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Biochar and heavy metals

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1. Introduction; heavy metals in the environment

1.1 Definitions

Aside from naturally occurring elevated concentrations of heavy metals, associated with geological weathering, anthropogenic activities have introduced both point and diffuse sources of heavy metals to the environment. Mining, smelting, industrial processing and waste disposal have impacted on rural and urban heavy metal concentrations alike, whilst fertilisers, herbicides and pesticides have contributed to the prevalence of high concentrations of heavy metals in some agricultural systems (Ross, 1994). In excessive concentration those heavy metals regarded as the most toxic and environmentally damaging are Cd, Cr, Cu, Hg, Ni, Pb and Zn (Ross, 1994) but several of these, especially those that are transition metals, are essential for plant metabolism (e.g. Cu, Ni, Zn). Heavy metals are a group of elements with specific gravities of > 5 g cm-3 (Ross, 1994) which are both industrially and biologically important (Alloway, 1995). Although not a heavy metal by chemical definition, the metalloid Arsenic (As) is given the status of 'risk element' or 'potentially toxic element' due to its carcinogenic effect on humans and toxicity to plants (Moreno-Jimenez et al, 2012). Excessive concentration of heavy metals and As that, through direct or secondary exposure, causes a toxic response to biota or humans resulting in an unacceptable level of environmental risk (Adriano, 2001; Abrahams, 2002; Vangronsveld et al., 2009) may be classed as pollutants. At ecosystem level heavy metal and As behaviour, mobility and toxicity are complex and, since this book is concerned with 'environmental management' we will focus on interactions between biochar and heavy metals in the environment, taking an applied approach, but covering the main mechanisms by which biochars affect heavy metals.

1.2 Exposure and risk

Heavy metals in soils and sediments are partitioned into a number of binding phases either (i) incorporated in the solid phase, (ii) bound to the surface of the solid phase, (iii) bound to ligands in solution or (iv) as free ions in solution. Only the free ions in solution (i.e. phase (iv)) can be taken up by organisms and, therefore, only the free ions are bioavailable (Di Toro et al., 2001; Thakali et al., 2006). In soils and sediments there is often disequilibrium between these four phases but the system always moves towards equilibrium. If the concentration of metal ions dissolved in solution decreases (for example, due to uptake), then the system re-equilibrates by more metals desorbing from the surfaces and complexes to increase the amount of metal ions in solution until a new equilibrium is reached. Likewise, if the surface area on which the metals can bind increases, then the system re-equilibrates and metals are removed from solution and sorbed on the surfaces. In order to cause a toxic effect, heavy metals must dissolve into solution, be taken up by an organism and be transported to cells where a toxic effect can occur. This complex interaction between organisms and contaminants can be described by a simple model known as the source-pathway-receptor model (Hodson, 2010). The source of the pollution is a heavy metal (e.g. Pb), the receptor is a biological organism (e.g. an earthworm), and the pathway is the process that leads to the contaminant being taken up by the organism (e.g. desorption of Pb from the soil surface into the soil solution and diffusion across the gut wall of the earthworm) (Sneddon et al., 2009). Therefore remediation of heavy metal contaminated sites can be performed by (i) removing all or part of the source, (ii) eliminating the pathway, or (iii) the modifying exposure of the receptor (Nathanail and Bardos, 2004). Thus remediation is achieved in heavy metal polluted environments by reducing the bioavailability of the metals to the receptor organisms (Semple et al., 2004) as lower metal bioavailability in biochar amended soils can result in reduced metal uptake by biological organisms and a lower probability of toxic effects (Park et al., 2011). Since heavy metals cannot be degraded or broken down (i.e. the source cannot be removed without also removing the substrate), and receptors often cannot be isolated in complex ecosystems, the only viable option to break the source-pathway-receptor linkage is to disrupt the pathway between the contaminant and the receptor. It is the manipulation of bioavailability, rendering them more or less available or mobile during environmental exposure that increasingly forms the basis of risk assessment and classification of polluted areas, rather than absolute concentrations in soils (Swarjes, 1999; Fernandez et al., 2005). As such, risk based regulatory systems concern themselves with the effect rather than concentration of heavy metals in soils (Beesley et al., 2011). Importantly, in the legislative context of most nations, it is this potential to cause harm to humans or ecosystems (the effect) that defines polluted sites and not the presence (concentration) of the contaminant per se. As we have identified that the effect is more important than the concentration, if biochars are to be deployed to heavy metal contaminated systems then their ability to break the pathway from source to receptor becomes a focal point (Figure 1).

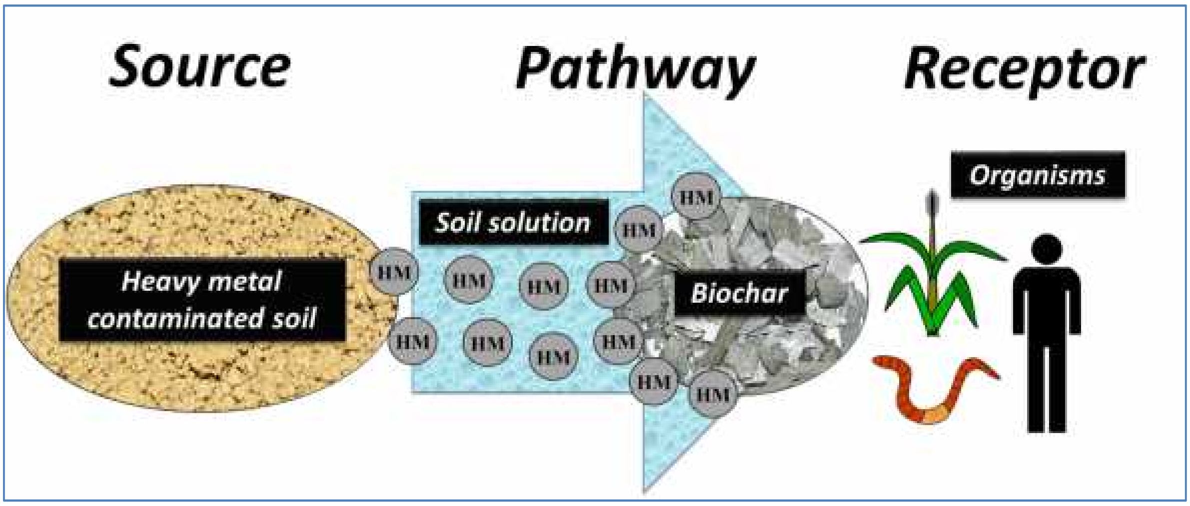

Figure 1. Schematic representation of biochar disrupting the pathway of heavy metals (HM) from their source to receptor organisms.

1.3 Biochar as a remedial amendment

Biochars are organic materials and organic amendments can render heavy metals immobile and non-bioavailable by various physico-chemical means (Bolan and Duraisamy, 2003; Bernal et al. 2006), disrupting the pathway of exposure and reducing risk. The application of organic amendments to soils, from a remedial point of view, has typically been justified by their relatively low cost, compared to ‘hard’ engineering solutions as well as their prevalence as a waste, ordinarily requiring other forms of disposal (burial in landfill, incineration etc). The pyrolysis of organic materials to produce biochar increases the surface area and effective cation exchange capacity (CEC) compared to the un-charred source, but has a lower decomposition rate than non-charred materials, theoretically requiring more infrequent additions to maintain efficacy than other, more labile organic materials, such as composts, manures etc. Therefore the justification for the addition of biochar to environmental matrices is that can work as a sorbent for metals in solution by establishing a new equilibrium between the concentrations sorbed to surfaces and that in solution and its greater resistance to degradation should render longevity of the effect. Before this chapter embarks on the detail of the mechanistic, advantageous and disadvantageous functions of biochar an important premise should be noted; the same features of biochar that render it suitable for remediation of heavy metal contaminated substrates may at once deem it unsuitable for application specifically where the desired effect is to increase availability of metals. The obvious example is Zn, an essential plant nutrient and important element to fortify food and feed but, in excess, a toxicant. Rather than considering absolute increases or decreases in heavy metal concentrations in substrates receiving biochars the emphasis should be placed on bioavailability, mobility and specific requirements related to land use.

2. Heavy metal-biochar interactions at the soil/water interface

2.1 Direct mechanisms

Direct mechanisms of heavy metal immobilisation by biochar include, but are not limited to, fundamental chemical and largely 'at-surface' processes, such as adsorption and complexation. It is widely acknowledged and discussed that biochars may both mobilise and immobilise heavy metals and As by direct means such as ion exchange, chemical and physical adsorption, precipitation etc; Gomez-Eyles et al, 2013). These mechanisms are discussed hence;

2.1.1 Chemical sorption

During exposure to the atmosphere, such as occurs during environmental weathering of freshly produced biochars applied to soils, the oxygenation of biochar surfaces occurs (Cheng et al. 2006) forming oxygen containing functional groups (e.g. carboxyl, hydroxyl, phenol and carbonyl groups) on the massive internal surface area of the biochar (Liang et al. 2006, Lee et al. 2010, Uchimiya et al. 2010b, Uchimiya et al. 2011b). These functional groups induce a negative charge and a high cation exchange capacity (CEC). CEC first increases, and then decreases, with increasing pyrolysis temperatures (Gaskin et al. 2008, Lee et al. 2010, Harvey et al. 2011, Mukherjee et al. 2011); a peak CEC of up to 45 $\text{cmol}_c\ \text{kg}^{-1}$ has been shown to occur between 250 and 350 ˚C, depending on source material (Figure 2). The lower oxygen:carbon ratio and reduced abundance of oxygenated (acid) functional groups lowers CEC after higher temperature pyrolysis (Cheng et al. 2006, Lee et al. 2010, Harvey et al. 2011, Uchimiya et al. 2011a, Shen et al. 2012). The capacity for metal immobilisation demonstrated by lower temperature (<500 ˚C), faster pyrolysis biochars (Beesley et al. 2010, Beesley and Marmiroli 2011) is therefore, in part, a result of high CEC of these biochars; biochar with a similar CEC to the soil it is applied to will not immobilise heavy metals as effectively as a biochar with greater CEC than the soil (Gomez-Eyles et al (2011). Soils from tropical regions that are highly weathered, acidic, low in organic carbon, and have their mineralogy dominated by kaolinite and Fe-or Al-oxyhydroxides, yield a low cation exchange capacity (Fontes and Alleoni, 2006; Schaefer et al., 2008). These soils are more readily phyto-toxic than soils from temperate regions due to their inherent inability to retain heavy metals (Naidu et al., 1998; Melo et al., 2011). In such soils it is more likely that adding biochar will increase CEC and be effective in immobilizing heavy metals. This was shown by Jiang et al. (2012), where the addition of 3% and 5% of rice straw derived biochar to an Oxisol (rich in Fe and Al-oxyhydroxides) increased the CEC, resulting a greater immobilization of Cu(II) and Pb(II).

