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RESEARCH ARTICLE

Increased bioavailability of metals in two contrasting agricultural soils treated with waste wood-derived biochar and ash

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Abstract Recycled waste wood is being increasingly used for energy production; however, organic and metal contaminants in by-products produced from the combustion/pyrolysis residue may pose a significant environmental risk if they are disposed of to land. Here we conducted a study to evaluate if highly polluted biochar (from pyrolysis) and ash (from incineration) derived from Cu-based preservative-treated wood led to different metal (e.g., Cu, As, Ni, Cd, Pb, and Zn) bioavailability and accumulation in sunflower (*Helianthus annuus* L.). In a pot experiment, biochar at a common rate of 2 % *w*/*w*, corresponding to ~50 t ha^{-1}, and an equivalent pre-combustion dose of wood ash (0.2 % *w*/*w*) were added to a Eutric Cambisol (pH 6.02) and a Haplic Podzol (pH 4.95), respectively. Both amendments initially raised soil pH, although this effect was relatively short-term, with pH returning close to the unamended control within about 7 weeks. The addition of both amendments resulted in an exceedance of soil Cu statutory limit, together with a significant increase of Cu and plant nutrient (e.g., K) bioavailability. The metal-sorbing capacity of the biochar, and the temporary increase in soil pH caused by adding the ash and biochar were insufficient to offset the amount of free metal released into solution. Sunflower plants were negatively affected by the addition of metal-treated wood-derived biochar and led to elevated concentration of metals in plant tissue, and reduced above- and below-ground biomass, while sunflower did not grow at all in the Haplic Podzol. Biochar and ash derived from wood treated with Cu-based preservatives can lead to extremely high Cu concentrations in soil and negatively affect plant growth. Identifying sources of contaminated wood in waste stream feedstocks is crucial before large-scale application of biochar or wood ash to soil is considered.

Keywords Arsenic · Black carbon · Contaminated land · Copper · Metal pollution · Wood preservatives

Introduction

Organic wastes are of global concern due to the large volumes produced and the need to dispose of them safely (Jones and Healey 2010). Traditionally, organic waste has been disposed of by incineration or landfill, but recently there has been a tendency to recycle waste and prevent and reduce biogenic waste by adopting a more sustainable waste management program (Vehlow et al. 2007; Del Borghi et al. 2009). Significant strategies for large-scale recycling of organic waste material include the production of safe and efficient soil amendments, e.g., through anaerobic digestion or composting, which can be incorporated into agricultural soils (Park et al. 2011; Williams 2005). This practice, in addition to reducing

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unnecessary landfill, can replenish soil organic matter reserves, provide plant nutrients, and help close the nutrient cycling loop between rural producers and urban consumers (Jones et al. 2013).

Pyrolysis or incineration of organic waste wood is an effective strategy to generate energy (Helsen and Van den Bulck 2005). These processes result in the production of biochar and ash, respectively, which can be applied to agricultural soils as either an organic amendment or liming agent (Campbell 1990; Lehmann 2007; Demeyer et al. 2001; Atkinson et al. 2010). In addition, adding biochar to soil can increase crop yields and reduce the leaching of nutrients, and act as a long-term recalcitrant store of carbon (Kookana et al. 2011). In contrast, wood ash is mainly used to raise the pH of acidic soils, although it can also provide a significant source of nutrients, particularly Ca, K, Mg, and P (Someshwar 1996), and benefit crop productivity (Patterson et al. 2004). However, both biochar and ash inherently contain varying levels of contaminants, including those generated during pyrolysis, e.g., polyaromatic hydrocarbons (PAHs), dioxins, and furans (Hale et al. 2012; Quilliam et al. 2013).

Preservative-treated wood may contain varying levels of metals, e.g., 5.2–16.3 mg As g^{-1}, 5.3–19.0 mg Cr g^{-1}, and 2.6–9.8 mg Cu g^{-1} (Helsen et al. 1999; Kartal 2003; Janin et al. 2009), and consequently if preservative-treated waste wood is used as the feedstock, biochar, and ash can contain significant amounts of heavy metals (Kim et al. 2012). One of the most common wood preservatives is chromated copper arsenate, although recently this has been replaced by less toxic Cu-based preservatives (Freeman and McIntyre 2008). High concentrations of metals in soil and increased metal accumulation in plant tissues following wood ash addition are well documented in the literature (Omil et al. 2007; Praharaj et al. 2002); whereas, there appear to be few major impacts following the addition of wood-derived biochar to soil, although biochar has the capacity to both sorb and release metals (Namgay et al. 2010; Uchimiya et al. 2010a, b). The pattern of metal leaching or retention may vary if biochar or ash are produced from metal-contaminated feedstock, but at present there are no studies available directly comparing the effects of biochar and wood ash produced from the same source materials.

The application of uncontaminated wood ash to soil can lead to the increased mobility of metals (Arvidsson and Lundkvist 2002; Pedersen 2003), whereas biochar has the potential to be a more sustainable strategy for recycling preservative-treated waste wood. Contamination of organic waste streams destined for application to agricultural soil can pose a significant risk to soil quality and crop production, therefore the aim of this study was to investigate the effect of soil amendment with biochar or ash produced from Cu-based preservative-treated waste wood on metal bioavailability and phytotoxicity. We hypothesized that total metal concentrations in the soil would increase following amendment with both biochar and ash, although this would not be accompanied by higher levels of plant uptake due to (1) the increase in pH decreasing the bioavailability of metals, and (2) the effective adsorption of heavy metals onto biochar (Su and Wong 2004; Chirenje et al. 2006; Namgay et al. 2010).

