



Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil

Luke Beesley^{a,*}, Eduardo Moreno-Jiménez^b, Jose L. Gomez-Eyles^c

^a Faculty of Science, Liverpool John Moores University, Liverpool L3 3AF, UK

^b Departamento de Química Agrícola, Universidad Autónoma de Madrid, 28049 Madrid, Spain

^c University of Reading, Department of Soil Science, Whiteknights, Reading RG6 6DW, UK

Biochar was more effective than greenwaste compost at reducing bioavailable fractions of phytotoxic Cd and Zn as well as the heavier, more toxicologically relevant PAHs.

ARTICLE INFO

Article history:

Received 21 December 2009

Received in revised form

2 February 2010

Accepted 7 February 2010

Keywords:

Biochar

Compost

Trace metals

PAHs

Pore water

ABSTRACT

Applying amendments to multi-element contaminated soils can have contradictory effects on the mobility, bioavailability and toxicity of specific elements, depending on the amendment. Trace elements and PAHs were monitored in a contaminated soil amended with biochar and greenwaste compost over 60 days field exposure, after which phytotoxicity was assessed by a simple bio-indicator test. Copper and As concentrations in soil pore water increased more than 30 fold after adding both amendments, associated with significant increases in dissolved organic carbon and pH, whereas Zn and Cd significantly decreased. Biochar was most effective, resulting in a 10 fold decrease of Cd in pore water and a resultant reduction in phytotoxicity. Concentrations of PAHs were also reduced by biochar, with greater than 50% decreases of the heavier, more toxicologically relevant PAHs. The results highlight the potential of biochar for contaminated land remediation.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Significantly elevated levels of inorganic and organic pollutants co-exist in soils from previously heavily industrialised areas. Soil characteristics as well as the individual geochemical associations of each element control whether these elevated concentrations are transferable to soluble, bioavailable and mobile fractions. Water-soluble fractions of trace metals and As in soils are the most ecologically relevant because they equate to those which are more readily mobile and bioavailable within the environment (Mench et al., 2009). Whilst the use of composted organic wastes as soil amendments, such as garden greenwaste, have been shown to have multiple benefits of improving vegetation establishment, reducing compaction, (Bernal et al., 2006), protecting against erosion (Craul, 1999; Whalen et al., 2003) and binding heavy metals (Song and Greenway, 2004), rapid mobilization and vertical transport of trace metals and As was also a consequence of adding this material to soil (Beesley and Dickinson, 2010).

Recent attention has been given to biochar as a soil amendment because of its potential soil conditioning properties and benefits to physico-chemical characteristics. Organic carbon contents of biochar have been reported to be as high as 90%, depending on the source material (Yin Chan and Xu, 2009), which encourages experimental application to soils to sequester C (Lehmann, 2007a, b). Further potential benefits of adding biochar to soil have also been reported; these include the adsorption of dissolved organic carbon (Pietikainen et al., 2000), increases in soil pH and key soil macro-elements, and reductions in trace metals in leachates (Novak et al., 2009). Unlike other soil amendments, biochar's longevity in soil reduces the possibility of heavy metal accumulation associated with repeated applications of other amendments (Lehmann and Joseph, 2009) such as sewage sludge.

Carbonaceous sorbents such as black carbon and activated carbon have been shown to have a very high affinity and capacity for sorbing organic compounds (Cornelissen and Gustafsson, 2005; Lohmann et al., 2005; Oen et al., 2006; Brandli et al., 2008). There are a number of studies that indicate that these materials can reduce the bioavailability of polycyclic aromatic hydrocarbons (PAHs) in soil and sediments (Cornelissen et al., 2006; Rhodes et al., 2008). Like other carbonaceous sorbents, biochar has a large surface area, several thousand fold greater than un-charred source

* Corresponding author. Tel.: +44 (0)151 231 2224.

E-mail address: L.Beesley@2007.ljmu.ac.uk (L. Beesley).

material (Thies and Rillig, 2009) and has also been shown to reduce the bioavailability of organic compounds (Yu et al., 2009).

In this study we investigate, by simple field pot trials and laboratory experiments, whether biochar is more effective than greenwaste compost at reducing mobile and potentially bioavailable fractions of trace metals and As and total and bioavailable fraction of PAHs in a multi-element contaminated soil.

2. Materials and methods

2.1. Study site

Soil was sourced from an embankment that separates two canals in Kidsgrove, Staffordshire, UK (Lat/Long: 53°05′23.0″N, 02°15′05.7″W). The history of the excess concentrations of trace metals in the soil is probably associated with an adjacent manufacturing industry during the 19th century. The former Kidsgrove gasworks, located near to the study site, is one possible source of the excess As concentrations found in the vicinity and potential above-background PAH levels, although these have not been previously investigated. It is thought that canal sediment was dredged and dumped onto the embankment without further treatment at an unknown period within the last century. The site has been previously studied with regards to the spontaneous vegetation found growing there. For example, *Salix caprea* has been found to selectively accumulate Cd in stems and leaves without apparent phytotoxic effects (Lepp and Madejón, 2007). High soil Fe content has been found to increase soluble Cd in this soil, in laboratory experiments (Hartley et al., 2004) which, along with Zn, leaches abundantly, vertically in the soil profile (Beesley et al., 2010). Arsenic concentrations are high but very limited transfer from soil to plant has been observed (Madejón and Lepp, 2007) because only a small fraction of the pseudo-total concentration of this metalloid was present in pore water (Beesley et al., 2010).