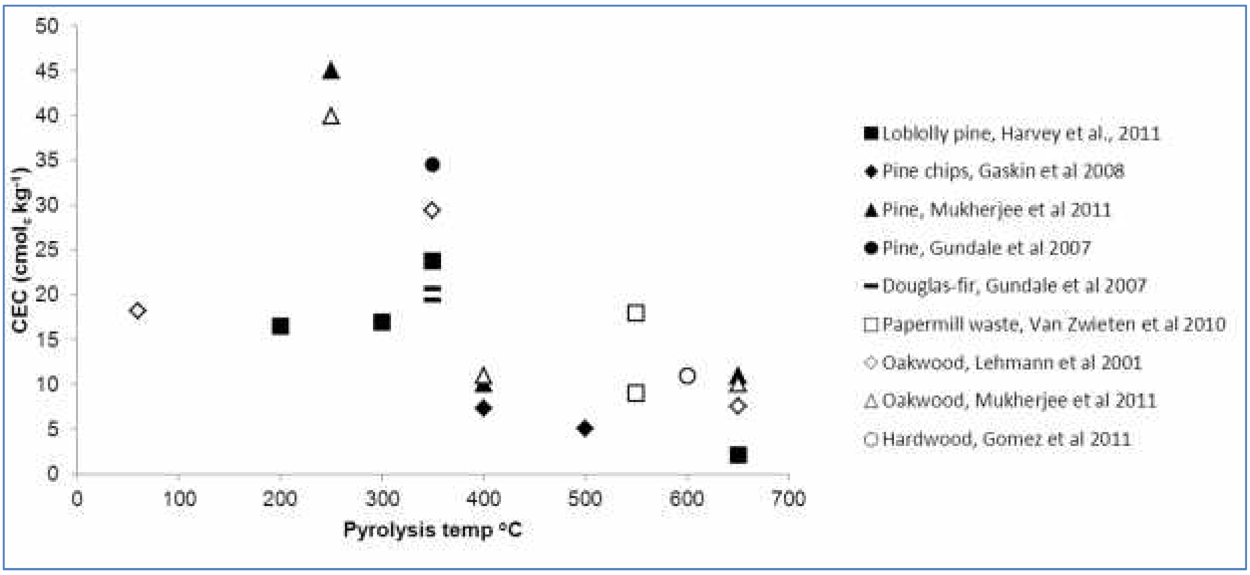

Figure 2. The relationship between cation exchange capacity (CEC) and pyrolysis temperature of woody biochars (reproduced in modified form from Gomez-Eyles et al., 2013).

Surface sorption of metals corresponds directly with the release of H+ ions from the biochar (Uchimiya et al. 2010b), but also of the release of Na, Ca, S, K and Mg (Uchimiya et al. 2011a) into solution which indicates retention of metals on protonated (acidic) functional groups but also metal exchange with other cations. In aqueous systems biochars usually show higher sorption capacity for a single metal than for multiple metals, because there is competition for binding sites between metals. Phosphorus- and sulphur-containing ligands influence the sorption of metal ions such as Pb and Hg that have a stronger affinity for phosphates and sulphates, respectively (Cao et al. 2009, Uchimiya et al. 2010b). Biochar surface oxygenated functional groups may impact on the oxidation of redox sensitive metals whilst biochar application to soils also changes soil porosity and modifies soil physical structure which may influence microscale redox condition. In these cases, redox sensitive elements will change their speciation and geochemistry; for instance, As(III) is found in anoxic environments (<100 mV) and is more mobile in soils and toxic than As(V) (Borch et al., 2010); Cr can get oxidized in aerobic environments (>300-400 mV) and Cr(VI) is more toxic than Cr(III) (Kotas and Stasika, 2000) whilst Cu(I) can also be found under anoxic conditions (Borch et al., 2010). Elaborating on the case of Cr, the application of a low temperature (250 ˚C) coconut derived biochar reduced Cr(VI) to Cr(III) completely after adsorption to biochar surface functional groups (Shen et al. 2012) whereas at higher pyrolysis temperature (350 ˚C and 600 ˚C) the same biochars removed less Cr from solution and reduction occurred before adsorption.

2.1.2 Physical sorption

Aside from a pure ion exchange between biochar surface and metal, a non-stoichiometric release of protons and other cations from the surface of biochars has been found (Uchimiya et al. 2010b, Harvey et al. 2011); more metals are adsorbed than protons or cations are released and sorption can occur at pH below the point of zero net charge (Sanchez-Polo and Rivera-Utrilla 2002). The immobilisation of metals by biochar cannot, in these instances, be purely attributed to ion exchange alone. Metal sorption to biochars is an endothermic physical process (Kannan and Rengasamy 2005, Liu and Zhang 2009, Harvey et al. 2011) and an electrostatic interaction between the positively charged metal cations and π-electrons associated with either C=O ligands or C=C of a shared electron ‘cloud’ on aromatic structures of biochars occurs (Swiatkowski et al. 2004, Cao et al. 2009, Uchimiya et al. 2010b, Harvey et al. 2011). Each carbon from a benzene ring donates an electron to the structure which is then ‘delocalized’ resulting in an 'electron cloud' or a π-cloud above and below the planar surface of that benzene ring. Metal cations are positively charged due to ‘missing’ electron(s) from their d-orbitals so when a positively charged cation approaches the benzene ring, the electron cloud becomes polarized and there is a weak electrostatic interaction between the negatively charged planar surface of the benzene ring and the positively charged metal cation. A representation is given in Figure 3. The bond energies of cation-π interactions are in the range 1 to 30 kcal mol^{-1}(Zarić 2003), while the bond energies of transition metal-carbon bonds are typically an order of magnitude higher (>100 kcal mol^{-1}) (Simoes and Beauchamp 1990).

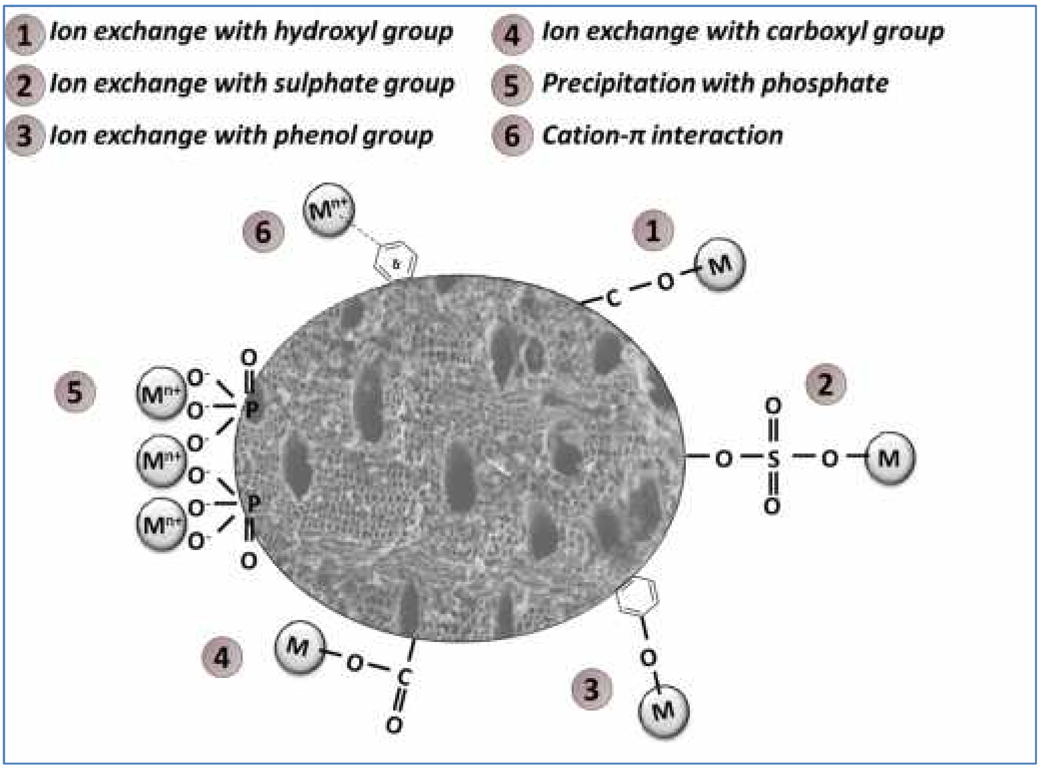

Figure 3. Mechanisms of metal (M) sorption to biochars.

An increase in pyrolysis temperature of biochars increases their aromaticity whilst the abundance of oxygenated functional groups decreases (Harvey et al. 2011, McBeath et al. 2011). So, increasing pyrolysis temperature increases the proportion of cations sorbed due to 'weak' electrostatic bonding (i.e. cation-π interactions) and decreases the proportion due to stronger chemisorption (i.e. by cation exchange). Therefore, lower temperature pyrolysis should result in effective short term metal immobilisation due to the formation of inner and outer sphere complexes with oxygenated (acid) functional groups, but with time these may diminish in the soil environment (within the first 90 days after application; Zimmerman et al. 2011).Thereafter there may be a release of metals back into solution. Higher pyrolysis temperatures result in a negative surface charge that should remain stable for longer but metals will be weakly (physically) adsorbed to biochar surfaces and immobilisation easily reversed. Melo et al. (un-published data) determined, in aqeous batch experiments, that biochar derived from sugar cane pyrolysed at 700 ^{o}C increased Cd and Zn sorption nearly 4-fold, compared to that produced at 400 ^{o}C. When the same biochar was applied to soil the effect of temperature on metal sorption was only observed in a sandy soil, and no difference was shown in a clay rich Oxisol.

A summary of selected batch sorption studies reporting the influence of pyrolysis temperature on heavy metal sorption is given in Table 1.

Table 1. Selected case studies detailing the influence of pyrolysis temperature on heavy metal sorption capacity, assessed by batch sorption experiments.

Experiment	Biochar preparation	Findings	Reference
Batch aqueous sorption of lead (Pb) and atrazine; to determine sorption capacity of biochars compared to manure and activated carbon (AC).	Dairy manure pyrolysed at 200 °C and 350 °C. Manure and woody plant derived activated carbon (AC) were used as controls.	Precipitation of Pb with phosphate and carbonate was the main retention mechanism (84-87%), with surface sorption accounting for 13-16% sorption. Lower temperature biochar sorbed more Pb than the higher temperature biochar and biochars were 6 times as effective as AC. Dairy manure biochars showed strong Pb retention capacity.	(Cao et al., 2009)
Batch aqueous sorption test using simulated rainfall spiked with Cd, Cu, Ni and Pb added to reactors of acidic sandy soil amended with 10% (w:w) biochar amendment.	Cottonseed hulls pyrolysed at 350, 500, 650 and 800 °C.	Lower temperature biochars (350, 500 and 650 °C) retained most Cd, Cu, Ni and Pb (> 4 fold higher sorption than soil without biochar). For Cd and Ni highest temperature biochar (800 °C) resulted in lower sortive capacity than soil without biochar. High oxygen-containing functional groups associated with lower temperature biochars enhanced the heavy metal sequestration ability of biochar when added to soil.	(Uchimiya et al., 2011b)
Batch aqueous sorption of Cu and Zn solution added to 1, 5, 10 and 50 g biochar	Biochar produced by pyrolysis of hardwood at 450 °C and corn straw at 600 °C.	Percentage heavy metal removal increased with amount of biochar added in solutions (<20% with 1 $g\ l^{-1}$ biochar to >90% for 50 $g\ l^{-1}$ biochar), whilst removal efficiency decreased (mg metal removed/g biochar), attributed to aggregation of biochar particles in solutions. Higher temperature biochar removed highest percentage of both Cu and Zn (>90% at 600°C to 80% at 450°C). Adding more biochar to heavy metal contaminated solutions can increase metal removal, but aggregation of biochar particles can reduce efficiency.	(Chen et al., 2011)

2.1.3 Precipitation

Biochar source materials are unlikely to be 100% organic in nature and contain minerals which remain entrained in the biochar matrix after pyrolysis resulting in a non-organic (or ash) fraction in biochar. Source material mineral contents can range from <1% for woody biomass, up to ~25% for manure or crop residues. Following high temperature pyrolysis the ash content of biochars can be upto 50% for manure-derived, or 85% for bonemeal-derived biochars (Amonette and Joseph 2009). Thus mineral salts of Na, K, Ca, Mg, P, S, Si and C are found in abundance in the ash fraction, usually in an oxidised form, their concentrations of which increase with pyrolysis temperature (Gaskin et al. 2008). Uchimiya et al. (2010b) found lead phosphate precipitates effective in immobilising Pb in a broiler litter-derived biochar whilst precipitation of Pb with phosphates contributed to as much as 87% of total Pb sorption to a dairy manure-derived biochar (Cao et al. 2009). Lead-phosphate minerals contributing to sorption in biochars include hydrocerussite and hydroxypyromorphite (Cao et al. 2011), lead phosphate, and lead hydroxyapatite (Chen et al. 2006). Lead-phosphate minerals have a very low solubility so their formation could result in increased capability of biochars to adsorb higher concentrations of Pb, compared to other divalent cations (Namgay et al. 2010, Uchimiya et al. 2010b, Trakal et al. 2011). Precipitation may also occur with other metals such as Cu, Cd, or Zn which precipitate as insoluble phosphate and carbonate salts, mainly at high pH (Lindsay, 1979) (Figure 3).