Material and methods

Biochar and wood ash production

Waste wood (Norway Spruce; *Picea abies* L.) that had been pressure-treated with a Cu-based preservative was used to produce biochar and wood ash. The wood (35×120×2,500 mm) had previously been used outdoors in North Wales, UK (mean annual temp 11 °C; 1,800 sunshine h $year^{-1}$; 840 mm rain $year^{-1}$) for 4 years prior to disposal and subsequent reclamation. Biochar was produced by pyrolysis under limiting O_2 conditions, and ash produced by combustion. Both processes were carried out at 550 °C for 1 h. Biochar was ground and sieved to pass 5 mm before use. The ash was in a powder form following combustion and did not require further grinding.

Experimental design

The experiment was conducted in pots by comparing two contrasting soils, a sandy clay loam textured Eutric Cambisol (7.5±0.2 % organic matter) and a sandy loam textured Haplic Podzol (12.1±0.3 % organic matter) collected from the University Experimental Station at Abergwyngregyn, Wales (53°14′ N, 4°01′ W). The freely draining Eutric Cambisol supports a sheep-grazed (ca. 10 ewes ha^{-1}) grassland sward dominated by *Lolium perenne* L. and *Trifolium repens* L. and receives regular fertilizer applications (120 kg N ha^{-1} $year^{-1}$). The freely draining Haplic Podzol supports a sheep-grazed (ca. 0.1 ewe ha^{-1}) grassland sward dominated by *Festuca ovina* L. and *Pteridium aquilinum* (L.) Kuhn and commonly receives no fertilizer or lime. Soil was sampled from 0–30 cm depth and sieved to pass 5 mm before use. Further details of the soils and their physiochemical properties are presented in Table 1.

Biochar was added to the Eutric Cambisol at a rate equivalent to 50 t ha^{-1} (2 % *w*/*w*, considering a depth of 0.2 m), which in a previous experiment was effective in increasing soil pH and its nutritional status (Jones et al. 2012), while the wood ash was added to the Haplic Podzol at a rate of 5 t ha^{-1} (0.2 % *w*/*w*). The high ash content of the biochar (~10 % *w*/*w*) made biochar and ash application rates directly comparable for Cu supply, albeit the responses were in different soil types. The application rates chosen also reflects those adopted for C sequestration purposes with biochar (Sohi et al. 2010; Jones et al. 2012) and as a liming agent for wood ash (Pitman 2006). Wood ash was not added to the Eutric Cambisol as this was predicted to cause excessive alkalinization, while biochar was

Table 1 Properties of both soils with or without biochar or wood ash application

	Eutric Cambisol	Eutric Cambisol +biochar	Haplic Podzol	Haplic Podzol +wood ash
pH (initial)	$6.02 \pm 0.02^{(c)}$	$6.97 \pm 0.01^{(a)}$	$4.95 \pm 0.01^{(d)}$	$6.48 \pm 0.04^{(b)}$
pH (end)	$5.94 \pm 0.07^{(b)}$	$6.29 \pm 0.09^{(a)}$	$4.73 \pm 0.05^{(d)}$	$5.06 \pm 0.08^{(c)}$
EC (μS cm^{-1})	$20.4 \pm 1.2^{(c)}$	$31.3 \pm 0.5^{(b)}$	$16.7 \pm 1.2^{(c)}$	$39.5 \pm 1.5^{(a)}$
Moisture (%)	$17.2 \pm 0.6^{(c)}$	$15.2 \pm 0.2^{(c)}$	$27.5 \pm 1.1^{(b)}$	$20.4 \pm 0.4^{(a)}$
Na (mg kg^{-1})	$46.84 \pm 2.51^{(c)}$	$85.35 \pm 2.45^{(b)}$	$46.67 \pm 0.50^{(c)}$	$123 \pm 1.68^{(a)}$
K (mg kg^{-1})	$31.5 \pm 0.17^{(d)}$	$136 \pm 3.67^{(b)}$	$16.04 \pm 0.66^{(c)}$	$158 \pm 5.25^{(a)}$
Ca (mg kg^{-1})	$5{,}967 \pm 33^{(b)}$	$6{,}817 \pm 130^{(a)}$	$28.33 \pm 1.67^{(d)}$	$180 \pm 2.89^{(c)}$
As (mg kg^{-1})	$9.44 \pm 0.12^{(b)}$	$10.29 \pm 0.72^{(ab)}$	$15.08 \pm 1.15^{(a)}$	$14.45 \pm 1.93^{(a)}$
Cd (mg kg^{-1})	$0.65 \pm 0.06^{(a)}$	$0.67 \pm 0.06^{(a)}$	$0.71 \pm 0.06^{(a)}$	$0.70 \pm 0.11^{(a)}$
Cu (mg kg^{-1})	$11.49 \pm 0.78^{(c)}$	$181 \pm 17.2^{(b)}$	$7.31 \pm 0.57^{(c)}$	$351 \pm 11.86^{(a)}$
Ni (mg kg^{-1})	$9.18 \pm 0.37^{(a)}$	$8.21 \pm 0.79^{(ab)}$	$7.51 \pm 0.61^{(ab)}$	$6.66 \pm 0.93^{(b)}$
Pb (mg kg^{-1})	$16.71 \pm 0.79^{(a)}$	$17.27 \pm 0.95^{(a)}$	$9.09 \pm 0.66^{(b)}$	$9.90 \pm 0.56^{(b)}$
Zn (mg kg^{-1})	$37.56 \pm 1.86^{(a)}$	$38.21 \pm 3.76^{(a)}$	$33.19 \pm 3.43^{(a)}$	$31.63 \pm 4.12^{(a)}$

Values represent the mean of five replicates ± SEM. Different letters within each row indicate statistically significant differences between treatments (HSD test, $P \leq 0.05$)

not added to the Haplic Podzol since it had no effect on pH or plant growth during preliminary trials.