2.2. Experimental design and procedure

Soil was collected from 15 to 30 cm soil depth on the canal embankment, avoiding a narrow litter horizon above, and sampling an area not disturbed by previous soil sampling. Soil was air dried at 20–25 °C for 2 weeks, sieved to <2 mm and any biological debris was removed. Soil was then homogenized and thoroughly hand mixed with greenwaste compost (Whitemoss Horticulture, Merseyside, UK) and hardwood-derived biochar (Bodfari Charcoal, Denbigh, UK) in the following proportions, before being placed into 1000 mL PVC pots. Each treatment was carried out in triplicate.

- S: 600 mL of soil per pot.
- S + C: 400 mL of soil and 200 mL of compost per pot.
- S + B: 400 mL of soil and 200 mL of biochar per pot.
- S + C + B: 200 mL of soil, 200 mL of compost and 200 mL of biochar per pot.

Mixing was carried out on a volume basis to account for the various densities of the soil and amendments (1.8 g ml⁻¹ for soil, 0.45 g ml⁻¹ for compost and 0.3 g ml⁻¹ for biochar).

Pots were equilibrated by saturating the soils with de-ionised water (pH 5.5) for 3 days in the laboratory, after which natural drainage was allowed. One rhizon sampler (Eijkkelkamp Agri-search Equipment, Netherlands) was inserted into each pot to collect pore water. The pots were then placed outdoors under environmental conditions at the university campus field location in Liverpool, for 60 days. Pore water was collected during the 60 days field exposure, at 7, 14, 28 and 56 day intervals by connecting removable 13 mL vacuum tubes to the rhizon samplers. At the last sampling (after 56 days) some of the replicates failed to extract any pore water, but at least one sampler from each triplicate had worked. Rainfall and soil temperature data were obtained from Met Office Weather station number 7326 (Ness Botanical Gardens, Wirral, Lat 53°20′N, Long 3°5′W) which is 12 km south-west of the field location. Daily mean values were calculated for the days preceding sample collection. After the 60 day field exposure and pore water collection, the material in the pots was collected and air dried as previously described, prior to being analysed for pseudo-total trace metals and arsenic, PAHs and phytotoxicity, assessed by a bio-indicator test.

2.3. Analytical procedures for soil characterisation

After soil and treatments had been initially mixed and equilibrated, but prior to field exposure, soil characteristics were determined. Soil pH was measured in a 1:2.5 suspension of soil in de-ionised water. Total organic carbon (TOC) was determined using an SSM-5000A/TOC-VE analyser (Shimadzu, Tokyo). Water extracts were then prepared using 1:10 suspensions, shaken for 3 h, centrifuged for 10 min at 3000 rpm and screened using a fine nylon mesh to remove any suspended particulate material which could interfere with analysis. These extracts were analysed for water-soluble total carbon (WSC) and water-soluble total nitrogen (WSN) using a TOC-VE water analyser (Shimadzu, Tokyo) and water-extractable trace metals and As by ICP-MS

(XSERIES 2 ICP-MS; Thermo Scientific, MA, USA). Pseudo-total trace metals and As determination was by microwave digestion of 0.2 g soil samples in concentrated 14 M, GPR grade HNO₃, also analysed using ICP-MS. Certified reference material (CMI 7004) was used to verify accuracy, with recoveries consistently greater than 75%. Further details of the geochemical fractionation of Cd, Zn and As in this soil can be found in Beesley et al. (2010).

Dissolved organic carbon (DOC) and dissolved total nitrogen (DTN) in pore water were determined using the same equipment as previously detailed for WSC and WSN. Trace metals and As concentrations in pore water were measured by ICP-MS as above. A rhodium standard (1 ppm) was added to each sample to verify and optimise instrument efficiency during analysis.

2.4. Analysis of total and bioavailable PAHs

Total concentrations of PAHs were determined by agitating three replicate 5 g samples of each soil after 60 days field exposure, in 10 mL of 1:1 (vol:vol) acetone/hexane mixture for 2 h on an orbital shaker at 200 rpm. After extraction the samples were left to settle for 30 min, after which 2 mL of solution was placed in a test tube containing 0.1 g of dry sodium sulphate before transferring to gas chromatography (GC) vials for GC-MS analysis (Gomez-Eyles et al., 2010). This method was adapted from a mechanical shaking method previously reported to give better recoveries than a Soxhlet extraction (Song et al., 2002).