2.2 Indirect mechanisms [effects]

Indirect mechanisms can also be defined as the effects biochar has on soil characteristics (physical, biological and chemical) that then impact on heavy metal retention or release. The addition of biochar to soils can increase soil pH, microbial biomass, organic carbon, water holding capacity and nutrient use efficiency (Chan and Xu 2009, Major et al. 2009, Atkinson et al. 2010, Sohi et al. 2010,; Karami et al, 2011; Lehmann et al. 2011), which may in turn impact of heavy metal retention and release.

2.2.1 pH changes

It is widely reported that addition of biochars to soils has resulted in pH increases (Yamato et al., 2006; Chan et al., 2007; Uchimiya et al., 2010a; Van Zweiten et al., 2010; Bell and Worrall, 2011); metal solubility changes according to pH, generally being lower at higher pH. For metalloids the geochemistry is somewhat opposing, with higher pH conditions reducing retention (Adriano, 2001). Arsenic solubility and availability increases when pH in soils rises, in most cases, since arsenic binds to positively charged surfaces such as Fe and Mn oxides in soils and anion exchange capacity (AEC) is inversely related to pH (Moreno-Jiménez et al., 2012). Cationic metals (e.g. Cu, Zn, Pb), which are bound to the negatively charged surfaces of soils such as clay minerals and organic matter, increase in solubility as pH decreases because CEC is positively related to pH. When the soil pH is increased metals are increasingly bound to negatively charged surfaces. Contrary to cationic metals, As is released from positively charged soil surfaces when the soil pH is increased; an increase of soil pH has thus been reported to increase As mobility and uptake by organisms (Fitz and Wenzel 2002, Moreno-Jiménez et al. 2012). Antimony (Sb) and molybdenum (Mo) geochemistry is more similar to As than to metals (showing anionic and uncharged species in soils), so we might expect similar pH effects, although to date there is not enough information to draw conclusions regarding the effect of biochar on Sb and Mo.

Studies have reported that soil pore water pH increases after biochar application to circumneutral and acidic contaminated substrates (Beesley et al. 2010, Beesley et al. 2011; Beesley and Dickinson, 2011; Karami et al, 2011; Zheng et al, 2012; Beesley et al. 2013), explaining changes in metal and As mobility in pore water. Various other studies report a soil liming effect of biochars, often resulting from alkaline biochars (Namgay et al, 2010; Fellet et al, 2011; Sizmur et al, 2011). Sizmur et al (2011) noted an especially beneficial increase in soil pH of more than 4 units when a nettle-derived biochar was added to a mine soil (pH 2.7). Jones et al (2012) report a liming effect of adding woody biochar (450 ˚C) to a rotational maize/grass planted agricultural soil (pH increased from 6.86 to 7.18 after 2 years, but back to 6.6 after 3 years). The pH of biochar recovered from the soil (aged) decreased by 2 units over the 3 year experimental duration, showing that biochars liming effect may be transient, thus the effects on metals and mealloids may also be transient. A summary of pH effects of biochars on heavy metal extractability, by different methods, following biochar amendment to contaminated soils is given in Table 2.

Table 2. Selected case studies detailing pH effects of biochars on heavy metal extractability, assessed by different methods.

Experiment	Soils and biochars	Extraction procedure	Findings	Reported in reference
Laboratory batch testing to establish whether biochar could be used to reduce readily extractable concentrations of heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) from unprotected, unstable mine tailings.	Orchard prune residue derived biochar (500 °C) mixed with contaminated pyrite mine tailings (pH 8.1) at 0, 1, 5 and 10% (w:w).	Single leachability testing (TCLP) and bioavailability (DTPA).	Adding 1, 5 and 10% biochar increased pH by ~2 units from pH ~8 in control mine tailings, to pH ~10 at 10% biochar addition. CEC also increased by adding biochar. Biochar significantly reduced bioavailable Cd, Pb and Zn but significantly increased bioavailable Cr and Cu at the highest (10%) biochar application. There was no effect on Ni. The most notable decreases in leachability were noted for Cd, Cr and Pb with the highest (10%) biochar application rate. Biochar most effective for reducing Cd bioavailability and leachability.	Fellet et al (2011)
Column leaching test to determine the efficacy of biochar to scrub excess leachate concentrations of As, Cd and Zn from a contaminated industrially impacted sediment derived soil adjacent to a canal.	Hardwood derived biochar (450°C) and sandy, poorly structured sediment derived soil (pH 6.2).	Continuous extraction with de-ionised water (pH 5.5) of soil and resultant leachate passed through biochar columns. Arsenic and metal concentrations determined from soil leachates before and after passage through biochar. Scanning Electron Microscope (SEM) element mapping of scrubbing biochar following experiment to determine surface sorption.	Biochar significantly increased leachate pH by ~2 units (soil leachate pH ~6 and after passing through biochar columns pH ~8). Soil leachate Cd and Zn concentrations greatly reduced after passing through biochar column; 300 and 45 fold for Cd and Zn respectively. Arsenic concentrations not significantly impacted by biochar. Biochar surface retention of Cd and Zn confirmed by SEM element scanning. Biochar can rapidly immobilise and retain Cd and Zn leached from soil.	Beesley and Marmiroli. (2011)
Pot trial to determine whether biochar as effective at reducing mobile/soluble Cu and Pb from a mine soil.	Hardwood derived biochar (450°C) mixed with Cu and Pb contaminated acidic mine soil (pH 5.4) at 20% (vol:vol).	Multiple pore water extractions (once per month for 3 months) by rhizon samplers (one per pot).	Pore water pH increased by biochar application (peak of pH 5 in control to pH 6.5 in biochar amended soil). DOC concentration not significantly increased by biochar. Both Cu and Pb concentrations significantly and sharply decreased by biochar (4 and 3 fold respectively); decreases greater, compared to control, in month 2 and 3. Biochar effective for sustained reductions in pore water Cu and Pb concentrations.	Karami et al. (2011)

2.2.2 Organic matter/soluble carbon

Biochar applied to soils can increase concentrations of organic matter, especially water-extractable fractions (Lin et al. in-press). Increases in stable organic matter, priming effects (where the input of new organic matter stimulates degradation of existing organic matter in soils) both positive and negative and increased or decreased dissolved organic carbon (DOC) concentrations have been noted as results of biochar application to soils (Cheng et al, 2008; Hartley et al, 2009; Novak et al, 2009; Gomez-Eyles et al, 2011; Bell and Worrall, 2011; Zimmerman et al, 2011; Zheng et al, 2012). Since several metals (eg Cu) form stable complexes with organic matter, adding biochars especially to soils low in organic matter, such as those in arid or semi-arid regions, could result in the occurrence of stabilised organo-metal complexes. However, mineralisation of organic matter in soils results in the often considerable generation of dissolved organic matter/carbon; even in short term column leaching experiments high concentrations of DOC have been leached from biochars (Beesley and Marmiroli, 2011), although it is debatable whether this is the result of mineralisation *in-situ* or leaching of unstable surface organic fractions on biochar surfaces, possibly complexed to mineral fractions in the ash. In biochar amended soils co-mobilisation of DOC and metals, especially Cu and As, have been noted both in pot trials (Beesley et al, 2010) and in the field (Beesley and Dickinson, 2011). In the case of Beesley and Dickinson (2011), a hardwood biochar (400°C) was applied both as a surface mulch (depth of 30 cm top dressing) and mixed (in lysimeters) into an urban soil. Both application methods induced increases in DOC concentrations in soil pore waters (<100 to >300 mg l^{-1}) with the surface application affecting pore water DOC concentrations at up to 25 cm soil depth below the biochar application. In other field (Jones et al, 2012) and pot (Karami et al. 2011) studies there were no significant difference in DOC concentrations attributed to biochar application.

The mechanisms for the co-mobilization of As and soluble organic matter are less clear than for metals, although Mikutta and Kretzschmar (2011) observed ternary complex formation between arsenate and ferric iron complexes of humic substances which could be responsible for the increasing As mobility with increasing DOC. Alternatively, DOC may compete with arsenic directly for retention sites on soil surfaces (Fitz and Wenzel 2002), resulting in an increase in soluble As with increasing concentrations of DOC (Hartley et al. 2009). Arsenic is methylated in soil in the presence of (non-charred) organic matter (Oremland and Stolz 2003) and methylated As species are less toxic than inorganic ones (Hughes 2002), but As speciation in biochar amended soils is yet to be reported.

2.2.3 Availability of phosphorus

Several studies have reported the effects of biochars on available P. Biochars can be sources of P (Sohi et al. 2010) or enhance P bioavailability (Cui et al, 2011; Ippolito et al, 2012) which may be associated with the ash fraction, and more rapidly leached (Wang et al. 2012). Yao et al. (2011) demonstrated that sugar beet-derived biochar adsorbs phosphate. Beck et al (2011) found that the addition of a mixed (greenwaste and car tyres) biochar was able to reduce phosphate and total P leaching from an amended green roof. Jones et al. (2012), in a 3 year field trial, found no significant changes in available P after a 50 t ha^{-1} biochar application. Quilliam et al (2012) noted the same effect after a single application to a 3 year field trial but found that a re-application of biochar after 3 years was able to boost P in field plots again. Hass et al (2012) conducted an 8 week incubation study with soils amended with 5, 10, 20 and 40 g kg^{-1} chicken manure biochar produced at 350 and 700 ^{o}C with and without steam-activation. At both temperatures, with and without activation, an increase in biochar application rate significantly increased extractable P (Mehlich-3 extraction), especially at upwards of 10 g kg^{-1} biochar application rate. Therefore the effect of biochar additions on P availability seems to be largely dependent on the source material.