Black PVC pots (1,000 cm^3, height 20 cm) were filled with field-moist soil from each of the four treatments: (1) Eutric Cambisol, (2) Eutric Cambisol + biochar, (3) Haplic Podzol, and (4) Haplic Podzol + wood ash. The replicate pots ($n = 5$) were then transferred to a glasshouse (20±2 °C with natural daylight) at Bangor University (Wales) and left to equilibrate for 7 days. Four sunflower seeds (*Helianthus annuus* L., cv. Sunburst) were sown in each pot, and watered every day with up to 100 ml of distilled. A commercial fertilizer (MiracleGro®, N-P_2O_5-K_2O 24-8-16; Great Garden Supply, Boston, MA) was applied (50 kg of N, 16 kg P_2O_5, and 33 kg K_2O on a per hectare basis) at 14 days after sowing. At 21 days after sowing, seedlings were thinned to two per pot, and at 45 days after sowing all plants were harvested.

Substrate analysis

Biochar and wood ash pH and electrical conductivity (EC) were determined with standard electrodes in 1:10 *w*/*v* and 1:1 *w*/*v* with distilled water, respectively. Both pH and EC were determined on field-moist soil both at the beginning (sowing) and at the end of the experiment. Total As, heavy metals (Cd, Cu, Ni, Pb, and Zn) and cation (Na, K, and Ca) pseudo-total contents of the ash and biochar were determined by a Agilent 700 Series ICP-OES (Varian Inc., Palo Alto, CA) after digestion in concentrated HNO_3 and filtration through nylon 0.45-μm syringe filters according to US-EPA (1995a). Moisture content was determined by drying at 105 °C for 24 h. Exchangeable cations (K, Na, and Ca) were extracted in 1:5 (*w*/*v*) fresh soil suspension using 1 M NH_4OAc (pH 7) after shaking at 250 rev min^{-1} for 1 h (Helmke and Sparks 1996), and analyzed by flame photometry (410 Flame Photometer; Sherwood Scientific, Cambridge UK).

Nutrients and metal bioavailability were measured at the beginning and at end of the experiment, according to Lambrechts et al. (2010); briefly, 25 ml of 0.01 M $CaCl_2$ was added to 2.5 g of air-dried soil, shaken for 24 h, centrifuged (3,000×*g*, 15 min), filtered through successive Whatman 42 filter papers and 0.45 μm nylon syringe filters and analyzed by ICP-OES. The extraction solution was left unbuffered to avoid altering metal speciation and solubility in soil (Houba et al. 2000; Meers et al. 2007). Arsenic bioavailability was measured with the same method, since As concentration in shoot and root is well correlated to the $CaCl_2$-extractable fraction (Vázquez et al. 2008).

Metal speciation modeling

The amount of free metal (i.e., uncomplexed) in soil solution in response to the addition of metal-contaminated wood ash or biochar was predicted using the chemical speciation program Geochem-EZ for Windows v1.0 (Shaff et al. 2010). The initial soil metal-loading rates were taken from Table 1 (Eutric Cambisol + biochar and Haplic Podzol + wood ash) and the model was run over the range of fixed pH values observed in the experiments. Solids were allowed to precipitate within the model runs, which typically took between two and seven iterations to achieve convergence. P and S contents of the biochar/ash were also included in the model and the input data used were based on Barrelet et al. (2006), although it was assumed that all S was lost during wood ash formation. Cl^- and NO_3^- were assumed to balance any excess cationic charge in solution. Dissolved organic matter was not included in the calculations due to uncertainties over its chemical composition and pH-dependent charge, although we acknowledge that this would also lower free metal concentrations.

Metal sorption to soil

Sorption of Cu, Ni, Pb, and Zn to the soil's solid phase was measured at sowing by batch extraction according to Namgay et al. (2010) in both amended soils and untreated controls. Briefly, 25 ml of 0.01 M $Ca(NO_3)_2$ containing an equimolar (0.25 mM) concentration of $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Pb(NO_3)_2$, and $Zn(NO_3)_2$ was added to 1 g of air-dried soil (sieved to <2 mm), the suspension shaken (75 rev min^{-1}, 24 h), and the pH measured. The samples were then centrifuged, filtered, and metal concentration determined by ICP-OES as described above. Solid-to-solution metal partition coefficients (K_d) were determined by dividing the amount sorbed to the solid phase (mmol kg^{-1}) by the equilibrium solution concentration (mmol l^{-1}).

Plant analysis

At plant harvest (45 days after sowing), shoot height and root length were measured, and dry weight determined after oven drying (80 °C, 48 h). Total As and metal (Cd, Cu, Ni, Pb, and Zn) concentrations in leaves and roots were measured after microwave digestion with a Synthos 3000 (Anton-Paar, Graz, Austria) according to US-EPA (1995b). Prior to ICP-OES analysis, all samples were filtered as described above. In order to avoid external metal contamination, collected taproots were gently brushed and washed with distilled water to remove any soil particle.