The bioavailable fraction was determined by cyclodextrin extractions (Stokes et al., 2005). Triplicate, 1.5 g samples of each soil after 60 days field exposure were mixed with a 25 mL solution of 60-mM HPCD (Sigma Aldrich, Poole, UK) in de-ionised water and agitated for 20 h in an orbital shaker. The mixture was then centrifuged at 2500 rpm for 30 min and the supernatant discarded. The resulting soil pellet was shaken with 25 mL of de-ionised water for 10 s, centrifuged again and the supernatant again discarded to remove any remaining HPCD solution. The soil pellet was then exhaustively extracted using the acetone/hexane mechanical shaking extraction described above and GC-MS analysis of this exhaustive extraction measured the PAHs remaining in the soil after HPCD extraction. GC-MS analysis was performed using a Thermo Trace GC Ultra system equipped with a Thermo TR-5MS capillary column (dimensions: 30 m × 250 μm × 0.25 μm; Thermo Scientific, Runcorn, UK) operating with helium as a carrier gas, coupled to a Thermo ITQ 1100 mass spectrometer (MS) through a heated transfer line (300 °C). The GC injector (220 °C) was operated in a pulsed splitless mode, 1 μl aliquots were injected using an autosampler, and the GC oven was programmed to hold 60 °C for 3 min then raise the temperature by 15 °C/min to 290 °C, which was held for 10 min. The MS was operated with the ion source at 220 °C and a damping flow of 0.3 ml min⁻¹.

2.5. Phytotoxicity bio-indicator test

A shoot emergence test, using *Lolium perenne* L. var Cadix was performed as a bio-indicator of phytotoxicity. Plant seed germination is sensitive to both available inorganic (Munzuroglu and Geckil, 2002) and organic pollutants (Henner et al., 1999), but, given that toxicity of inorganics is usually linked to soluble fractions but organics are poorly water-soluble, the shoot emergence test was performed directly in the soil rather than using soil extracts. Triplicate petri dishes were filled with 30 g of soil collected after 60 days field exposure and watered to saturation. After 6 h, 20 seeds were placed over the soil surface. Petri dishes were incubated for 96 h under darkness at 28 °C and 60% relative humidity in environmental chambers (Conviron, USA). Successfully emerged plants (those with shoots longer than 1 cm) were counted and the emergence success was calculated as a percentage of the 20 seeds applied to the surface of each soil.

2.6. Statistical analyses

Differences between soil treatments were analysed by ANOVA using Tukey's test for means comparison ($p < 0.05$) and linear regressions were performed using concentrations of water-soluble trace elements, pH, DOC, DTN, trace elements in pore water and pseudo-total trace element concentrations in soils. All statistical analysis was carried out using SPSS v.14.

3. Results

3.1. Properties of soil and amendments

Soil pH was mildly acidic, but each amendment reduced acidity significantly (Table 1). Combining compost and biochar resulted in the greatest pH increase (to ~ pH 8). Similarly TOC and WSC (Table 1) significantly increased with the application of both of the amendments, as did DOC in pore water (data not shown). Water-soluble nitrogen (WSN) and concentrations of DTN in pore water were also elevated above those in the control soil by adding compost, but biochar had no effect on these parameters (data not shown).

Table 1
Physico-chemical characteristics and water-extractable trace metals and As in soils prior to 60 days field exposure (Different letters equal significant differences between treatments; $p < 0.05^*$, $<0.01^{**}$, $<0.001^{***}$, ns = not significant).

	S ^a	S + C	S + B	S + C + B	ANOVA
pH	5.45 a	6.19 b	7.56 c	7.88 d	***
TOC (%)	4.60 a	6.80 b	8.10 c	12 d	***
WSC (mg kg ⁻¹)	49 a	66 b	89 c	129 d	***
Water-extractable and pseudo-total ^b (in parentheses) (mg kg ⁻¹)					
As	0.01 a (96 c)	0.13 b (75 ab)	0.41 d (85 bc)	0.26 c (63 a)	*** (*)
Cd	1.10 b (119 b)	0.37 a (77 a)	0.38 a (123 b)	0.26 a (73 a)	*** (**)
Cu	0.01 a (58 b)	0.13 ab (46 a)	0.27 b (60 b)	0.34 b (47 a)	*** (*)
Pb	0.01 a (157 a)	0.14 b (140 a)	0.03 a (143 a)	0.03 a (136 a)	** (ns)
Zn	1.49 b (249 b)	0.73 a (205 a)	1.32 b (258 b)	0.83 a (202 a)	** (*)

^a Soil texture was 8.4% clay, 48% silt, 43% sand (after Beesley et al., 2010).

^b Note that trace metal and As pseudo-total concentrations (in parentheses) were measured after 60 days field exposure.

All of the water-extractable trace metal and As concentrations were significantly affected by the amendments (Table 1). Water-extraction yielded far lower concentrations of each element in soil compared to the pseudo-total (Table 1), with Cd being the most soluble (~1% of pseudo-total) and Zn the second most soluble (~0.5% of the pseudo-total). All amendments reduced water-extractable Cd significantly, but enhanced water-extractable As and Cu. There were mixed effects on both water-extractable Zn and Pb (Table 1), compost reducing the former but enhancing the latter. Pseudo-total Pb concentrations measured after field exposure were not significantly affected by soil amendments. The other elements' pseudo-total concentrations were variously affected, Cd to the greatest extent after compost application (Table 1). Biochar and compost amendments themselves contained far lower levels of both organic and inorganic contaminants than soil; for organics this was close to or below the limit of detection and for heavy metals and As, far below current statutory guidelines for residential soils (DEFRA, 2002).