Phosphate is chemically analogous to As (V), so increases in P availability result in the release of As from soil surfaces, into solution and uptake into plants via phosphate ion channels (Meharg and Macnair 1992). Although arsenate is desorbed from soil surfaces by phosphate (Cao et al., 2003), it is not always available for plant uptake since P and As will compete again for the same root transporter (Meharg et al. 1992). Therefore, As (V) uptake into plants can be avoided by high concentrations of soluble P (Moreno-Jiménez et al. 2012) but if the soluble fraction of As is not taken up by plants, there is a risk it may leach to surface and groundwaters (Fitz and Wenzel 2002). Phosphate rich compounds applied to Pb contaminated soils have also been found to reduce Pb bioavailability (Brown et al, 2003). In contaminated mine soils Karami et al (2011) noted a decrease in available P after biochar amendment to a mine soil in a pot experiment, suggesting that phosphate precipitation was responsible for large reduction in soluble Pb measured in pore water. Fellet et al (2011) noted that an orchard prune residue biochar (550^{o}C) increased total P when amended into a mine soil as this biochar's total P concentration was ~45 times greater than that of the soil. Beesley et al (2013) also found pore water P concentrations of the same biochar to be ~14 times greater than the contaminated mine soil it was applied to in a pot trial, suggesting biochar as source of soluble P.

2.2.4 Reduction/oxidation (Redox)

Increased soil porosity has resulted from biochar application to soils (Warnock et al., 2007; Atkinson et al., 2010), whilst root proliferation in water-filled biochar pores has also been observed (Joseph et al., 2010) though it is unclear whether biochars' pore networks could harbour anaerobic conditions. If this were the case soil hydrological changes due to biochar amendments, and the resultant redox fluctuations, could render an increased risk of biotic contact with reduced, and more toxic forms of elements, for example arsenite (As III) (Gomez-Eyles et al., 2013). Such mechanisms have been suggested to explain changes in As mobility after biochar amendment (Beesley et al, 2013) and work has shown that Cr toxicity and bioavailability is mitigated by biochar due to the reduction of Cr (VI) to the nontoxic Cr (III) form in the presence of biochar (Choppala et al., 2013).

2.2.5 Modification of biochars

Biochars have heavy metals inherent within their structure, derived from their source material, which may be accumulated and concentrated in ash fractions during pyrolysis. These may contribute to a heavy metal loading in soils they are applied to as well as reducing their metal sorption capacity. One of the most comprehensive screening exercise to determine heavy metal concentrations of biochars was reported by Freddo et al. (2012) who analysed heavy metal concentrations in nine dissimilar biochars (rice straw, maize, bamboo, redwood and an unspecified softwood produced at 300-600 ^{o}C); other studies are summarised in Table 3, with comparison to typically measured soil heavy metal concentrations across Europe. In all cases some biochars exceed the median European topsoil total concentrations suggesting that they may contribute heavy metal loadings to soils, but reported aqueous concentrations are typically very low implying low leaching risk from entrained heavy metals. Quilliam et al (un-published data) amended agricultural pasture soils with biochar derived from Norway spruce (*Picea albies* (L.)) which had been pressure treated with a Cu based wood preservative several years prior to pyrolysis, comparing it to the same biochar that had not been Cu treated. Treated wood biochar had greater pseudo-total Cu and bioavailable ($CaCl_2$ extraction) Cu concentrations than untreated wood biochar. Debela et al. (2012) experimented with manipulation of source material, co-pyrolysing sawdust and a metal contaminated soil, thereafter determined metal leachability. Their results showed that leaching of Cd and Zn could be reduced by up to 93%, and Pb leaching by up to 43%, the latter without added sawdust. Contrastingly As leaching was enhanced up to 10 fold by the co-pyrolysis process. Mendez et al. (2012) produced biochar from sewage sludge to determine whether the pyrolysis process could render reduced leachability and bioavailabilty of heavy metals from the sludge, for application to agricultural soils. The pseudo-total concentrations of metals increased after pyrolysis, attributed to their accumulation in the ash fraction, but plant-available concentrations of Cu, Ni, Pb and Zn and the mobility of Cd additionally decreased. A degree of caution should therefore be exercised when applying biochars made from source materials contaminated with heavy metals, to soils to avoid introducing toxicity issues.

Biochars may be modify either during production or when applying them to soils using inorganic amendments, a common practice when napplying other organic amendments to soils to produce better results than applying the amendments individually (Mench et al. 2003). Iron oxides (FeOx) and other metal oxides (Al, Mn etc) are effective binding surfaces for metals and metalloids such as As, Hg, Se, Cr, Pb, etc, and are used in remediation of heavy metal contaminated substrates (Warren et al. 2003, Waychunas et al. 2005). The formation of chemical bonds with surface atoms (chemisorption), forming covalent, ionic or hydrogen bonds by inner and outer sphere complexation retains metals (Waychunas et al. 2005). Iron-oxides effectively immobilise As (Dixit and Hering 2003). Iron-oxide impregnated sorbents have been used in waters and activated carbons have been impregnated with iron-oxide to enhanced the iron-oxides effectiveness (ie an increase surface area) (Reed 2000, Vaughan and Reed 2005). Soaking the source material with iron chloride solution before pyrolysis entrains the iron-oxide into the biochar structure (Chen et al. 2011a). Alternatively, the biochar may be soaked in an iron solution after pyrolysis (Muñiz et al. 2009, Chang et al. 2010). The cost of producing these biochars will be greater than unmodified biochar, so they may only be suitable for specific small scale applications. Lin et al. (2012) experimented with the incubation (aging) of an Fe rich soil (ferrosol) with biochars, suggesting the observed retention of Al and Fe during the 'aging' indicated the formation of mineral-biochar (organic) complexes related to decreasing surface C and corresponding increasing surface oxidation of the biochars. Arsenic is widely known to be immobilised by Fe rich materials as they provide anion exchange sites (Masscheleyn et al. 1991), so optimising biochar for metal and As retention may be possible by modifying its characteristics during production or pre-application.

Table 3. Summary of range of selected heavy metal concentrations in biochars according to extraction method.

Heavy metal/metalloid	*Background European topsoil concentrations (mg kg^{-1})^{a}*	Range of concentrations measured in biochars (mg kg^{-1})	Extractant	As reported in reference
As	*6*	0.01-8.8	Acid	Hossain et al. (2010); Freddo et al. (2012); Bird et al. (2012)
		<100 (μg l^{-1})	Aqueous	Beesley & Marmiroli (2011); Beesley et al. (2013)
		<0.1 (μg g^{-1})		Zheng et al (2012)
Cd	*0.2*	<0.01-8.1	Acid	He et al. (2010); Hossain et al. (2010); Freddo et al. (2012); Bird et al. (2012); Gasco et al. (2012); Knowles et al. (2011)
		<100 (μg l^{-1}) 0.01 (μg g^{-1})	Aqueous	Beesley & Marmiroli (2011); Mendez et al. (2012); Zheng et al (2012)
Cr	*22*	0.02-230	Acid	Hossain et al. (2010); Freddo et al. (2012); Bird et al. (2012)
Cu	*14*	<0.01-2100	Acid/Base	He et al. (2010); Hossain et al. (2010); Freddo et al. (2012); Bird et al. (2012); Gasco et al. (2012); Mankansingh et al. (2011); Knowles et al. (2011); Graber et al. (2010); Mendez et al. (2012)
		<0.01- 0.18	Aqueous	Graber et al. (2010); Chen et al. (in-press)
		70	XRF	Hartley et al. (2009)
Pb	*16*	0.12-196	Acid	He et al. (2010); Hossain et al. (2010); Freddo et al. (2012); Bird et al. (2012); Gasco et al. (2012); Knowles et al. (2011); Mendez et al. (2012)
Zn	*52*	0.64-3300	Acid/Base	He et al. (2010); Hossain et al. (2010); Freddo et al. (2012); Bird et al. (2012); Gasco et al. (2012); Mankansingh et al. (2011) Knowles et al. (2011); Graber et al. (2010); Mendez et al. (2012)
		<0.01-0.95	Aqueous	Graber et al. (2010); Chen et al. (in press)
		<300 (μg l^{-1})		Zheng et al. (2012)
		6.3-6.5 (μg g^{-1})		Beesley & Marmiroli (2011)
		70	XRF	Hartley et al. (2009)

[a] Source: Lado et al. (2008) based on 1588 samples across 26 EU member states; data reported are median values.

3. Toxicity

3.1 Phytotoxicity

3.1.1 Metals

Experiments involving plants and biochars can be grouped according to those concerned with enhancing biomass only (i.e. biochar as a fertiliser or growth medium) or also managing trace element/nutrient bioavailability. Enhanced plant growth due to liming effects, increased water holding capacity and improved soil structure have been reported after the amendment of agricultural soils with biochars (Chan and Xu 2009; Blackwell et al., 2009; Atkinson et al., 2010 and Sohi et al., 2010) but such benefits are often only seen when fertiliser is added together with the biochar soil amendment, suggesting that biochar alone is not able to stimulate re-vegetation (Yamato et al., 2006; Chan et al., 2007; Steiner et al., 2007; Asai et al., 2009; van Zwieten et al., 2010). In a review of the suitability of biochars for remediating contaminated soils Beesley et al. (2011) suggest that the combination of biochars with composts, manures and other amendments may be the most effective way to revegetate bare soils.

Managing heavy metal toxicity (i.e. the impact on plant health and mortality) is a means by which biochars could help to stimulate revegetation of contaminated soils. Biochar produced from hardwoods has been demonstrated to increase germination success of Ryegrass (*Lolium perenne*) on Cd and Zn contaminated soils (Beesley et al. 2010), attributed to decreases in the concentration of phytotoxic heavy metals; Cd and Zn concentrations were dramatically reduced in the pore water of a biochar amended, contaminated canal bank soil, compared to the control without biochar. Karami et al. (2011) amended a Cu and Pb contaminated mine soil with 30% (vol:vol) of a hardwood biochar, and studied germination and uptake of metals to Ryegrass (*Lolium perenne*). In that study pore water concentrations of Cu and Pb were reduced by ~7 and ~3 fold respectively, which in turn reduced shoot concentrations by ~2 and ~3 fold respectively. The effect was to minimise metal phytotoxicity of this soil leading to the conclusion that biochar could be used to aid revegetation of heavily contaminated sites where biomass yields are not important, but inhibition of germination is a barrier to remediation attempts (Beesley et al. 2011). The results of selected studies reporting heavy metal uptake to plants in soils amended with biochars are reported in Table 4.

The possibility exists that, depending on source material composition, biochars themselves are phyto-toxic. In this case, even if their effects were to immobilise large concentrations of heavy metals, seed germination would still be inhibited. Gell et al. (2011) screened 8 biochars for their phytotoxicity to lettuce (*Lactuca sativa L.*), raddish (*Raphanus sativus L.*) and wheat (*Triticum aestivum L.)* (germination shoot and root elongation measurements) finding that only one biochar, produced from pig co-digestate, was significantly phytotoxic due to a high soluble salt content or water-soluble phytotoxic organic compounds . Beesley et al. (2013) took another approach, loading a nutrient solution with various proportions of an orchard prune residue biochar and measuring germination and shoot elongation of tomato (*Solanum lycopersicum L.*), with the aim of discovering if there was a toxic threshold after which adding more biochar adversely affected germination. They found that germination success was decreased relative to the amount of biochar added to nutrient solution. Biochar added at 0, 1, 30, 50 and 100% resulted in 100, 80, 60. 60 and 0% germination rates respectively. This suggests that biochar may itself be phytotoxic if added in high doses, although the effect of nutrient immobilisation by biochar may also explain this effect. Brennan and Moreno *(un-published data)* tested the effect of two biochars (produced at 350^{o}C) applied to Hg-polluted soil (>1000 mg kg^{-1}) by assessing germination success of *Lolium. perenne*. Pine-derived biochar slightly increased plant germination whereas olive-derived biochar (with greater ash fraction than pine) doubled the germination, but neither had an effect on pH or electrical conductivity of soil. Biochar therefore may decrease phytoavailability and phytotoxicity in Hg-polluted soils, but the evidence base is as yet small to draw any conclusions to this effect.

