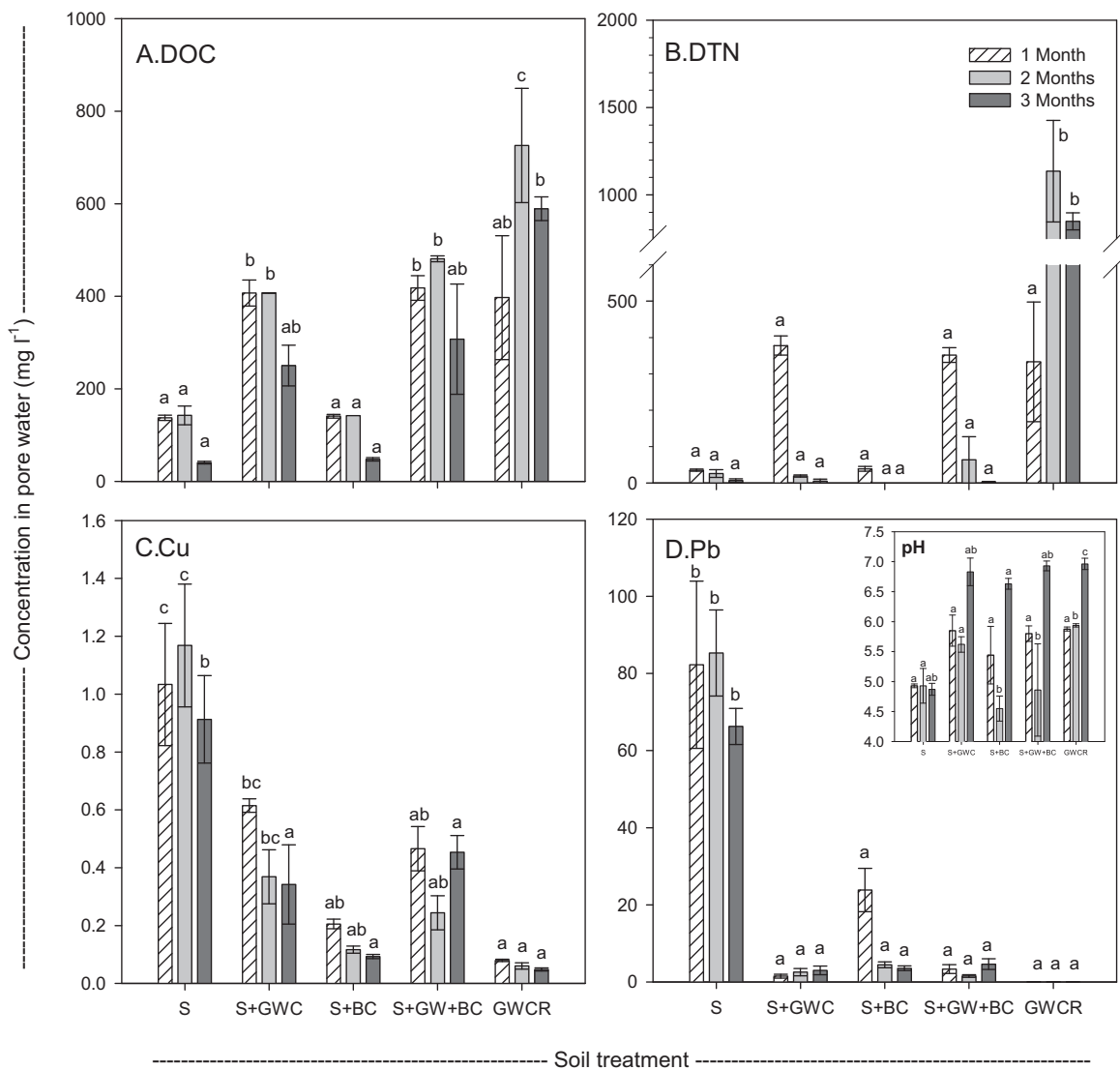


Fig. 2. Concentration of DOC (A), DTN (B), Cu (C) and Pb (D) in pore water for each soil treatment and (inset) pH of pore water (S = untreated soil, S + GWC = soil plus green waste compost, S + BC = soil plus biochar, S + GWC + BC = soil plus green waste compost and biochar combined, and GWCR = green waste compost reference) in successive collections. Different letters indicate significant differences between treatments in the same month ($p < 0.05$).