Statistical analysis

After checking for normality and homogeneity of variances, differences in treatments were compared by one-way ANOVA and Tukey HSD test using SPSS v.14 (SPSS Inc., Chicago, IL). *T* tests were used to test for differences between biochar and ash chemical properties.

Results

Chemical properties of biochar and wood ash

Properties of the biochar and ash are presented in Table 2. Overall, complete combustion caused metals to become significantly more concentrated in the ash relative to the partially combusted biochar ($P<0.05$). Of particular note was the significantly higher EC and pH of the wood ash relative to the biochar and soils (Tables 1 and 2). Cu, the dominant heavy metal, represented almost 2 and 20 % of the total dry weight of the biochar and wood ash, respectively. In addition, the concentration of K, Na, and heavy metals in the wood ash and biochar were significantly ($P\leq0.05$) higher than in either of the soils (Tables 1 and 2).

Soil properties and metal concentrations

The addition of both biochar and wood ash to soil resulted in an immediate increase in soil pH and EC ($P<0.05$), however, this response was not sustained and by the end of the experiment the pH had fallen back close to the unamended soil value (Table 1). The concentrations of Na, K, and Ca were all increased in soils amended with both biochar and wood ash. There was also a significant increase in the concentration of total Cu following amendment by both biochar and wood ash ($P<0.05$). Although inherent differences did exist between the two soil types, total concentrations of the potentially toxic elements Zn, Cd, As, and Pb remained unaffected by the addition of either biochar or wood ash. In contrast, the concentration of total Ni was slightly reduced in both soil types following amendment by either biochar or wood ash.

Bioavailability of heavy metals and cations

Bioavailability of heavy metals and cations in soil measured at both plant sowing and harvest are shown in Fig. 1. The concentration of bioavailable metals in soil were one to two orders of magnitude lower than the total metal concentrations reported in Table 1, and most treatment trends appeared consistent between the two extractions. Overall, the bioavailability of Ca, As, Pb, Zn, Cd, and Ni remained relatively unchanged immediately after the addition of either biochar or

Table 2 Chemical properties and total cation and heavy metal concentrations of biochar and wood ash

Parameter	Biochar	Wood ash
pH	9.77±0.13	10.75±0.02*
EC (mS cm^{-1})	1.66±0.03	13.58±0.15*
Na (g kg^{-1})	2.1±0.3	14.5±0.1*
K (g kg^{-1})	5.7±0.6	24.5±0.2*
Ca (g kg^{-1})	7.1±1.5	31.0±0.3*
Cu (g kg^{-1})	22.1±2.4	198.6±3.2*
Zn (g kg^{-1})	0.19±0.02	2.97±0.09*
As (mg kg^{-1})	9.01±1.34	125±2.62*
Cd (mg kg^{-1})	0.35±0.12	5.25±0.13*
Ni (mg kg^{-1})	1.7±0.2	21.5±1.1*
Pb (mg kg^{-1})	13.4±1.3	76.5±2.4*

Values represent the mean of three replicates ± SEM

*$P\leq0.05$ (indicates statistically significant differences between the two amendments; HSD test)

wood ash to soil (Fig. 1). After 45 days, however, the concentrations of available Zn and Cd in soil had significantly increased in the wood ash treatment relative to the unamended control soil, while no such effect was observed in the biochar treatment. In contrast to the other heavy metals, there was an immediate large increase in bioavailable Cu after Cu-treated wood ash application to the Haplic Podzol soil. After 45 days, the availability of Cu had continued to increase in the wood ash-treated Haplic Podzol soil, while a significant increase was also apparent in the biochar-treated Eutric Cambisol ($P < 0.05$). There was an immediate and significant increase in Na and K bioavailability in both soil types ($P < 0.05$) following addition of biochar and wood ash, however, this effect was much less pronounced by day 45.

Metal speciation modeling

The predicted amount of free metal in soil solution in response to biochar or wood ash addition is shown in Fig. 2. In the Haplic Podzol the addition of wood ash and the resultant increase in pH was predicted to initially cause a large reduction in free Cu^{2+}, Pb^{2+}, and Zn^{2+}, while having no major effect on the availability of Ni^{2+}, $HAsO_4^{2-}$, and Cd^{2+}. Modeling indicated that most of the reduction in free metal concentration was due to the formation of insoluble metal complexes (e.g., $Cu(OH)_2$), $Zn_3(PO_4)_2$, $Pb_3(PO_4)_2$, and $Cu_3(AsO_4)_2$), although some soluble metal complexes were also present. At the end of the experiment, when the pH effect of the ash had been reduced, we predicted little effect of the ash on free metal availability in comparison to the unamended soil.

The liming effect of biochar in the Eutric Cambisol was also initially predicted to greatly reduce free metal concentrations (i.e., Cu^{2+}, Pb^{2+}, and Zn^{2+}), but it had no effect on Ni^{2+} or Cd^{2+}. Where reductions were predicted to occur, the effect became significantly diminished from the start to the end of the experiment. Due to the higher pH of the Eutric Cambisol in comparison to the Haplic Podzol, the addition of biochar was predicted to somewhat increase the solubility of As and to decrease those of Pb and Zn. Significant differences in metal response to pH between the two treatments was caused by differences in initial soil chemistry (e.g., base cation concentration) as well as the chemical nature of the amendment (e.g., S content).

Heavy metal sorption

Heavy metals were strongly adsorbed by both soils and followed the series Pb>Cu>Zn=Ni (Table 3). Generally, the presence of biochar and wood ash had little effect (at the time of sowing) on the solid-to-solution partitioning of the metals as described by the $\log_{10} K_d$ values, with the exception of Pb and Zn sorption, which was increased in the presence of both biochar and wood ash ($P < 0.01$), and Ni in the presence of biochar ($P < 0.01$).