Table 4. Selected case studies detailing pot trial soil-plant biomass and heavy metal uptake experiments utilising biochars [plus other organic amendments].

Experiment	Soil	Biochar	Findings	Reported in reference
To determine bio-fortification of crop plants (Zn) grown in biosolid amended soil with added biochar. Bioavailable (Ca $(NO_3)_2$ extraction) and pseudo-total soil and plant metal concentrations determined (HNO_3 extraction). Cadmium, Cr, Cu and Pb also determined.	Acid (pH 5.6) silt-loam soil.	Pine chip biochar produced at 350ºC applied by mixing into soil at 20% (vol:vol) and 11 crops grown; beetroot (*Beta vulgaris*), spinach (*Spinacia oleracea*), radish (*Raphanus sativus*), broccoli (*Brassica oleracea*), carrot (*Daucus carota*), leek (*Allium ampeloprsum*), onion (*Allium cepa*), lettuce (*Lactuca sativa*), corn (*Zea mays*), tomato (*Solanum lycopersicum*), and courgette (*Cucurbita pepo*).	When biochar added alone to soil i) bioavailable Cd, Cu and Zn ii) nor any measured heavy metal pseudo-total concentrations iii) nor aboveground dry biomass of any crop (except for beetroot) significantly different to control soil. Zinc fortification only occurred for raddish due to biochar alone treatment 9 out of 11 crops were significantly fortified by the combined biosolids and biochar treatment (compared to 8 for biosolids alone). Biochar alone ineffective at increasing biomass and heavy metal uptake.	Gartler et al. (in-press)
To examine the impact of biochars (type and rate of application) on growth, bioavailability (extraction with $CaCl_2$) and uptake of Cd to a wetland Rush species.	Circumneutral (pH 6.9) sandy loam soil with low Cd concentration, spiked with 0, 10 and 50 mg kg^{-1} Cd solution. biochars.	Oil mallee and wheat chaf biochars produced at 550*o*C mixed into Cd spiked soil at 0.5 and 5% (w:w) and wetland rush species (*Juncus subsecundas*) transplanted to spiked soil-biochar mixtures.	Soil pH significantly increased by all biochar rates and types. Bioavailable soil Cd reduced by 96% at 5% biochar addition. In non-Cd spiked control biochar significantly reduced shoot number, root length and total (above plus belowground) biomass but in spiked soil there was no significant difference with or without biochar. Total removal of Cd by whole plants (Cd in plant tissues/Cd added as spike) significantly reduced in all spike biochar/biochar rate combinations except 0.5% wheat chaf biochar at 10 mg kg^{-1} Cd spike. Biochars effective for Cd immobilisation, and to reduce uptake, but not promote growth of this wetland species.	Zhang et al. (2013)
To determine whether Cu toxicity can be mitigated by adding biochar. Bioavailable soil ($NaNO_3$ extraction) and plant pseudo-total (HNO_3) concentrations determined and plant biomass measured in response to Cu dose and biochar added.	Initial germination of 'pseudo-cereal' *Chenopodium quinoa* Willd. in fertilised potting media (pH 5.8) and then growth in coarse sand. Spiked with 50 and 200 ug g^{-1} Cu solution.	Forest greenwaste biochar produced at 600-800 ºC, mixed at 2 and 4% (w:w) into soil.	Soil bioavailable Cu reduced 5-6 fold by 2 and 4% biochar addition (at 50 ug g^{-1} Cu spike) and 11 and 42 fold by 2 and 4% biochar addition (at 200 ug g^{-1} Cu spike). Complete mortality of plants occurred at 200 ug g-^{1} Cu spike without biochar.With 2 and 4% biochar leaf Cu concentration reduced at both the lower and upper Cu spike dose. The 4% biochar addition increased root but decreased shoot Cu concentrations after the upper spike Cu dose. Biochar effective to reduce bioavailable Cu and mitigate Cu toxicity, alleviating plant stress symptoms.	Buss et al. (2012)

3.1.2 Metalloids

Metalloid, or semi-metals, have properties of metals and non-metals and different geochemistry to metals. Due to its toxicity and potentially carcinogenic effects several studies have examined the impacts of biochars added to As contaminated soils demonstrating that biochar induced pH increases increase this metalloid's concentration in soil pore water after amendment (Beesley et al. (2011). Hartley et al. (2009) reported that this effect did not result in a significantly increased foliar uptake of As, or impact on biomass of *Miscanthus giganteous.* After the amendment of a heavily As contaminated mine soil with an orchard prune residue biochar, Beesley et al. (2013) reported ~5 fold and ~9 fold increases respectively in As concentrations in pore water, planted with and without tomato (*Solanum lycopersicum L.*). No significant differences in biomass yields could be attributed to biochar, but despite the increase in pore water concentrations of As, both root and shoot As concentrations were significantly reduced, whilst fruit As content was very low (2.5 $\mu g\ kg^{-1}$). The authors speculated the apparent increase in potentially bioavailable As, but the reduced uptake to root and shoots may have been a result of increased Fe concentrations in the rhizosphere, rendering As immobile at root level; Lin et al. (2012) reported evidence of Fe retention by biochars. Iron based amendments have also been used to immobilise antimony (Sb) present in soils as a result of spent munitions debris (Sneddon et al., 2009; Okkenhaug et al, *un-published data*) but there is currently no data available on that or other metalloids' behaviour (germanium (Ge), selenium (Se), quebomium (Qb) etc) as a result of biochar additions to soils.

3.2 Toxicity to soil organisms

Earthworms are important soil organisms because of their role in (i) increasing microbial biomass and diversity, (ii) creating drainage channels in the soil, (iii) accelerating the rate of organic matter decomposition, and (iv) increasing nutrient availability to plants. Earthworms are therefore often referred to as soil ecosystem engineers (Jones et al., 1994; Jouquet et al., 2006) and key species (Jordán, 2009) in the soil environment. Special attention to earthworms and their behaviour in contaminated soils has been paid because ecosystem functioning is adversely affected by their absence (Smith et al., 2005). Therefore, the majority of studies carried out to assess the effect of biochar on the toxicity of heavy metals to soil organisms have focused on earthworms, in particular the soil ecotoxicology model earthworm species *Eisenia fetida*. Gomez-Eyles et al. (2011) report that the uptake of Cu by *E. fetida* was decreased by the amendment of a hardwood biochar because the biochar decreased the concentration of soluble organic carbon. Cao et al. (2011) report that the addition of a dairy manure biochar decreased Pb bioaccumulation in *E. fetida* by up to 79% because the phosphate minerals in the biochar precipitated the Pb as insoluble hydropyromorphite.

Recently, evidence has emerged that the chemical changes that occur upon passage of soil through the earthworm gut result in an increase in the bioavailability of metals in the soil environment (Sizmur and Hodson, 2009; Sizmur et al., 2011c). Since the mechanisms for the immobilisation of heavy metals by biochar are similar to the immobilisation of metals by soil organic and inorganic constituents (i.e. cation exchange), earthworms may potentially cause metal desorption from biochar surfaces. Therefore, when considering the effect of biochar on the bioavailability of metals to soil organisms there are three important questions to address:

1. Do soil organisms ingest biochar?
2. What is the effect of earthworms on the bioavailability of metals sorbed to biochar surfaces?
3. Are there any other effects of biochar on earthworm activity besides a change in metal bioavailability?

3.2.1 Do soil organisms ingest biochar?

The ingestion of biochar by soil organisms is dependent upon the size of the biochar particles. Many laboratory experiments investigating either the effect of biochar on soil organisms or investigating the use of biochar as a remedial treatment grind the biochar to a fine powder (e.g. sieved to <2 mm; Gomez-Eyles et al. (2011)) before addition to experimental vessels. However, grinding biochar to a fine powder is unlikely to be replicated during field studies because of (i) the energy required to grind the biochar into a powder, (ii) the loss of biochar from the surface of the soil upon application due to wind, and (iii) the increased risk that airborne biochar powder may cause irritation by inhalation or dermal contact.

There is considerable evidence that the geophagous tropical earthworm *Pontoscolex corethrurus* consumes biochar particles in soils mixed with char (Ponge et al., 2006; Topoliantz and Ponge, 2003, 2005). Rather than ingesting the biochar particles alone, the earthworm ingests a mixture of biochar and mineral soil particles. This is achieved by pushing aside the lighter biochar particles and selectively ingesting the soil (Topoliantz and Ponge, 2003). The earthworm favoured the mixture of biochar and soil to either biochar alone or soil alone (Ponge et al., 2006). There is no evidence that the earthworm uses biochar as a source of nutrition (Topoliantz and Ponge, 2003). Conversely, Collembola can consume carbonised materials and complete their life cycle using biochar as their sole food source (Salem et al., 2013).

3.2.2 Effect of earthworms on the bioavailability of metals

The passage of soil through the gut of an earthworm increases the mobility (and thus the bioavailability) of heavy metals in contaminated soils (Sizmur et al., 2011a). This increase is achieved largely due to an increase in the solubility of organic carbon (Sizmur et al., 2011a; Sizmur et al., 2011b); Figure 4. Therefore, considering the evidence presented above suggesting that earthworms ingest biochar particles, one can speculate that the activity of earthworms in contaminated soil remediated with biochar may either mix the biochar with the mineral soil and promote the sorption of heavy metals on the surface of the biochar, or change the chemistry of the soil-biochar mixture and cause the desorption of heavy metals from the biochar surfaces. Each of these possibilities may be assisted by fragmentation of the biochar, which can increase effective surface area either for adsorption of heavy metals or [microbial activity and] generation of DOC.

Beesley and Dickinson (2011) found that the addition of *Lumbricus terrestris* earthworms to soil contaminated with heavy metals decreased the concentration of dissolved organic carbon and, thus decreased the mobility of As, Cu, and Pb in biochar amended soil. Using the same species of earthworm, Sizmur et al. (2011d) found that the addition of earthworms to contaminated soil remediated with biochar had no effect on the mobility or bioavailability of Cu, Pb or Zn. The effect of the biochar on the mobility of the metals was so large (more than an order of magnitude) that the relatively smaller effect of the earthworms was buffered by the presence of the biochar. Gomez-Eyles et al. (2011) inoculated the earthworm *E. fetida* into a contaminated soil both with or without biochar addition; the earthworms increased the mobility of metals in the non-remediated soils but had less effect in the remediated soil. The mobility of As and Cd was lowest in the soils that were both amended with biochar and inoculated with earthworms. Therefore, it seems that earthworms do not increase the mobility of metals in soils after amendment with biochar. Instead, if they have any effect, they decrease the mobility probably because they ingest biochar particles and facilitate the mixing of biochar with the mineral soil. A schematic summary of earthworms' effects on heavy metals in biochar amended soils is given in Figure 4.