During field exposure of the soils, rainfall was very low and soil temperature was high in the days preceding all of the pore water

collections and therefore net throughflow of water in the pots was probably low (mean rainfall was less than 2 mm and soil temperature was 11.3–13.3 °C for each sampling time).

3.2. Trace metals and As in pore water

Cadmium and Zn concentrations were the highest of all trace elements measured in the pore water from untreated soil (Fig. 1, $p < 0.05$), in common with their water-extractable concentrations (Table 1). In contrast both As and Cu concentrations in pore water were consistently very low ($<20 \mu\text{g l}^{-1}$; Fig. 1). Lead was increased by the addition of compost, and to a lesser extent, biochar ($p < 0.05$; data not shown). Cadmium concentrations were reduced significantly by both compost and biochar during the 56 days, with biochar having the greatest effect (Fig. 1). In contrast, concentrations of Zn fluctuated, with an increase after 28 days where biochar was added, despite the initially large decrease associated with this amendment; the same effect was not seen with compost. Changes in As concentration were not time dependant as for the trace

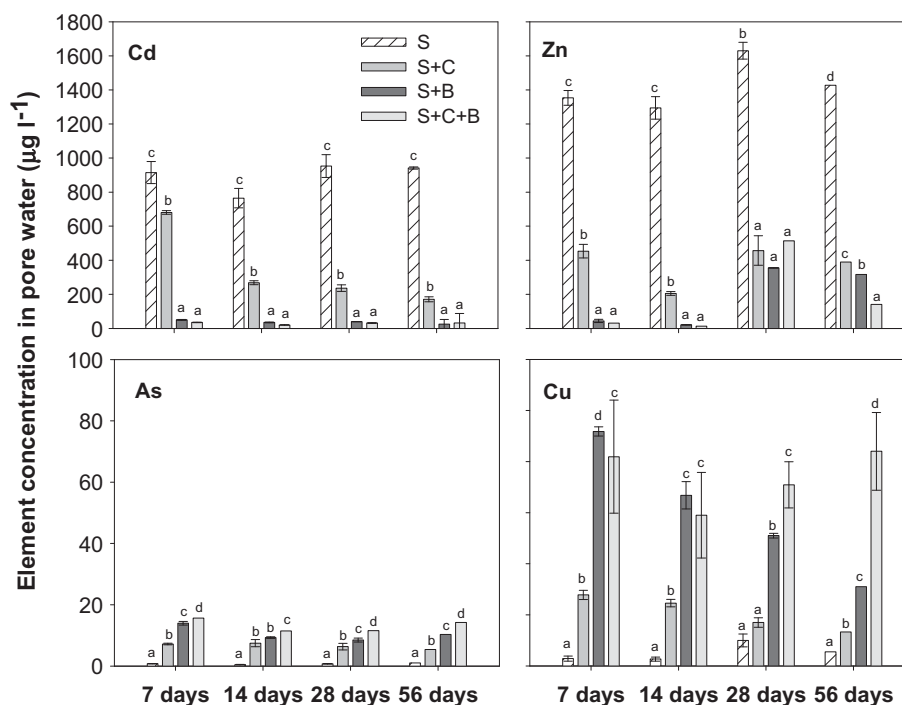


Fig. 1. Concentrations of selected trace metals and As in soil pore water from soil (S), soil with compost (S + C), soil with biochar (S + B) and soil with compost and biochar (S + C + B), during 60 days field exposure ($n = 3$; error bars represent standard error). Different letters indicate significant differences in concentration between treatments within each sampling period ($p < 0.05$).

metals, but each amendment increased concentrations above that of the untreated soil. Copper concentrations responded to a greater extent to the amendments; biochar initially increased Cu in pore water, which subsequently consistently decreased over the 56 days, although concentrations were still significantly greater than the control soil ($p < 0.05$; Fig. 1).

3.3. Total and bioavailable PAH concentrations

Following 60 days field exposure of soils, biochar treatment was most effective at reducing the concentrations of both total and bioavailable PAH groups; more than 50% relative to the untreated soil for the heavier 4- and 5-ringed PAHs and over 40% for the lighter 2- and 3-ringed PAHs (Fig. 2). Differences relative to the untreated soil were only statistically significant for the total and bioavailable fractions of the 2-ringed PAHs and the total concentration of the 5-ringed PAHs ($p < 0.05$). Total PAH concentrations for all groups were reduced in the biochar treated soil significantly more than both those in the compost and combined biochar with compost treatments, with the exception of the 5-ringed PAHs in the combined treatment ($p < 0.05$). The bioavailable PAH concentrations responded similarly but only the 2- and 3-ringed PAHs were significantly reduced after 60 days ($p < 0.05$). The compost treatment reduced both the total and bioavailable PAH concentrations by over 25% and was also generally more effective than the combined biochar with compost treatment (Fig. 2). However, the total and bioavailable PAH concentrations were only significantly smaller relative to the untreated soil for the 2- and 3-ringed PAHs ($p < 0.05$).