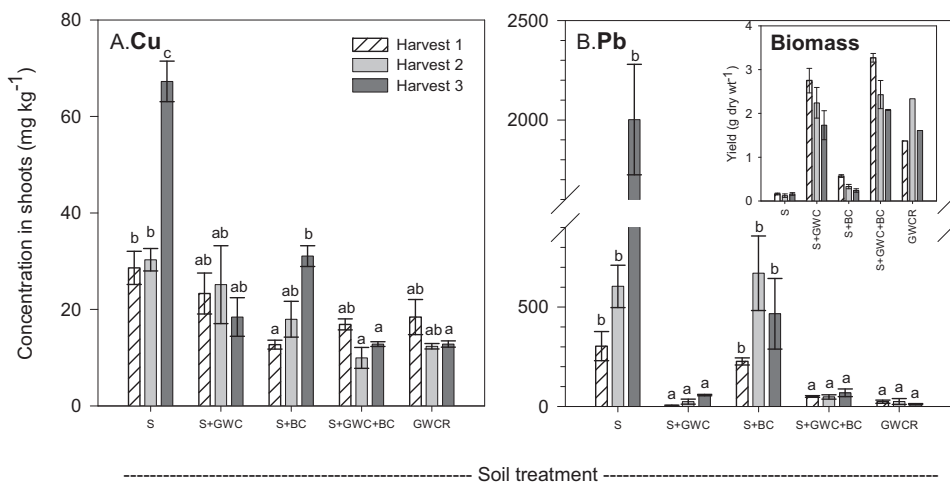


Fig. 3. Concentrations of Cu (A) and Pb (B) in ryegrass shoots and biomass yield (inset) (S = untreated soil, S + GWC = soil plus green waste compost, S + BC = soil plus biochar, S + GWC + BC = soil plus green waste compost and biochar combined, and GWCR = green waste compost reference). Different letters indicate significant differences between treatments in the same harvest ($p < 0.05$).

Table 1

Physico-chemical characteristics of soil, green waste compost and amended soils (Soil = untreated soil, S + GWC = soil plus green waste compost, S + BC = soil plus biochar, S + GWC + BC = soil plus green waste compost and biochar combined, and GWCR = green waste compost reference) ($n = 3$, \pm SE).

| Treatment | Soil | S + GWC | S + BC | S + GWC + BC | GWCR | ANOVA |
|---|-----------------|----------------|----------------|----------------|--------------------------|-------|
| pH | 5.4 (0.03) a | 6.7 (0.01) b | 5.6 (0.0) a | 6.9 (0.01) c | 8.1 (0.02) c | *** |
| Organic matter (LOI %) | 4.3 (0.2) a | 6.6 (0.4) a | 5.2 (0.1) a | 14 (1.5) b | 23 (0.5) c ^a | *** |
| WSC (mg kg ⁻¹) | 1220 (120) a | 5270 (220) b | 1690 (1) a | 11,280 (10) c | 24,520 (880) d | ** |
| WSN (mg kg ⁻¹) | 20 (3) a | 990 (57) b | 59 (6) a | 2080 (100) c | 10,670 (320) d | *** |
| P _{available} (mg kg ⁻¹) | 108 (15) a | 156 (14) ab | 35 (15) a | 278 (52) b | 1473 (271) c | ** |
| Pb (mg kg ⁻¹) | 20,703 (2501) b | 16,142 (322) b | 17,607 (979) b | 14,821 (333) b | 142 (0.9) a ^a | ** |
| Cu (mg kg ⁻¹) | 603 (23) d | 451 (23) c | 453 (11) c | 333 (21) b | 62 (1.3) a ^a | *** |

Different letters indicate statistical differences between treatments (evaluated by Tukey's test) where *, ** and *** indicate significance at $p < 0.05$, 0.01 and 0.001, respectively.

^a Data from Beesley and Dickinson [22].