3.2.3 Effects of biochar on earthworm activity

Manures applied to agricultural soils often contain elevated concentrations of heavy metals that accumulate in the soil (Nicholson et al., 2003). By pyrolysing the manure to biochar the organic content is decreased and the concentration of the (non-volatile) heavy metals is greater in the resulting biochar compared to the feedstock (Cantrell et al., 2012). Liesch et al. (2010) investigated the toxicity of two different biochars to the earthworm *E. fetida*. While the concentrations of heavy metals (As, Cu, Zn) in the poultry litter derived biochar were high (52, 177 and 1080 mg kg-1 respectively) it was concluded that these were sub-lethal concentrations. Instead, mortality occurred after high application rates of poultry litter derived biochar because of the presence of ammonia gas and an elevated soil pH. Both Li et al. (2011) and Gomez-Eyles et al. (2011) report weight loss by *E. fetida* in soil amended with wood chips, while Liesch et al. (2010) report no significant effect. There is evidence to suggest that the reason for weight loss and avoidance of biochar amended soils by *E. fetida* is due to desiccation and that desiccation can be overcome by pre-wetting biochar prior to application (Li et al., 2011). These short term experiments reveal that although some types of biochar (particularly biochars derived from manures) may be toxic immediately after application, the long term effect of biochar on the earthworm populations and activity is rather negligible (Weyers and Spokas, 2011).

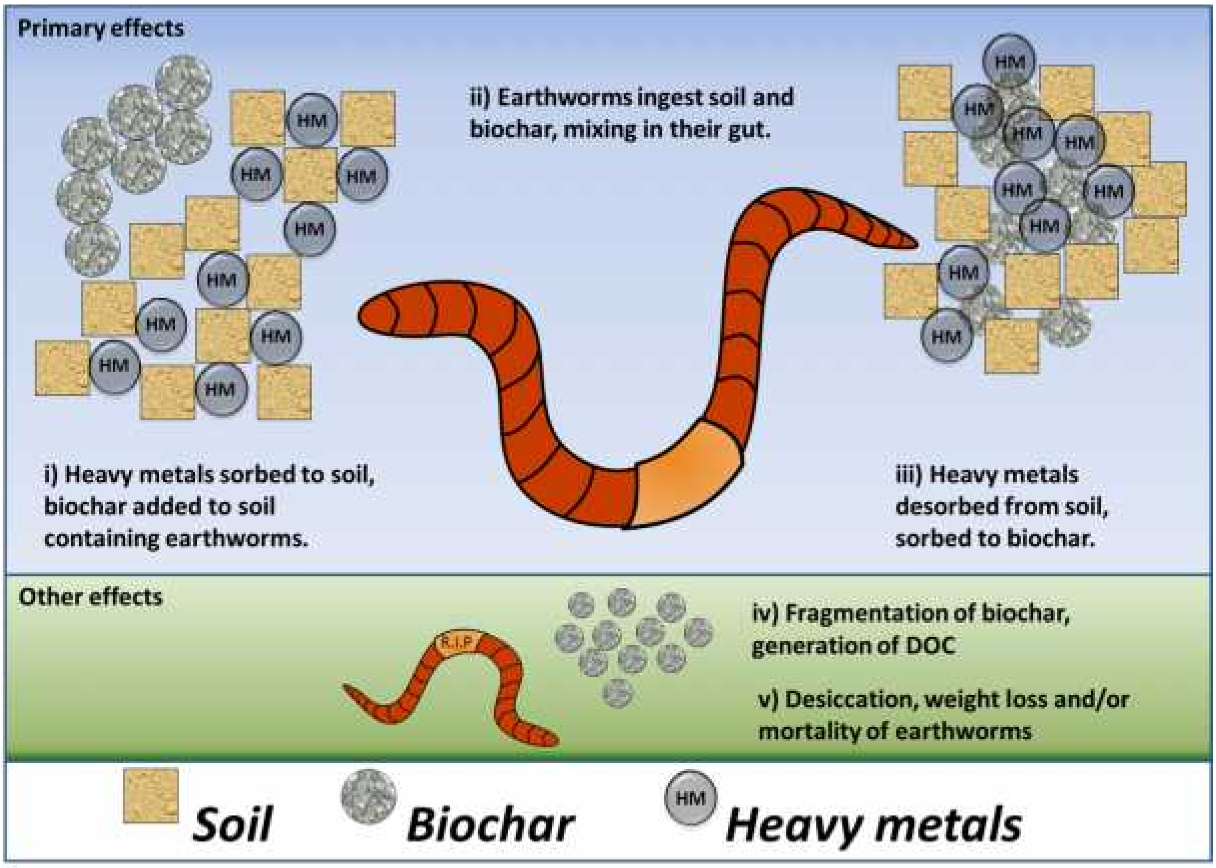

Figure 4. Schematic summary of earthworm effects on heavy metals in soil

4. Remediation

4.1 Degraded lands and their functionality

Technosols are soils containing or covered by a large quantity of man-made products and are now a recognised soil type (World Reference Base classification (WRB); Rossiter, 2007), thus afforded the same importance for their functionality as other soils. These soils vary widely in their levels of disturbance and heterogeneity because of human intervention and their profiles are so strongly impacted by direct human action that the original horizon sequences may be all but completely destroyed (Hollis, 1991) often resulting in a characteristic lack of topsoil (Ennis et al. 2012). This is the case where soils have been deepened historically through waste disposal (Davidson et al., 2006; He and Zhang, 2006) and/or contain a predominance of artefacts of anthropogenic origin, not all of them benign. Contaminated, industrially impacted, mining and urban lands are not only characterised by young, poorly developed soils but by their sparse or absence of vegetation cover (Mench et al. 2010) often associated with a pollution legacy. Re-vegetation of contaminated soils is key to its stabilisation and remediation (Arienzo et al. 2004; Ruttens et al. 2006), as the presence of a vegetative cover over bare soil reduces the potential for migration of contaminants to proximal watercourses or inhalation by receptor organisms (Tordoff et al. 2000), as well the restoration of natural cycling of organic matter and nutrients. Barriers to re-vegetation and thus remediation are phyto-toxic concentrations of heavy metals-in this context those which plants may not be able to immobilise at the root level (Pulford and Watson, 2003)-and poor functionality (organic matter [cycling], nutrient status, structure of soils, water-holding capacity).

We have discussed how biochars can adsorb heavy metals in batch systems, and evaluated how this relates to changes in mobile and bioavailable concentrations of heavy metals in soil matrices with biochar incorporation; biochars have been shown to reduce phyto-toxicity. We also know biochar has several well documented effects on soil quality which should promote functionality and the recovery of degraded land either directly or by indirect mechanisms; liming effects, increased water holding capacity and improved soil structure (Blackwell et al. 2009; Atkinson et al. 2010; Sohi et al. 2010).

However, many benefits are only seen when organic or inorganic fertilisers are added together with the biochar amendment, suggesting that biochar alone is often unsuitable as a soil amendment to stimulate re-vegetation (Yamato et al. 2006; Chan et al. 2007; Steiner et al. 2008; Asai et al. 2009; van Zwieten et al. 2010). As degraded soils often lack basic functionality, such as sufficient nutrient capital to restart natural processes, biochars may not be the most suitable single amendment. Infact some studies report a decrease in plant growth after amendment of soils with biochars (Kishimoto and Sugiura, 1985; Mikan and Abrams, 1995), although others report agronomic benefits when biochar is exclusively added to soils (Novak et al. 2009). Connectivity between i) biochars efficiency for adjusting the equilibrium between mobile/bioavailable and stable/complexed heavy metals (toxicity) and ii) soil functionality is the final aspect to consider in biochars application to contaminated sites (Figure 5).

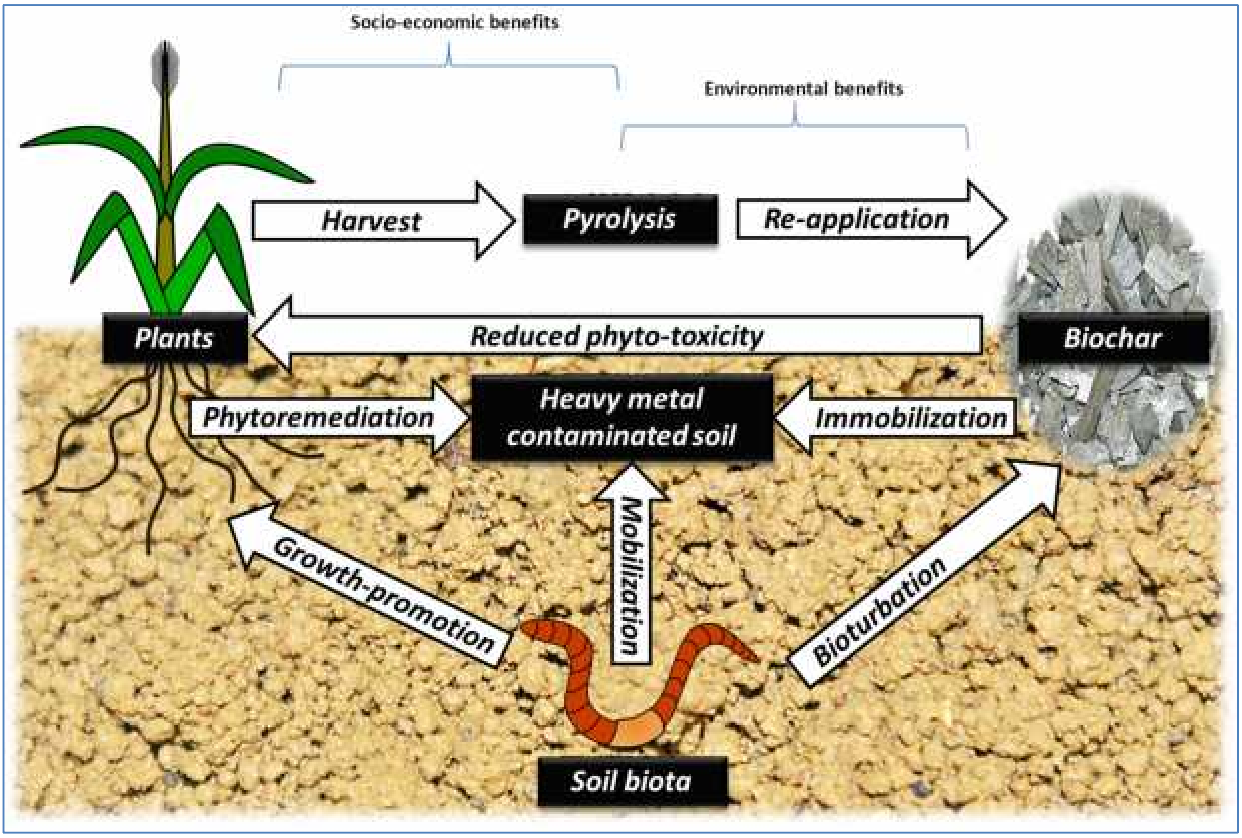

Figure 5. Schematic summary of a remediation system in which biochar is deployed to immobilise heavy metals reduce phyto-toxicity, improve biomass yield. Biomass may be pyrolysed and re-applied to soils, maintaining a closed system.

4.2 Former industrial sites

Soils of former industrial sites are often characterised by materials left after abandonment, such as construction debris, which may be alkaline in nature. Soils may be shallow, overlying impermeable bases with poor drainage and abandoned heaps of waste material can leave hotspots of elevated heavy metal concentration. Several studies have documented the effect of biochars on heavy metal and As mobility, bioavailability and plant uptake on former industrial sites.