3.4. Phytotoxicity assessment

Compost, biochar or the combined application of these amendments significantly ($p < 0.05$) increased shoot emergence from 61% in the untreated soil to 75–78% in the amendment treated soil (Table 3). Individual application of amendments, rather than their combination, was slightly more effective at increasing shoot length, although the difference was not significant.

4. Discussion

4.1. Influence of amendments on heavy metals and As in pore water

Increased Cu concentrations in pore water (Fig. 1) were associated with elevated concentrations of soluble carbon from compost and biochar (Table 1), with both DOC and pH influencing concentrations of this metal significantly (Table 2). Applying the amendments individually or in combination resulted in initially high Cu concentrations, but these reduced with time, reflecting the same

trend in dissolved organic carbon (DOC), which also reduced in pore water over time (data not shown). Associations between Cu and DOC were previously found by Bernal et al. (2009). Increases in As in pore water (Fig. 1) were associated with the increase in pH, especially where biochar and compost were applied in combination (Table 1); increased As solubility with more alkaline pH at soil pH > 7 has previously been reported (O'Neill, 1990; Fitz and Wenzel, 2002). In the present study, arsenic concentration in pore water was found to be both a function of pH and DOC (Table 2), although the latter was probably less influential because, unlike Cu, As concentrations did not consistently reduce with time (Fig. 1). A further influence on As mobility in the presence of soil amendments could have been soluble phosphorous; P levels are generally elevated in compost (for example, Curtis and Claassen, 2009).

The contrasting effect of the amendments on Cd and Zn, compared to As and Cu, was related to the former being present abundantly as water-soluble fractions and the latter in more stable complexes in this soil (Beesley et al., 2010). In a previous study by Clemente and Bernal (2006), Zn was immobilized in an acid soil, by humic acids isolated from organic materials, whilst Cu mobility was enhanced by the same humic acids. Zinc and Cd are generally relatively insoluble at pH > 7 (Ross, 1994), so increases in pH with the application of the amendments in the present study (Table 1) would have reduced the solubility of these metals. Additionally, concentrations of Cd and Zn in pore water from environmentally exposed greenwaste compost are generally low ($< 1 \mu\text{g l}^{-1}$ and $< 200 \mu\text{g l}^{-1}$ respectively), whilst concentrations of Cu and As are greater ($180 \mu\text{g l}^{-1}$ and $300 \mu\text{g l}^{-1}$ respectively; Beesley and Dickinson, 2010). Therefore it is possible that at least part of the increase in Cu and As in pore water (Fig. 1) could be attributed to the direct contribution of the amendments. In comparison to greenwaste compost, biochar was previously found to have lower Zn but higher Cu concentrations (determined by XRF analysis; Hartley et al., 2009), which explains why Cu concentrations in pore water were increased furthest after 7 days where biochar was added to soil in the present study (Fig. 1). Hartley et al. (2009) also found that biochar did not significantly increase plant biomass yield. In the present study, shoot emergence (indicating phytotoxicity) was significantly increased equally by biochar and greenwaste compost treatment (Table 3). This was not related to changes in soluble nitrogen in soil, because only compost increased WSN and DTN above untreated soil, so it was probably predominantly due to the fact that both biochar and compost reduced water-soluble phytotoxic element concentrations sufficiently to promote successful germination.

After 60 days field exposure, pseudo-total trace metal and As concentrations were found to be significantly lower where compost

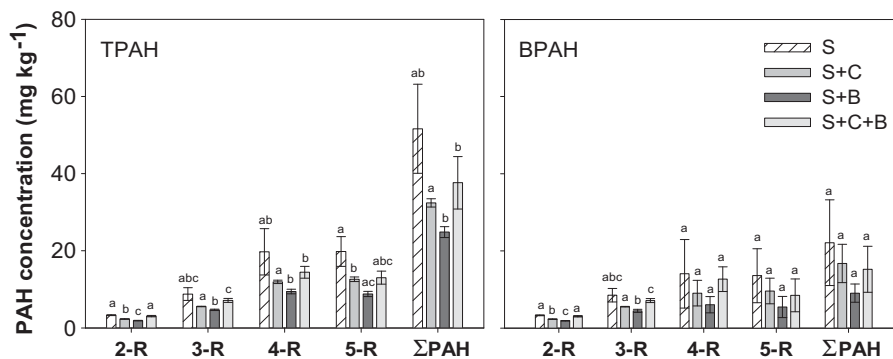


Fig. 2. Total (TPAH) and bioavailable (BPAH) concentrations of 2-ringed (2-R), 3-ringed (3-R), 4-ringed (4-R), 5-ringed (5-R) PAHs and the sum of all PAHs (Σ PAH) in soil (S), soil with compost (S + C), soil with biochar (S + B) and soil with compost and biochar (S + C + B) after 60 days field exposure ($n = 3$; error bars represent standard error). Different letters indicate significant differences in concentration between treatments within each PAH group ($p < 0.05$).