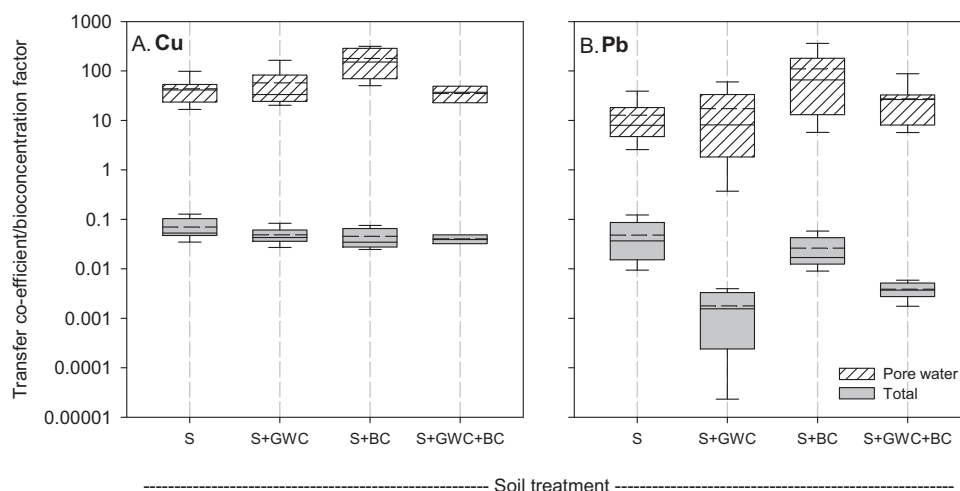


Fig. 4. Transfer of Cu (A) and Pb (B) to ryegrass according to total (shoot concentration/pseudo-total concentration; transfer co-efficient) pore water (shoot concentration/pore water concentration; bioconcentration factor) (S = untreated soil, S + GWC = soil plus green waste compost, S + BC = soil plus biochar and S + GWC + BC = soil plus green waste compost and biochar combined). Note that the compost reference (GWCR) is not included here. Dashed line is the mean value, solid line is median, box is the upper and lower quartile and whiskers are the 10th and 90th percentiles ($n = 9$).

Transfer coefficients numerically depict the efficiency at which plants take up metals from the soil. When concentrations in labile forms (e.g., pore water) instead of total soil concentrations are used to calculate the transfer coefficient it can be referred to as bioconcentration factor [27]. Amendments generally increased the mean bioconcentration factor of Cu but decreased transfer coefficient compared to the untreated soil (Fig. 4A). For lead, green waste compost and green waste compost and biochar combined treatments reduced transfer coefficients sharply compared to untreated soil but increased mean bioconcentration factors (Fig. 4B). In general the range of values for Pb was far wider than for Cu (Fig. 4). Biochar raised bioconcentration factors of both Cu and Pb from pore water furthest of all treatments but its effects on transfer coefficients were more muted (Fig. 4).

When biomass differences were considered, and metal uptake was represented on a per pot basis (here referred to as harvestable amount of metal), green waste compost alone produced the lowest harvestable amount of Pb, but the highest harvestable amount of Cu compared to untreated soil ($p < 0.05$, Fig. 5A and B). Whilst Cu concentrations were highest in ryegrass shoots in untreated soil (Fig. 3A) the smallest harvestable amount was recorded in this case (Fig. 5A) as biomass was lowest in untreated soil (Fig. 3 inset). Similarly, combining compost and biochar significantly reduced both Cu and Pb concentrations in shoots, compared to untreated soil ($p < 0.05$; Fig. 3A and B) but did not significantly reduce Pb per pot (Fig. 5B; $p < 0.05$), compared to untreated soil.

4. Discussion

4.1. Effects of amendments on pore water characteristics

Solubility of Pb in soils is usually very restricted [28]. However, remarkably high levels of Pb in pore water were found in the present work ($>80 \text{ mg l}^{-1}$) compared to the previously published results of many Pb-contaminated soil studies [29–31]. Such an elevated concentration of Pb in soil solution can be only explained according to the extremely high pseudo-total concentrations found in this soil together with its particular properties (e.g., acidic pH and lack of a well-developed structure). Free ion activity, commonly used in toxicology studies and solubility calculations, for Pb ($p[\text{Pb}^{2+}]$) in untreated soil in the present work would be close to 3 (assuming most of the Pb in pore water is present as free Pb^{2+}). This is almost an order of magnitude higher than data compiled previously at pH 3 [29] and 2–3 orders of magnitude higher than in soils with the same pH as those found in the current work. However, when the organic amendments were added to the soil, this activity fell to $p[\text{Pb}_{\text{Soil}}]$ around 4–7. Levels of Cu in pore water were not as unusually high as those of Pb in untreated soil [29,31], with activities ($p[\text{Cu}_{\text{Soil}}]$) around 5–6. Both copper and lead have a high affinity for organic matter [8,14,32] whilst their stability in soils generally decreases with increasing acidity [12,33]. Compost and combined compost and biochar amendments would have assisted reductions in metal concentrations in the present study due to both increases in soil organic matter content (Table 1) and increases in soil and