Plant biomass and heavy metal uptake

In contrast to plant grown in the Eutric Cambisol, above- and below-ground growth remained very poor in the Haplic Podzol, irrespective of wood ash application, resulting in extremely stunted plants. Consequently, only biomass and metal contents were determined in the Eutric Cambisol grown plants. While the plants were of similar heights and the roots of similar length, the addition of biochar to the Eutric Cambisol reduced total biomass by approximately 40 % with a significant reduction observed in both root and shoot dry weights ($P < 0.05$; Table 4). Cu-treated wood-derived biochar application had no significant effect on the accumulation of As, Cd, Zn, Ni, and Pb in roots or leaves; however, it did result in a 4-fold increase in foliar Cu concentrations and a 40-fold increase in total root Cu concentration ($P < 0.05$). In addition, plant accumulation of Cu (milligrams per plant) was higher in the biochar-treated soil despite their lower biomass (data not shown).

Discussion

Biochar and wood ash metal content and the potential for soil contamination

Reclaimed waste wood is being increasingly used for energy generation, while the products of pyrolysis and combustion are increasingly being recognized as valuable soil amendments; however, the waste-wood stream is also known to contain significant amounts of organic (e.g., PAHs) and metal contaminants (e.g., Cu, Cr, and As). Recent work has shown that during pyrolysis or combustion, metals (i.e., Cu and Cr) are rarely transferred into bio-oil or become volatilized, thereby contaminant enrichment within the solid end-products (ash or biochar) is inevitable (Matsuura et al. 2009; Kim et al. 2012). In this study we have used an environmental source of waste wood that had been treated with Cu-based preservatives; rather than using an experimentally contaminated biochar, this has demonstrated the real potential for contaminated wood material entering waste streams. High levels of Cu contamination were present in the biochar (>20 g Cu kg^{-1}) and ash (~200 g Cu kg^{-1}) produced from this waste wood, which were far in excess of those typically found in agricultural soils (0.001–0.1 g Cu kg^{-1}; McLaughlin 2002) and above the maximum permissible limits for other common organic wastes (e.g., biosolids, 0.50–5.0 g Cu kg^{-1}; composts, 0.2 g Cu kg^{-1}; US-EPA 1993; BSI 2011). Based on the typical field application rates used here, ash and biochar would both result in annual Cu loading rates (1,000 kg Cu ha^{-1}) significantly above regulatory annual limits for Cu loadings to agricultural land (75 kg Cu ha^{-1} $year^{-1}$), although remain below lifetime loading rates (1,500 kg Cu ha^{-1}) (US-EPA