Table 2

Linear regressions between trace element concentration and other parameters (pH, DOC, and DTN) in pore water (pw), water-extractable trace element concentrations (sol) and pseudo-total trace element concentrations (tot) ($n = 36$). Parameters were ordered by significance in the model according to the independent parameter. Those parameters with least significance ($p > 0.1$) were removed from the linear model.

Model	<i>r</i>	sig	<i>F</i> -value
$[\text{As}]_{\text{pw}} = -11.2 + 2.28 \cdot \text{pH} + 0.022 \cdot \text{DOC}$	0.944	***	134
$[\text{Cd}]_{\text{pw}} = 2454 - 321 \cdot \text{pH}$	0.967	***	482
$[\text{Cu}]_{\text{pw}} = -113 - 0.18 \cdot \text{DOC} + 10.9 \cdot \text{pH} + 0.99 \cdot [\text{Cu}]_{\text{tot}}$	0.940	***	81
$[\text{Pb}]_{\text{sol}} = 35.7 + 0.57 \cdot \text{DTN} - 0.28 \cdot \text{DOC}$	0.782	***	26
$[\text{Zn}]_{\text{sol}} = 3572 - 460 \cdot \text{pH}$	0.910	***	161

amendment had been applied, but not where biochar had been used (Table 1), despite the latter reducing soluble concentrations furthest. There could have been a dilution effect of the compost, which was greater in mass than biochar applied on the same volume basis and was probably more easily incorporated into the soil during field exposure. However, as it is the soil solution concentrations, rather than the total in soil that determines the environmental impact of trace metals (Temminghoff et al., 1998), this effect was not of great importance to the interpretation of effectiveness of each of the amendments.

4.2. Influence of amendments on total and bioavailable PAH concentrations

Despite a lack of statistically significant differences between some of the treatments, the fact that biochar consistently reduced the total and bioavailable fraction to the greatest extent for all PAH groups (Fig. 2) is generally encouraging in the context of remediation of PAH contaminated soils. Other carbonaceous sorbents like activated carbon have previously been shown to reduce the bioavailable fraction of PAHs. Brandli et al. (2008) found that freely dissolved PAH concentrations measured using Polyoxymethylene (POM) strips were reduced by the addition of activated carbon whilst Yu et al. (2009) found that the sorbing properties of biochar itself reduced the bioavailability of organic pesticides to plants. However this reduction was only in the bioavailable fraction, as pesticide residues were found to persist for longer in the presence of biochar. The fact that the total PAH concentration as well as the bioavailable concentration was reduced by biochar in the present study (Fig. 2) could be explained by the possibility that the acetone/hexane extraction was not exhaustive enough to extract the PAHs that were more strongly bound to the added soil amendments, suggesting that these more strongly bound PAHs are not readily bioavailable and are thus unlikely to pose an environmental risk. Alternatively the addition of biochar could have increased the degradation of PAHs; biochar has been shown to increase microbial activity in soil (Steinbeiss et al., 2009) which can stimulate PAH degradation. However, this seems unlikely as other carbonaceous sorbents (for example black carbon) have been found to decrease

Table 3

Percentage of seeds with emerging shoot lengths of >1 cm, as an indicator of phytotoxicity (mean \pm SE, $n = 3$). Significant differences between treatments are indicated by different letters ($p < 0.05$).

	% Shoot lengths of >1 cm
S	61 \pm 3 a
S + C	78 \pm 4 b
S + B	78 \pm 2 b
S + C + B	75 \pm 4 b
ANOVA	0.033

PAH mineralisation by reducing PAH bioavailability for microbial degradation (Rhodes et al., 2008).

The addition of compost alone also reduced total and bioavailable PAH concentrations (Fig. 2). Compost has been shown to enhance PAH degradation in a number of studies by improving soil texture, oxygen transfer, and providing energy to the microbial population (Haritash and Kaushik, 2009). It is this increased degradation potential of the microbial community that is believed to decrease PAH concentrations, not the increased sorption to organic matter (Kaestner and Mahro, 1996). Biochar and compost could therefore reduce PAH concentrations by different mechanisms in the soil which would explain why, when added in combination, they generally worked less effectively than when added individually (Fig. 2). The reduced PAH bioavailability caused by the addition of biochar may have an antagonistic interaction with the increased microbial activity caused by the addition of compost, by reducing the substrate available for the microbes. Although the biochar and compost were consistently found to work less effectively in combination than in isolation in both reducing the total and bioavailable PAH concentration, it is important to highlight that differences were not statistically significant, warranting the need for further investigation before drawing definitive conclusions.

Unlike pore water extraction, for which an unknown soil to solute ratio and contact time exists (Beesley et al., 2010), some of the reduction in PAH concentrations could also have been caused by the dilution effect of adding the virtually PAH free amendments to the soil; biochar addition of 30% by volume only constituted an addition of less than 10% by weight because the biochar was 6 times less dense than soil. However, as PAH concentrations were consistently reduced by more than 40% when biochar was added to soil, the dilution was not thought to be a largely influential mechanism of reduction.