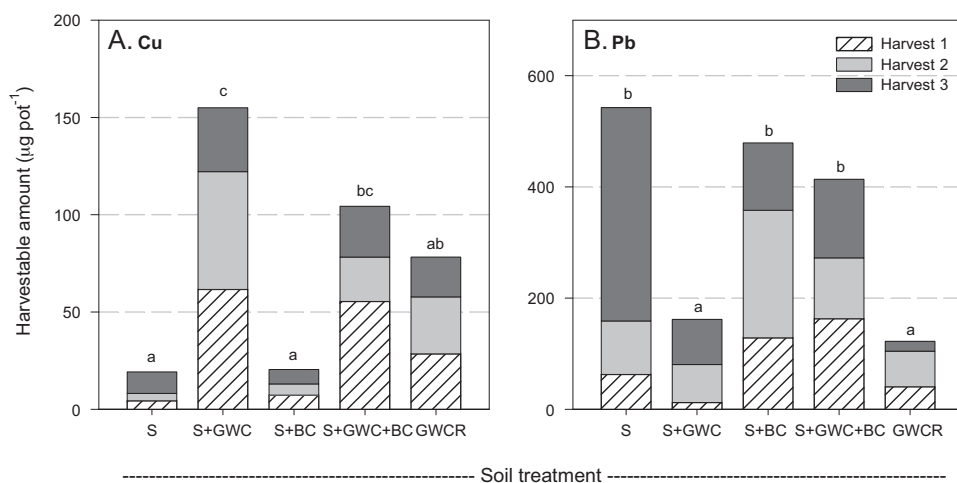


Fig. 5. Harvestable amounts of Cu (A) and Pb (B) in ryegrass (S=untreated soil, S+GWC=soil plus green waste compost, S+BC=soil plus biochar, S+GWC+BC=soil plus green waste compost and biochar combined, and GWCR=green waste compost reference). Different letters indicate significant differences in total harvestable metal amounts between treatments ($p < 0.05$).

Table 2
Linear regression equations between trace element concentrations in pore water (pw) and other parameters in pore water (pH, DOC, DTN) and soil (OM, available P [P]_{Av}, pseudo-total metal concentrations [Cu/Pb]_{Tot}) (data from all pore water samples except those from green waste compost reference; $n = 48$).

| Equations | R^2_{adj} | Sig | F-value |
|--|-------------|--------|---------|
| $[Cu]_{pw} = 0.291 - 0.077 \cdot OM + 0.003 \cdot [P]_{Av} + 0.001 \cdot [Cu]_{Tot}$ | 0.47 | <0.001 | 12.9 |
| $[Pb]_{pw} = 125 - 15.1 \cdot pH - 0.060 \cdot DOC$ | 0.40 | <0.001 | 14.5 |

pore water pH (for pore water >2 units; Fig. 2 inset). However adding amendments increased DOC concentrations in pore water significantly above the untreated soil (Fig. 2A); several studies have attributed increased metal solubility, mobility and bioavailability in soils treated with organic amendments to the formation of soluble organo-metallic complexes with DOC [22,32,34]. In the present study large amounts of DOC (Fig. 2A) but very low levels of Cu and Pb (Fig. 2C and D) were released from the green waste compost reference during the experiment, in common with previous work [22], which rules out the direct contribution of this material to the pool of these soluble metals, and supports the validity of the effects of the amendments at reducing the huge pore water Pb levels. Biochar reduced Cu in pore water to a greater extent than the green waste compost whereas the opposite was true for Pb, but concentrations were still appreciably lower than the untreated soil (Fig. 2D). Phosphate rich compounds applied to Pb contaminated soils can form pyromorphite and effectively limit Pb availability [14]. Some composts are known to be rich in P and Fe [14,32] whilst XRF analysis of biochar has found its P and Fe concentrations approximately twice the concentrations of those of green waste compost analysed by the same method [35]. The large reductions in Pb solubility in the present soils, compared to Cu, may therefore be related to humified complexes and high concentrations of P in compost or biochar.

Laird et al. [36] added biochar to swine manure in a column leaching test to examine nutrient retention effects, finding that biochar reduced total N and dissolved P by 11 and 69%, respectively. Given that biochar has also been shown to adsorb DOC [37] it could be the case that both DOC and P dynamics controlled Cu and Pb mobility, respectively in biochar amended soil. Given the labile supply of DOC, N and P from compost but their possible retention by biochar, it would be expected that combining amendments would reduce DOC, N and P supply from compost as it was immobilised by biochar. However, it could be the case that priming effects, where fresh additions of organic matter stimulate the degradation of older and more recalcitrant fractions [38] could have occurred as the

amendments were mixed, explaining higher concentrations of DOC than when applied singly (Fig. 2A).

Linear regression equations calculated from pore water concentrations of Cu and Pb and other soil and pore water parameters (Table 2) confirmed the dependence of Cu solubility primarily on soil OM content and that of Pb primarily on pore water pH and to a lesser extent on DOC.