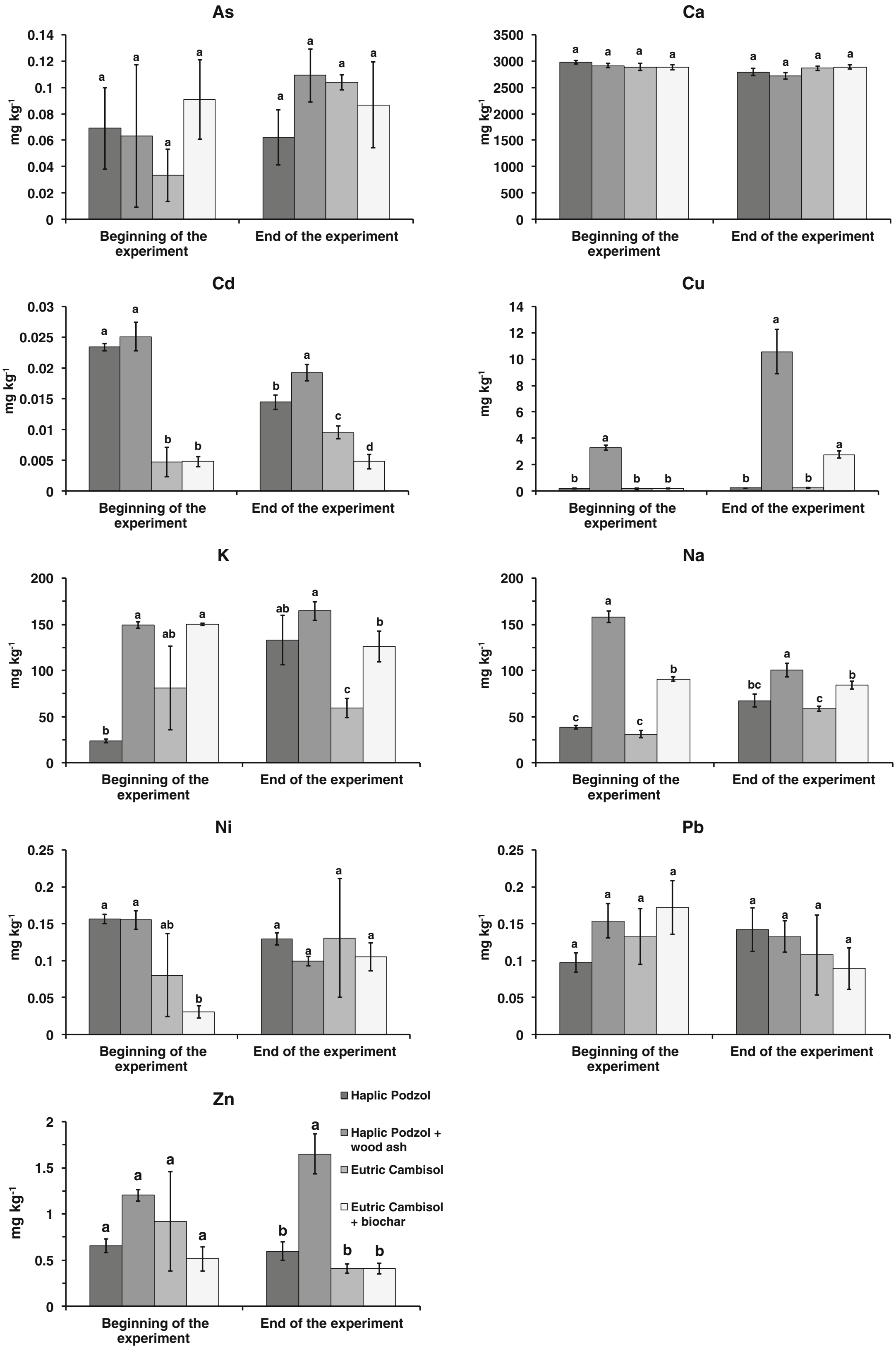

Fig. 1 Nutrient and heavy metal bioavailability in two soils (Eutric Cambisol and Haplic Podzol) amended with either biochar or wood ash at the start and end of the experiment. *Values* represent means ± SEM while *different letters* indicate statistically significant differences between treatments ($P < 0.05$) for each date. The legend is the same for all panels

1993). The resulting total soil Cu concentrations measured here after application (0.18–0.35 g Cu kg^{-1}) were much greater than soil Cu guidance limits designated as being of "negligible risk of environmental contamination" (0.01–0.07 g Cu kg^{-1}) and within the trigger limits for "unacceptable risk" (0.1–1.0 g Cu kg^{-1}) as designated by various EU member states (Carlon 2007).

If biochar or ash derived from non-treated wood is destined for land application, our results indicate that contamination levels of waste wood streams by metal-treated timber should be set very low (≤1 % of Cu) to minimize environmental risk. The main challenge for the industry is to separate preservative-treated wood from the bulk waste wood stream, although this is logistically very difficult and still represents the major obstacle for sustainably recycling organic waste (Townsend et al. 2005).

Biochar and wood ash effects on soil pH

The addition of liming agents to soils and the resulting increase in pH towards neutrality typically results in soil improvement due to an increase in nitrification, a reduction in rhizotoxic Al^{3+} and a concomitant increase in plant productivity (Kemmitt et al. 2006). Here we showed that both wood