5. Conclusions

Clear potential exists for both greenwaste compost and biochar to diminish water-soluble Cd and Zn in this soil, significantly reducing their phytotoxic effect. However, low initial water-soluble Cu and As concentrations in this soil, combined with some mobilization of these elements with increases in DOC and pH associated with soil amendments, make firm conclusions as to effects on As and Cu less definitive. What is clear is that both compost and biochar amendments can usefully reduce PAH concentrations, especially the heavier and more toxicologically relevant ones, with the affinity of biochar for these organic contaminants being particularly encouraging for the remediation of contaminated soils. Therefore, taken on balance, biochar has greater potential to beneficially reduce bioavailability of both organic and inorganic contaminants than greenwaste compost in this multi-element contaminated soil, being especially effective at reducing phytotoxic concentrations of water-soluble Cd and Zn as well as heavier PAH groups. Its targeted application to contaminated soils in field trials, as well as the mechanisms by which it immobilized selected pollutants, should now be the focus of further work.

Acknowledgements

The authors would like to acknowledge the support of COST Action 859 (STSM) and reviewers for their helpful comments and suggestions.

References

- Beesley, L., Moreno-Jimenez, E., Clemente, R., Lepp, N., Dickinson, N., 2010. Mobility of arsenic, cadmium and zinc in a multi-element contaminated soil profile assessed by *in-situ* soil pore water sampling, column leaching and sequential extraction. *Environmental Pollution* 158, 155–160.
- Beesley, L., Dickinson, N.M., 2010. Carbon and trace element mobility in an urban soil amended with green waste compost. *Journal of Soils and Sediments* 10, 215–222.
- Bernal, M.P., Clemente, R., Walker, D.J., 2006. The role of organic amendment in the bioremediation of heavy metal polluted soils. In: Gore, R.W. (Ed.), *Environmental Research at the Leading Edge*. Nova Science, pp. 1–60.
- Bernal, M.P., Clemente, R., Walker, D.J., 2009. Interactions of heavy metals with soil organic matter in relation to phytoremediation. In: Navarro-Aviño, J.P. (Ed.), *Phytoremediation: the Green Salvation of the World*. Research Signpost, Kerala, India, pp. 109–129.
- Brandli, R.C., Hartnik, T., Henriksen, T., Cornelissen, G., 2008. Sorption of native polycyclic aromatic hydrocarbons (PAH) to black carbon and amended activated carbon in soil. *Chemosphere* 73, 1805–1810.
- Clemente, R., Bernal, M.P., 2006. Fractionation of heavy metals and distribution of organic carbon in two contaminated soils amended with humic acids. *Chemosphere* 64, 1264–1273.
- Cornelissen, G., Breedveld, G.D., Naes, K., Oen, A.M.P., Ruus, A., 2006. Bioaccumulation of native polycyclic aromatic hydrocarbons from sediment by a polychaete and a gastropod: freely dissolved concentrations and activated carbon amendment. *Environmental Toxicology and Chemistry* 25, 2349–2355.
- Cornelissen, G., Gustafsson, O., 2005. Importance of unburned coal carbon, black carbon, and amorphous organic carbon to phenanthrene sorption in sediments. *Environmental Science & Technology* 39, 764–769.
- Craul, P.J., 1999. *Urban Soils: Applications and Practices*. Wiley, London.
- Curtis, M.J., Claassen, V.P., 2009. Regenerating topsoil functionality in four drastically disturbed soil types by compost incorporation. *Restoration Ecology* 17 (1), 24–32.
- DEFRA, 2002. Soil Guideline Values for Arsenic Contamination. Available from The R&D Dissemination Centre. WRc plc, Swindon, Wilts, UK.
- Fitz, W.J., Wenzel, W.W., 2002. Arsenic transformations in the soil–rhizosphere—plant system: fundamentals and potential application to phytoremediation. *Journal of Biotechnology* 99, 259–278.
- Gomez-Eyles, J.L., Collins, C.D., Hodson, M.E., 2010. Relative proportions of polycyclic aromatic hydrocarbons differ between accumulation bioassays and chemical methods to predict bioavailability. *Environmental Pollution* 158, 278–284.
- Hartley, W., Lepp, N.W., Edwards, R., 2004. Arsenic and heavy metal mobility in iron oxide-amended contaminated soil evaluated by short and long-term leaching tests. *Environmental Pollution* 131, 495–504.
- Hartley, W., Dickinson, N.M., Riby, P., Lepp, N.W., 2009. Arsenic mobility in brownfield soils amended with green waste compost or biochar with *Miscanthus*. *Environmental Pollution* 157, 2654–2662.
- Haritash, A.K., Kaushik, C.P., 2009. Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): a review. *Journal of Hazardous Materials* 169, 1–15.