Case study 1: Northwest England (UK)

Hartley et al (2009) mixed hardwood derived biochar (400°C) into three alkaline substrates (pH > 7) collected from old industrial manufacturing and waste disposal sites in the northwest of England (UK). The sites were primarily As contaminated (pseudo-total >60 mg kg^{-1}) but, in common with many such sites, contained elevated concentrations of metals such as Cd, Cu and Zn. Miscanthus giganteous rhizones were transplanted into the soil and biochar mixture and grown for 8 months; short rotational coppice (SRC) species, like Miscanthus, are often favoured during phytoremediation due to their rapid uptake of metals and end use as a biomass burn crop. Since no great increase in either As mobility (pore water) or uptake (foliar As concentration) was found in this study the authors concluded that the low transfer co-efficient (soil-plant) of As deemed these soils feasible for growing bioenergy crops. However, if this was the intended soft end use of these sites, a lack of biomass yield improvement after biochar was added to soil would deem the application of the biochar questionable, unless metal mobility and uptake were substantially impacted upon. If uptake of metals was increased by adding biochar to these soils then the short growth cycle and rapid extraction of metals by Miscanthus could yield a decreased soil metal concentration over time. Alternatively, if metal uptake was decreased then the bioenergy crop may be deemed safer to burn, leaving lower residual ash concentrations of metals to be disposed of.

Case study 2: North Midlands (UK)

A similar evaluation to that of Hartley et al (2009), albeit without plant uptake, was carried out with acidic (pH 5.5) sediment derived soil from a canal bank site in the Midlands region of England (Beesley et al, 2010). At this site suspected heavy metal rich effluent had been discharged into the canal and concentrated Cd and Zn in the sediment. Soil was amended with hardwood derived biochar (400^{o}C) at 30% (vol:vol) and pore water concentrations of As, Cd, Cu and Zn measured over a 56 day period. In the case of this site it was hypothesised that biochar may arrest a leaching and toxicity risk identified previously by considerable vertical mobility of Cd and Zn down the profile as a result of a soluble or weakly surface sorbed fractions of metals. A Ryegrass (Lolium perenne) root emergence toxicity test was used to indicate whether biochar could be effective in reducing phytotoxicity and promoting re-vegetation of the soil (Moreno-Jimenez et al. 2011).

Immediate and considerable reductions in pore water concentrations of Cd and Zn were accompanied by similarly rapid increases in As and Cu concentrations (Figure 6),the latter attributed to a pH increase and an increase in DOC. Root emergence was significantly increased, as indicated by the phytotoxicity test, after applying biochar to the soil.

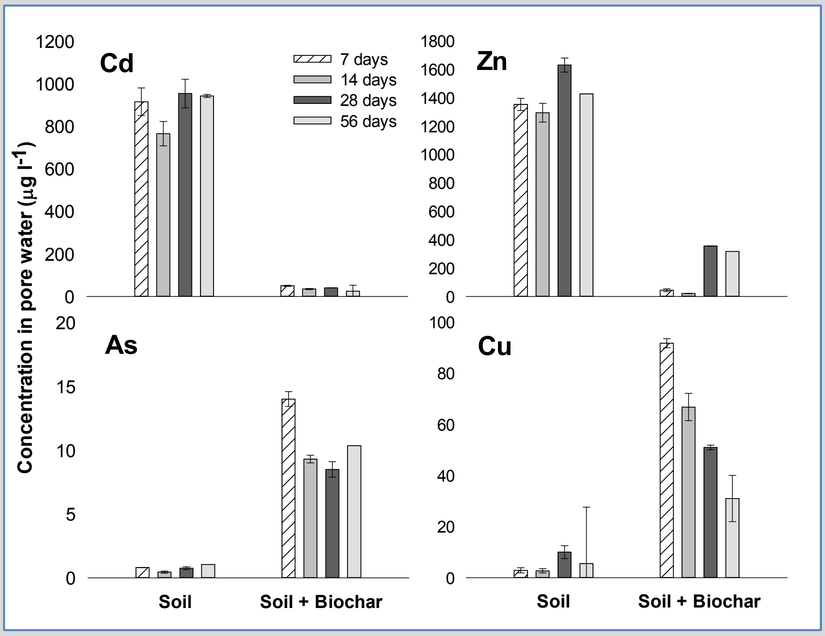

Figure 6. Pore water concentrations of heavy metals and As measured during 56 days in soil from a former industrial area mixed with biochar; note contrasting behaviours of Cd and Zn compared to As and Cu (reproduced in modified form from Beesley et al, 2010)

In this situation biochar deployment to topsoil could restrict the migration of soluble Cd and Zn lower in the soil profile to the rhizosphere. The lower fraction of water soluble As and Cu in this soil probably renders a low risk that adding biochar would substantially mobilise those elements down the profile as they would be retained by organo-mineral complexion. Adding biochar deeper within the soil profile would require disturbance and ultimately endure higher costs and, as the modern remediation agenda seeks to engineer natural processes in the most cost-efficient ways possible, a surface application may be the only viable application method.

Case study 3: South England (UK)

A facet of the assessment of remediation success, in terms of restoring soil functionality, is measuring invertebrate populations' size and diversity; this can also be used as a proxy for relative resilience of colonising populations to introduced, or non-native soil constituents, such as biochars. Functional soils should be able to support diversity of microbial and invertebrate populations. However it is necessarily difficult to develop universal biological indicators for this purpose (Harley et al, 2008). Gomez-Eyles et al (2011) amended a multi-element contaminated soil (As, Cd, Co, Cu, Ni, Pb and Zn) taken from a gasworks site in the south of England (UK) with a hardwood biochar (600oc) on a 10% (w:w) basis. During the 56 day pot experiment pore water concentrations of heavy metals, arsenic, and WSOC (water soluble organic carbon; DOC) were measured. Half of the treatments received 10 adult earthworms (E. fetida), and half did not. No additional organic material was added. It has been suggested that adding biochar alone, without additional organic materials may not be able to effectively meet the needs of gross pollutant immobilisation and net remediation goals (Beesley et al, 2011), including restoring and maintaining soil functionality. Gomez-Eyles et al (2011) found that the earthworm weight loss after 28 days exposure to biochar was significantly greater than without biochar. After 56 days exposure weight loss had further increased significantly. However, as earthworms effectively mobilised Co, Cu and Ni, but adding biochar immobilised these metals, it could be suggested that biochar's role in this situation was to mitigate the effects of earthworms on pollutant mobility. Furthermore earthworm tissue concentrations of most measured metals were not significantly increased by adding biochar. Thus, if biochar was added solely to this soil heavy metal mobility could be mitigated, but this would make no attempt to restore soil functionality. Adding earthworms alone mobilised heavy metals, so it is efficacious to combine earthworms and biochar.

4.3 Former mine sites

Skeletal or weakly structured soils supplemented by waste tailings are common at former mine sites (Wong, 2003) and the original soil horizon sequences may be buried deeply below waste. In temperate marine climatic regions, with predominance of surface organic (O) horizons, the loss of the surface organic material can induce erosion, limit buffering capacity and minimise available nutrients; in such cases heavily acidic leaching waters can supply elevated concentrations of heavy metals beyond administrative boundaries. In semi-arid and arid regions, with a lack of organic matter, well adapted species of plants may have colonised sites, providing, by natural processes, a supply of organic material immediately to their surroundings. Therefore supplying organic matter, and/or increasing the pH of mine soils, reduces toxicity and creates soil functionality conducive to the restarting of natural processes, and eventual formation of horizonated soils. Composts, manures and sludges can be employed on former mine sites as sources of slow release nutrients (Wong, 2003) but biochars' highly variable C:N ratio (7-400:1; Chan and Xu, 2009) requires that it may require a co-addition of organic or inorganic fertiliser. In agricultural contexts an optimum biomass yield should result from combining biochars with fertilisers, but for restoring degraded mine sites the aim is different. So long as [enhanced] vegetation cover is achieved, to stabilise soils and prevent re-entrainment of heavy metal loaded soils, then the measure can be judged successful. Creating over-fertile soils may encourage invasive and non-native species to colonise, so long as they can tolerate heavy metal rich conditions.

Case study 4: Copper and Lead contaminated site (UK)

Karami et al (2011) investigated Cu and Pb mobility (by pore water collection) and uptake by Ryegrass (Lolium perenne) in a pot experiment using a very heavily Pb contaminated (pseudo-total >20000 mg kg^{-1}) soil from a former mine site in Cheshire, England (UK) mixed with 20% (vol:vol) hardwood biochar (400^{o}C), with and without the addition of 30% (vol:vol) green waste compost. The investigation was focussed on determining i) biochar effects on metal mobility and ii) the impact of biochar on ryegrass biomass and metal transfer to vegetation. All three treatments (biochar, compost, and biochar plus compost) reduced Cu and Pb mobility (concentration measured in pore water samples), but had differential effects on ryegrass biomass and uptake; in general biochar alone failed to promote increased biomass yield compared to the control, whereas combining it with compost did so to a greater extent than with only compost (Figure 7).

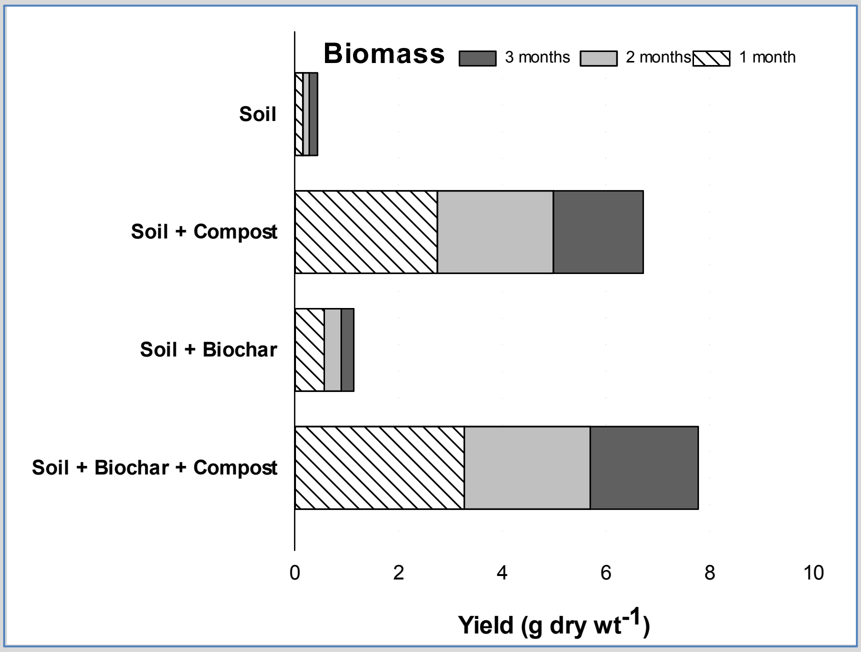

Figure 7. Monthly biomass (Lolium perenne) yield following a biochar amendment to a Cu and Pb contaminated mine soil (reproduced in modified form from Karami et al, 2011).

However, because the addition of biochar did not significantly increase the extractable (harvestable) amount of Cu and Pb per pot, in this case, biochar reduced potential leaching of metals from soil, but did not increase the risk of food chain transfer. So, it can be regarded as a suitable amendment at this site. In this particular case pH was acidic (pH 5.4) and organic matter content average for soils of this climatic region (4%).