4.2. Uptake and transfer of metals to ryegrass

Transfer coefficients and bioconcentration factors describe the proportion of the metal in soil (pseudo-total concentration), or in soil solution (pore water concentration), respectively, that is taken up into the plant (shoot concentration), allowing an ecological evaluation of potential risk to be made. Thus very low coefficients and/or factors indicate low plant uptake and/or high soil/pore water concentrations, equivalent to low risk to primary consumers. High values of these ratios therefore indicate greater uptake compared to lower soil/pore water concentrations, indicating an increased risk. In the case of the relationship between total Pb and shoot concentrations it is clear to see that the reduced shoot Pb levels (Fig. 3B) against the very high soil Pb levels resulted in stark lowering of transfer coefficients when soil was amended compared to the untreated soil (Fig. 4B). The same is true to explain the small reductions in Cu transfer coefficients (Fig. 4A).

In phytostabilisation terms, good plant development but minimal roots to shoot translocation of pollutants indicate the most suitable candidates [33,39,40] and good plant development is synonymous with increased biomass. In our study, compost-based (both itself or applied with biochar) treatments promoted plant growth and the biomass increased, indicating better conditions for plant establishment [7,33,41]. Poor biomass resulting from biochar amendment could be expected due to low levels of N (Table 1 and Fig. 2) and P (Table 1); deficiencies in N and P are often limiting factors in revegetation of former mine sites [42].

However, a trade-off exists because, on the basis of far reduced shoot concentrations of, especially Pb, compost based treatment would be adjudged as superior for safe revegetation with minimal risk to food chain transfer. This viewpoint is the classically accepted phytostabilisation approach where low concentration in shoots is supposed to equate to low risk for the food chain [1]. However greatly increased biomass associated with compost amendment out-weighted the reductions in concentrations in shoots, increasing harvestable Cu on a pot basis ($<25 \mu\text{g pot}^{-1}$ in untreated soil but $>150 \mu\text{g pot}^{-1}$ in compost amended soil; Fig. 5A). Similarly, for Pb, it appears from significant reductions in shoot concentrations (Fig. 3B; $p < 0.05$) that there would be massive reductions in potential transfer, but accounting for biomass increases, the combined compost and biochar treatment did not significantly reduce Pb uptake in harvestable terms compared to untreated soil (Fig. 5B; $p < 0.05$). Reductions of metal concentrations in edible plant tissues are of course desirable, but this should not be the only factor to consider during stabilisation. A complete evaluation of the risk requires integrating the total amount of metal in plant tissues and the total biomass available to primary consumers in one measure.

4.3. Viability of the amendments for contaminated land applications

Notwithstanding lower N and P capital, biochar has previously been demonstrated to successfully increase growth of ryegrass in common with green waste compost because it can reduce phytotoxic concentrations of Cd and Zn [21]. In this respect, in soils already possessing sufficient capability to sustain plant growth (i.e. available N, P and sufficient OM etc.) biochar could be useful in promoting additional growth by a reduction in the availability of certain trace elements. This is potentially valuable in the context of contaminated but nutrient rich soils, such as where sewage sludge has been applied. The combination of biochar with other amendments could be its most effective deployment even in nutrient poor soils; for example water soluble C and N and available P were significantly greater in the combined application than in the case of green waste compost applied singly (Table 1) supporting synergistic effects of the combination of materials. It can be envisaged, from the results of previous work that describe short term boosting of labile nutrients but large leaching losses after a relatively short time associated with amendments such as composts and manure, that biochar could provide a mechanism of regulation in its combination with such amendments. Further trials will help to determine this.

5. Conclusions

Enhancement of physico-chemical properties by adding composted green waste to this contaminated soil included reducing soil acidity, increasing soil OM, N and P, all of which facilitated the establishment and growth of perennial ryegrass. Biochar alone could not produce these effects, due to low N and P resulting in poor plant biomass. However, the combination of compost and biochar had a synergistic effect with a greater efficacy for reducing Pb concentrations in pore water and uptake to plants. Whilst superior in this aspect of remediation, the increased biomass of ryegrass associated with compost application and the enhanced nutrition it provided negated some of the large reductions in metals, on a harvestable basis, and may therefore increase the risk of food chain transfer. The balance between reductions in uptake and increases in biomass could be subtle but should be managed if transfer is to be avoided to higher trophic levels, whilst stabilising contaminated soils. The interaction between biochar and other organic

amendments in soil should now be the focus of further research if we are to maximise the potential benefits of both.

Acknowledgements

The authors thank Dr. William Hartley and Dr. Philip Riby (Liverpool John Moores University) for their contributions to experimental work and sample analysis.

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