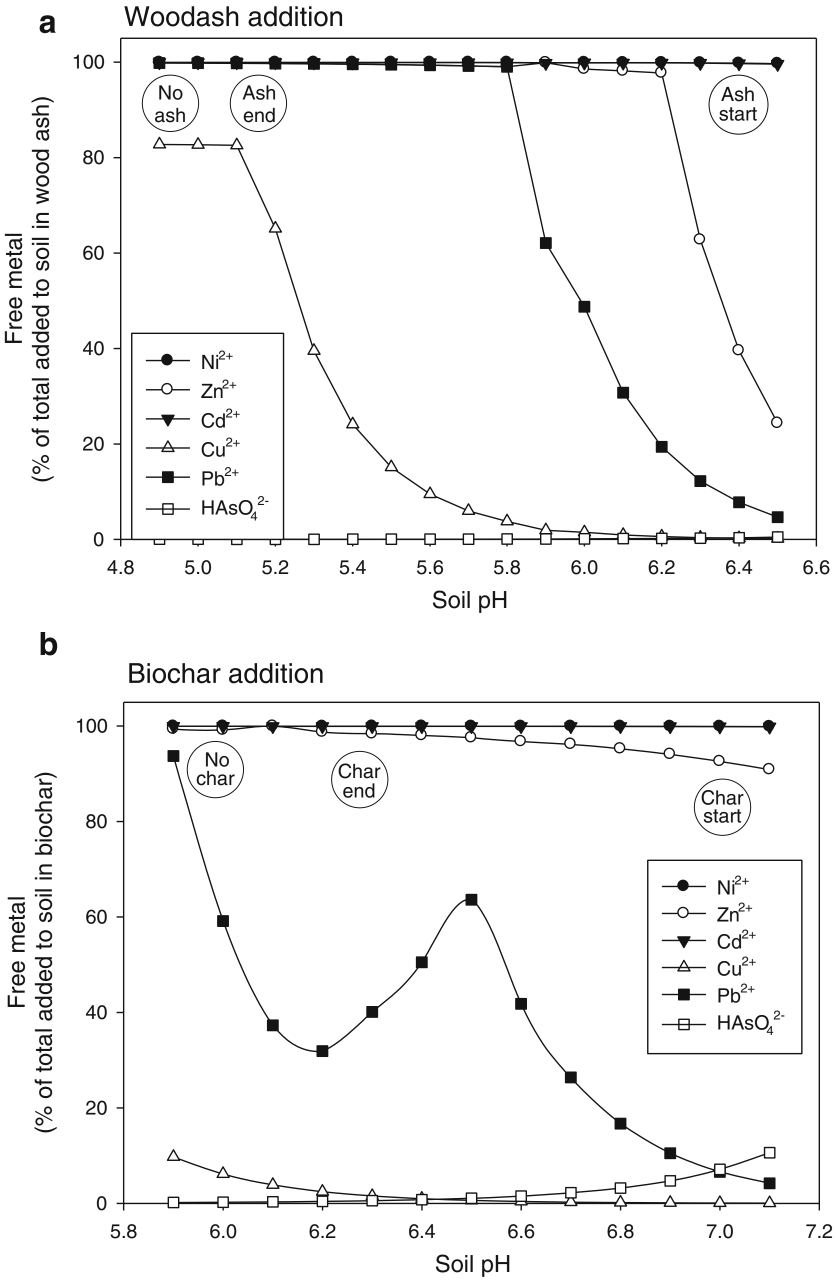

Fig. 2 Predicted effect of the shift in soil pH on the proportion of free metals in solution after the application of either metal-contaminated wood ash (**a**) or biochar (**b**) to soil. Metals not present in a free state were either present as metal–ligand complexes or had formed insoluble precipitates (e.g., $Cu(OH)_2$, $Zn_3(PO_4)_2$, $Pb_3(PO_4)_2$, and $Cu_3(AsO_4)_2$). The *circle with "No ash"* indicates the pH of the unamended soil, *with "Ash start"* indicates the soil pH immediately after wood ash addition, and *with "Ash end"* indicates the soil pH after 45 days (the labels follow a similar pattern for **b**). The initial amount of metal in the soil follows that shown in Table 1 and is different for the two soils (**a** Haplic Podzol + wood ash, **b** Eutric Cambisol + biochar)

Table 3 Solid-to-solution partition coefficients ($\log_{10} K_d$) describing the sorption of four heavy metals added to soil in the presence and absence of either Cu-treated wood-derived biochar or ash as measured at sowing

	Solid-to-solution partition coefficient ($\log K_d$)			
	Cu	Ni	Pb	Zn
Eutric Cambisol	3.74 ± 0.01^{a}	2.47 ± 0.01^{b}	4.57 ± 0.05^{b}	2.50 ± 0.01^{b}
Eutric Cambisol+biochar	3.67 ± 0.05^{a}	2.60 ± 0.02^{a}	4.80 ± 0.07^{a}	2.85 ± 0.03^{a}
Haplic Podzol	2.53 ± 0.09^{b}	1.91 ± 0.11^{c}	2.91 ± 0.08^{d}	1.72 ± 0.10^{d}
Haplic Podzol + wood ash	2.74 ± 0.01^{b}	2.00 ± 0.04^{c}	3.63 ± 0.06^{c}	1.85 ± 0.04^{c}

Values represent the mean of three replicates ± SEM. Different letters within each column indicate statistically significant differences between treatments ($P<0.01$)

ash and biochar can increase soil pH, but that this effect was relatively short lived. We ascribe this decline in pH to the gradual neutralization of the small amount of metal carbonates and oxides within the amendments. This pattern of pH response mirrors that seen in biochar field trials where an identical rate of application was used with this Eutric Cambisol soil (Quilliam et al. 2012). To achieve the optimal pH for sunflower cultivation in the Haplic Podzol (pH increase from 5.0 to 6.8) and Eutric Cambisol (pH increase from 6.0 to 6.8), the calculated dose of $CaCO_3$ required would be 10 and 5 t ha^{-1} respectively, while for $Ca(OH)_2$ it would be 14 and 7 t ha^{-1}. Given the metal cation content of our ash and char (Ca, Na, K, etc.), we estimate that we added the equivalent of approximately 1 t $CaCO_3$ ha^{-1} which explains why the amount added was insufficient to bring about a lasting change in soil pH. Overall, our results suggest that the positive liming effect of biochar and ash derived from Cu-contaminated wood does not offset the negative impacts of its high Cu content on soil quality and plant growth.

Effect of biochar and wood ash on metal cation availability

Heavy metals such as Cu^{2+} are known to strongly sorb to the surface of both soil organic matter and biochar, thus lowering free metal solution concentrations and limiting plant uptake (Ross 1994; Namgay et al. 2010). Indirectly, the high pH of biochar and wood ash can also increase the pH-dependent negative charge on soil surfaces stimulating further sorption as well as promoting metal precipitation (e.g., $Cu(OH)_2$) which readily occurs for several metals above pH 6.5 (Lindsay 2001) as predicted by our modeling. Biochar also contains significant amounts of dissolved organic C and HCO_3^- which may complex the free metals and render them non-phytotoxic (Jones et al. 2011). For these reasons, soil amendment with biochar has been advocated as a way to remediate metal-contaminated sites (Park et al. 2011). The effect of biochar on metal bioavailability, however, remains unclear as both increases and decreases in solution concentrations have been reported (Hua et al. 2009; Beesley et al. 2010; Fellet et al. 2011). In our study the very high intrinsic Cu content of the char and ash clearly overwhelmed the immobilization capacity of the soil and biochar, resulting in phytotoxic concentrations being reached (Harden 2011). Differences in toxicity at equal Cu addition were probably due to differences in the specific bioavailability in soil containing either biochar or ash, together with the soil type.