Case study 5: Arsenic contaminated site (Spain)

In semi-arid regions, such as Spain, organic matter contents of soils are low. Beesley et al (2013) determined As mobility (by pore water measurements) in an acidic (pH 5) arsenic contaminated mine soil (pseudo-total >6000 mg kg^{-1}) with low organic matter content (< 2%) amended with 30% (vol:vol) of an orchard prune residue biochar (500^{o}C). Uptake to Tomato (Solanum Lycopersicum L.) grown on the soil/biochar mixtures, fertilised and non-fertilised with NPK solution, was measured in terms of transfer from soil to root, shoots and fruit. A non-planted mixture was also included to account for a scenario where biochar was added without a re-vegetation attempt.

Biochar addition to this soil significantly increased As mobility, in pore water, to the greatest extent without plants, suggesting that plant uptake had occurred; this was shown not the case as biochar addition reduced both root and shoot As concentrations significantly (Figure 8),whilst fruit As concentration was very low (> 3 µg kg^{-1}). Fertilisation resulted in no significant reduction in root As compared to the control of soil only, and a significantly greater shoot As concentration than in the un-fertilised soil/biochar mixture (Figure 8).

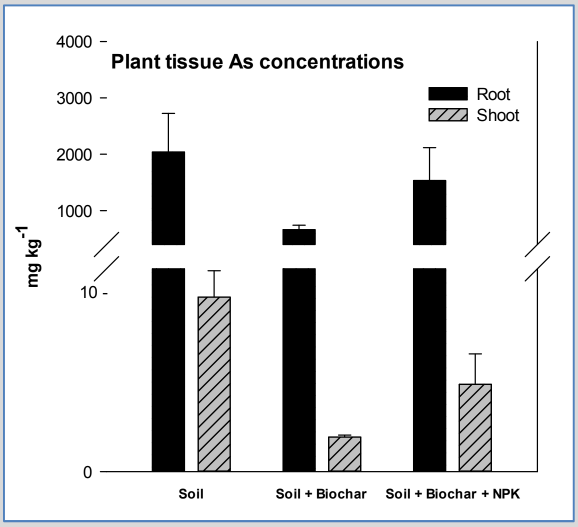

Figure 8. Concentration of arsenic in roots and shoots of tomato (Solanum Lycopersicum L.) grown in a contaminated mine soil with biochar and NPK amendment (reproduced in modified form from Beesley et al, 2013).

Fertilisation did, however significantly increase plant biomass yield to a greater extent than the un-fertilised soil/biochar mixture. These results suggests that adding inorganic fertiliser, to improve re-vegetation of this site, would reduce the effectiveness of biochar in restricting plant uptake of As and, combined with increased biomass, likely yield a potential transfer risk. Biochar did affect a useful naturalisation of pore water, although in this case this was causal in the increased As mobility after its addition.

Case study 6: Multi-element contaminated site (China)

In neutral soil (pH 7) adjacent to a mining area in Hunan province (China), biochar addition (5% w:w of rice straw, husk and bran biochars, 500°C) also significantly increased pore water As concentrations, but significantly decreased those of metals, related to an increase in pore water pH (Zheng et al, 2012). In this case rice (Oryza sativa L.) uptake mirrored pore water concentrations, decreasing compared to the control for Cd, Pb and Zn, and increasing for As. It has been recommended that biochars are applied in combination with Fe based amendments to As contaminated sites (Beesley et al, 2011; Gomez-Eyles et al, 2013) to restrict As mobility.

Thus, for mine site restoration biochars should be applied either i) with additional organic fertilisers, if the site is primarily metal contaminated or ii) with Fe based amendments if the site is As contaminated. The extent of these co-applications will need to be evaluated based on biomass requirements and after evaluation of the soluble fraction of contaminants, and may be approached on a site by site basis after prior physico-chemical analysis of soils.

4.4 Urban sites

Heavy metal in urban soils are more likely to have come from disperse sources, for example by aerial deposition, originating a large distance from the site, than at industrial or mining sites, where contamination is more likely to have originated on site. Such aerial deposition not only has an impact on heavy metal concentrations in topsoils, but through leaching occurring over decadal timescales, heavy metal concentrations in soils and pore waters can be elevated above background values at tens of centimetres depth (Clemente et al., 2008). Surface additions of organic materials, such as composts, can act as a source of DOC which may be leached through the urban soil profile acting as a carrier for heavy metals and redistributing the DOC-metal complex at lower depths (Beesley and Dickinson, 2010).

Case study 7: Churchyard site, close to old smelters (UK)

To establish whether the same DOC-metal co-mobilisation effect was impacted by biochar, Beesley and Dickinson (2011) applied a surface 30 cm amendment of a hardwood biochar (400^{o}C) to an urban soil in the centre of a medium sized conurbation in northwest England (UK); Figure 9. Soil pore water metals, As and DOC concentrations were monitored for 1 year hence at three depths below the surface amendment; 25, 50 and 75cm; Figure 9d. A comparison was made against similarly applied greenwaste compost and non-pyrolysed wood chips; Figure 9c. A parallel mesocosm experiment was performed using soil from the same site (0-25cm depth), but mixed at 30% (vol:vol) with biochar; pore water was monitored in the mesocosms for 6 months. The aim was to determine if the biochar amendment mobilised metals and As to the same degree as other commonly applied amendments and if application method was a determinant. The particular study site employed was a garden established on church land in the mid-17th century, but which had received considerable diffuse heavy metal input from increasingly encroaching industrial sources (ore smelting, refining etc) in the 19th and early 20th centuries, leaving a soil profile with various artifacts and an elevated heavy metal and As concentration throughout its 1 metre depth; Figure 9b. A previous study had identified a potential As toxicity risk, as concentrations of this metalloid in lettuce leaves exceeded contemporary food safety regulatory thresholds (Warren et al, 2003). Thus the application of amendments to this site should not have increased, but sought to decrease As bioavailability.

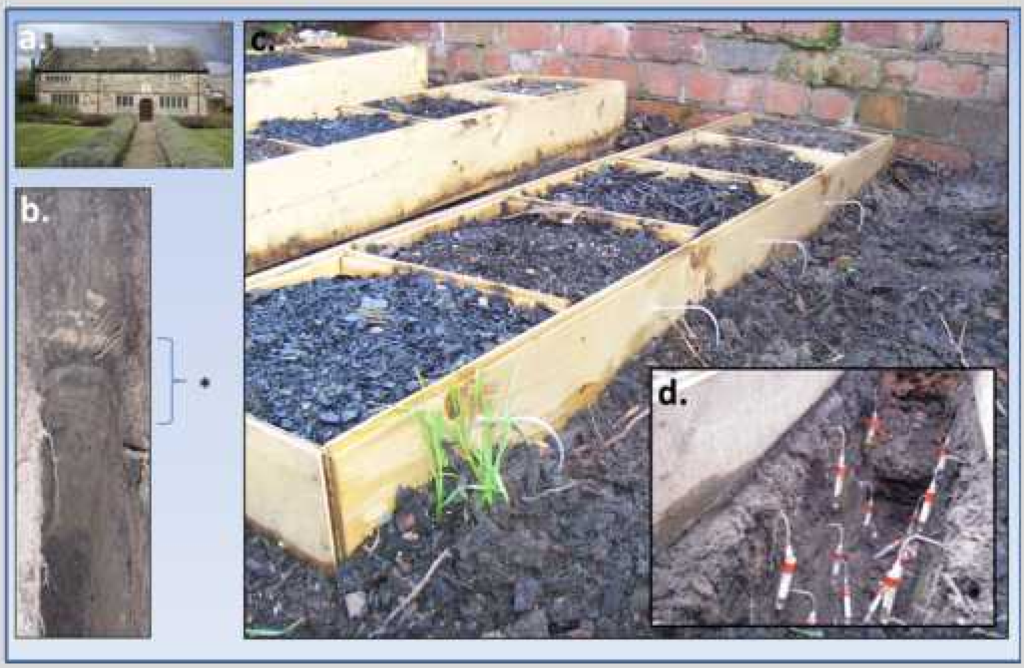

*Figure 9. Urban soil study site showing a.) view of the garden where experimental trenches were located, b.) excavated soil profile revealing now buried deposits of heavy metal rich soot at the surface of the soil circa. industrial era (marked *), c.) surface amendment matrices and d.) pore water samplers in place at 25, 50 and 75 cm depth.*

The addition of biochar to this urban soil, in common with compost and, to a lesser extent, non-pyrolysed wood chips, increased DOC concentrations in pore water collected from the upper 25 cm of the soil, but had little effect below that. At this depth a steady increase in As concentration was also recorded in pore water and a positive correlation between DOC and As concentrations in pore water statistically validated the trend; the same correlation was not seen after greenwaste compost amendment but was noted after amendment with non-pyrolysed wood chips. In the mesocosm experiment, after soil and amendments were mixed together, DOC concentrations were also greatly elevated compared to the control soil without amendment. For biochar, the concentration gradually decreased with time, but As concentrations increased. This would suggest that factors affecting the mobilisation of As after a surface applied biochar addition and a soil mixed application were different. After mixing there will be intimate soil-biochar contact whereas, after a surface amendment, *it is only the leachates from the biochar that impact on soil below and there is little soil-biochar interaction beyond that where the two substrates contact. Thus DOC loaded leachates percolating through the soil profile may redistribute contaminants, whereas pH effects may predominant after soil-biochar mixing, taking account of the often high pH of biochar and lower pH of soils. There may also be different hydrological effects of biochars mixed or surface applied to soils; after mixing biochar pores may be blocked by soil derived mineral or organic materials, reducing water-biochar contact. The same affect would not be seen if biochar was applied as a surface amendment and, in this case, DOC may be desorbed from biochar more readily and leach to soils below rapidly. Such practical factors require more investigation.*

5. Summary

Biochars as soil amendments are suitable for use as amendments to contaminated soils during remediation activities because:

1. Biochar has a very high surface area and some a high cation exchange capacity meaning they are capable of sorbing high concentrations of heavy metals, such as Cd and Zn.
2. The surface chemistry of biochars can be manipulated to sorb certain contaminants more effctively
3. Biochars are more stable in soils for longer periods of time than other commonly applied soil amendments, such as composts and sludges.
4. Biochar raises the pH of soils, making some nutrients more available to plants, immobilising some heavy metals and liming acid soils.
5. Biochars can assist the re-vegetation of some contaminated soils and the vegetation grown on those soils could be pyrolysed to produce more biochars to be returned to the soil.

Remediation strategy for industrial, mining impacted or urban soils could include biochars for reducing leaching of heavy metals, decreasing phyto-toxicity of substrates and assisting revegetation. In the case of arsenic contaminated sites, and especially where there is a potential that food crops may be cultivated (for example urban allotment sites), a greater degree of caution should be exercised not only in whether or not to apply biochar, but in what method of application and how much should be applied. Some biochars also contain elevated concentrations of heavy metals due to their source material; in these cases an evaluation would need to be made into the potential for introducing contaminants to soils by biochar application. It must also be remembered that most biochars appear inadequate as fertilisers if applied alone, so there may be a need to combine them with materials containing labile nutrients. At very heavily contaminated and denuded sites, such as former mine areas, particularly where there are surface leachates of heavy metals and unconsolidated soils and wastes, biochars may be useful to restrict the wider impact of contamination beyond site boundaries. Combination with other organic materials is likely to be required for affective phyto-stabilisation/remediation. At old industrial sites there may be sufficient native soil remaining, and recalcitrant nutrient capital that biochars can be applied alone to contamination hotspots to restart natural processes. In all cases an intelligent approach should be taken to biochar application to land after some data has been gleaned about the specific soil characteristics, heavy metals present in elevated concentrations, preferably their bioavailability and their wider dispersal and posed risk.

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