- Henner, P., Schiavon, M., Druelle, V., Lichtfouse, E., 1999. Phytotoxicity of ancient gaswork soils. Effect of polycyclic aromatic hydrocarbons (PAHs) on plant germination. *Organic Geochemistry* 30, 963–969.
- Kaestner, M., Mahro, B., 1996. Microbial degradation of polycyclic aromatic hydrocarbons in soils affected by the organic matrix of compost. *Applied Microbiology and Biotechnology* 44, 668–675.
- Lehmann, J., 2007a. A handful of carbon. *Nature* 447, 143–144.
- Lehmann, J., 2007b. Bio-energy in the black. *Frontiers in Ecology and the Environment* 5, 381–387.
- Lehmann, J., Joseph, S., 2009. *Biochar for Environmental Management*. Earthscan, U.S.A.
- Lepp, N.W., Madejon, P., 2007. Cadmium and zinc in vegetation and litter of a voluntary woodland that has developed on contaminated sediment-derived soil. *Journal of Environmental Quality* 36, 1123–1131.
- Lohmann, R., MacFarlane, J.K., Gschwend, P.M., 2005. Importance of black carbon to sorption of native PAHs, PCBs, and PCDDs in Boston and New York Harbor sediments. *Environmental Science & Technology* 39, 141–148.
- Madejón, P., Lepp, N.W., 2007. Arsenic in soils and plants of woodland regenerated on an arsenic-contaminated substrate: a sustainable natural remediation? *Science of the Total Environment* 379, 256–262.
- Mench, M., Schwitzguébel, J.-P., Schroeder, P., Bert, V., Gawronski, S., Gupta, S., 2009. Assessment of successful experiments and limitations of phytotechnologies: contaminant uptake, detoxification, and sequestration, and consequences to food safety. *Environmental Science & Pollution Research* 16, 876–900.
- Munzuruglu, O., Geckil, H., 2002. Effects of metals on seed germination, root elongation, and coleoptile and hypocotyl growth in *Triticum aestivum* and *Cucumis sativus*. *Archives of Environmental Contamination & Toxicology* 43, 203–213.
- Novak, J.M., Busscher, W.J., Laird, D.L., Ahmedna, M., Watts, D.W., Niandou, M.A.S., 2009. Impact of biochar amendment on fertility of a southeastern coastal plain soil. *Soil Science* 174, 105–112.
- Oen, A.M.P., Cornelissen, G., Breedveld, G.D., 2006. Relation between PAH and black carbon contents in size fractions of Norwegian harbor sediments. *Environmental Pollution* 141, 370–380.
- O'Neill, P., 1990. Arsenic. In: Alloway, B.J. (Ed.), *Heavy Metals in Soils*. Blackie, London, pp. 83–99.
- Pietikainen, J., Kiikkila, O., Fritze, H., 2000. Charcoal as a habitat for microbes and its effect on the microbial community of the underlying humus. *Oikos* 89, 231–242.
- Ross, S.M., 1994. *Toxic Metals in Soil–Plant Systems*. John Wiley & Sons, Chichester, UK.
- Rhodes, A.H., Carlin, A., Semple, K.T., 2008. Impact of black carbon in the extraction and mineralization of phenanthrene in soil. *Environmental Science & Technology* 42, 740–745.
- Song, Q.J., Greenway, G.M., 2004. A study of the elemental leachability and retention capability of compost. *Journal of Environmental Monitoring* 6, 31–37.
- Song, Y.F., Jing, X., Fleischmann, S., Wilke, B.M., 2002. Comparative study of extraction methods for the determination of PAHs from contaminated soils and sediments. *Chemosphere* 48, 993–1001.
- Steinbeiss, S., Gleixner, G., Antonietti, M., 2009. Effect of biochar amendment on soil carbon balance and soil microbial activity. *Soil Biology & Biochemistry* 41, 1301–1310.
- Stokes, J.D., Wilkinson, A., Reid, B.J., Jones, K.C., Semple, K.T., 2005. Prediction of polycyclic aromatic hydrocarbon biodegradation in contaminated soils using an aqueous hydroxypropyl-beta-cyclodextrin extraction technique. *Environmental Toxicology and Chemistry* 24, 1325–1330.
- Temminghoff, E.J.M., Van der Zee, S.E.A.T.M., Da Haan, F.A.M., 1998. Effects of dissolved organic matter on the mobility of copper in a contaminated sandy soil. *European Journal of Soil Science* 49, 617–628.
- Thies, J.E., Rillig, M.C., 2009. Characteristics of biochar: biological properties. In: Lehmann, J., Joseph, S. (Eds.), *Biochar for Environmental Management*. Earthscan, U.S.A.
- Whalen, J.K., Hu, Q., Liu, A., 2003. Compost applications increase water-stable aggregates in conventional and no-tillage systems. *Soil Science Society of America Journal* 67, 1842–1847.
- Yin Chan, K., Xu, Z., 2009. Biochar: nutrient properties and their enhancement. In: Lehmann, J., Joseph, S. (Eds.), *Biochar for Environmental Management*. Earthscan, U.S.A.
- Yu, X.Y., Ying, G.G., Kookana, R.S., 2009. Reduced plant uptake of pesticides with biochar additions to soil. *Chemosphere* 76, 665–671.