As regards the mobility of non-essential metals, like Cd, Ni, and Pb, we conclude that most of their bioavailable fraction originated from the soil rather than from the added char or ash. Due to the high cation content of the amendments, particularly K^+, Ca^{2+}, and Cu^{2+}, we hypothesized that their addition would stimulate desorption of the native metals, increasing their

Table 4 Growth characteristics and heavy metal concentration of sunflower shoots and roots after 45 days of growth in Eutric Cambisol soil either amended with or without metal-contaminated biochar

Parameter	Shoot		Root	
	Control	+Biochar	Control	+Biochar
Length (cm)	47.8±2.1	48.0±2.6	7.2±0.6	7.1±0.4
Biomass (g plant^{-1})	5.15±0.67*	3.05±0.39	0.73±0.11*	0.44±0.07
As (mg kg^{-1} dw)	0.79±0.12	0.68±0.25	2.18±0.53	3.37±0.76
Cd (mg kg^{-1} dw)	0.23±0.13	0.12±0.01	0.72±0.29	0.83±0.21
Cu (mg kg^{-1} dw)	3.62±0.33*	13.75±2.16	5.11±1.49*	202±52
Ni (mg kg^{-1} dw)	1.10±0.09	0.89±0.1	2.63±0.73	3.89±0.97
Pb (mg kg^{-1} dw)	0.61±0.09	0.43±0.14	5.36±0.67	5.46±0.87
Zn (mg kg^{-1} dw)	26.78±6.30	21.25±3.49	20.76±6.46	41.88±9.65

Values are expressed on a dry weight basis and represent the mean of four replicates ± SEM

*$P\leq0.05$ (indicates statistically significant differences between treatments; HSD test)

bioavailability. This could occur by direct exchange of cations on sorption surfaces (e.g., Ca^{2+} for Cd^{2+}), and indirectly through cation displacement of H^+ from exchange surfaces which lowers solution pH and makes metals more soluble (Namgay et al. 2010). The opposite response, however, was observed in our experiments with biochar stimulating Cd retention at the end of the experiment. Our findings contrast with those of Vergara and Schalscha (1992) and Vibhawari and Pandey (2010) who both found that high amounts of Cu^{2+} inhibited Cd^{2+} sorption, although with different soils. The sorption and desorption reactions of mixtures of heavy metals, however, are complex processes dependent on both soil properties and competition between metals for sorption sites (Cherqueira et al. 2011). Our results could suggest that Cd and Cu may occupy different sorption site profiles, as reported by Yobouet et al. (2010), with therefore negligible influence of Cu on Cd solubility (Uchimiya et al. 2010a).

It is clear from this study, that with the exception of Cu, biochar derived from Cu-treated wood appears to have minimal lasting effect on available heavy metal concentrations in soil. This supports the metal solubility predictions that showed little long-term effects of pH on metal bioavailability. In contrast, Cu-treated wood-derived ash application tends to increase the availability of native metals, suggesting that ash production would be a less favorable option for recycling metal-contaminated wood.

Effect of biochar and wood ash on metal oxyanion availability

Raising soil pH represents a major remediation option for most heavy metals (by rendering them insoluble); however, one of the negative consequences of this can be an increased availability of oxyanions (Beesley et al. 2013). Despite our chemical equilibria predictions, there was little experimental evidence to support an increase in As bioavailability in response to the biochar and wood-ash-induced rise in soil pH. While the amount of As in the biochar-amended soils were within guideline values (1–150 mg As kg^{-1}; mean 40 mg As kg^{-1}; Martin et al. 2009; Reimer and Cullen 2009; US-EPA 1994; Teaf et al. 2010), higher loading rates may occur with wood treated with As-based preservatives (e.g., Cu-Cr-As or monosodium methanearsonate). Although our feedstock material possessed a relatively low As concentration (<0.05 g As kg^{-1}), As-treated wood typically contains between 1 to 18 g As kg^{-1} (Hingston et al. 2006). During pyrolysis or incineration, some As will volatilize, however, significant quantities will be retained in the ash and char (ca. 30–40 % at 500–600 °C reducing to 10–20 % at 850–1,500 °C; Gray et al. 2001; Kim et al. 2012). At these higher concentrations (1–18 g As kg^{-1}), we estimate that the amount of As added to soil within ash or biochar will result in soil concentrations ranging from 1 to 100 mg As kg^{-1} exceeding regulatory limits for soils in many countries and effectively rendering the soil contaminated. In addition, the As sorption capacity ($S_{\max}$) of most soils will be readily saturated ($S_{\max}$ typically 0.01–0.1 mg As kg^{-1}; Burns et al. 2006) leading to high solution concentrations and a risk of leaching to groundwater. However, Cu readily precipitates with As and this may offer some protection against leaching and plant uptake. Wood-derived biochars are predominantly negatively charged, therefore their capacity for sorbing As is very low in comparison to metals such as Cu and Zn (Beesley and Marmiroli 2011). The lack of potential for the added biochar to help lock up As is supported by a range of studies showing little effect in reducing soil bioavailable As concentrations or plant uptake (Beesley and Marmiroli 2011). Although Cu-Cr-As treatment is, or has been, phased out in many countries, it will be present in many waste wood streams for decades to come.

Conclusions

Our results show that waste wood materials containing high levels of copper can lead to different levels of soil metal bioavailability and phytotoxicity depending on the treatment (pyrolysis or combustion) and soil type. At the same Cu load, biochar is less phytotoxic than ash and more efficient for retention of Pb and Zn. Cu-contaminated biochar and especially wood ash increase the bioavailability of this metal, and this is of concern for leaching and subsequent groundwater and food chain contamination. Application to soil may also exacerbate the bioavailability of previously non-bioavailable oxyanions such as As. Biochar and ash derived from wood treated with Cu-based preservatives can lead to extremely high Cu concentrations in soil and negatively affect plant growth. Waste wood may also contain significant quantities of other metals (e.g., Cr, As, and Pb), therefore, identifying contamination in waste stream feedstocks is crucial before large-scale application of biochar or wood ash to soil is considered.

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