



Biochar and heavy metals

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1 **Biochar and heavy metals**

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13 ***1. Introduction; heavy metals in the environment***

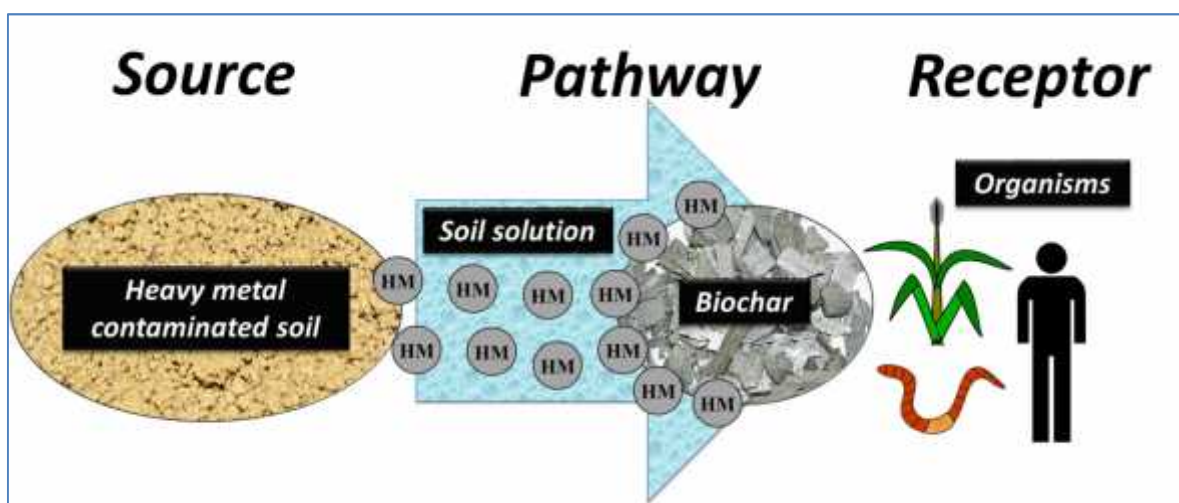
14 *1.1 Definitions*

15 Aside from naturally occurring elevated concentrations of heavy metals, associated with geological
16 weathering, anthropogenic activities have introduced both point and diffuse sources of heavy metals
17 to the environment. Mining, smelting, industrial processing and waste disposal have impacted on rural
18 and urban heavy metal concentrations alike, whilst fertilisers, herbicides and pesticides have
19 contributed to the prevalence of high concentrations of heavy metals in some agricultural systems
20 (Ross, 1994). In excessive concentration those heavy metals regarded as the most toxic and
21 environmentally damaging are Cd, Cr, Cu, Hg, Ni, Pb and Zn (Ross, 1994) but several of these,
22 especially those that are transition metals, are essential for plant metabolism (e.g. Cu, Ni, Zn). Heavy
23 metals are a group of elements with specific gravities of $> 5 \text{ g cm}^{-3}$ (Ross, 1994) which are both
24 industrially and biologically important (Alloway, 1995). Although not a heavy metal by chemical
25 definition, the metalloid Arsenic (As) is given the status of ‘risk element’ or ‘potentially toxic
26 element’ due to its carcinogenic effect on humans and toxicity to plants (Moreno-Jimenez et al, 2012).
27 Excessive concentration of heavy metals and As that, through direct or secondary exposure, causes a
28 toxic response to biota or humans resulting in an unacceptable level of environmental risk (Adriano,
29 2001; Abrahams, 2002; Vangronsveld et al., 2009) may be classed as pollutants. At ecosystem level
30 heavy metal and As behaviour, mobility and toxicity are complex and, since this book is concerned
31 with ‘environmental management’ we will focus on interactions between biochar and heavy metals in
32 the environment, taking an applied approach, but covering the main mechanisms by which biochars
33 affect heavy metals.

34 *1.2 Exposure and risk*

35 Heavy metals in soils and sediments are partitioned into a number of binding phases either (i)
36 incorporated in the solid phase, (ii) bound to the surface of the solid phase, (iii) bound to ligands in
37 solution or (iv) as free ions in solution. Only the free ions in solution (i.e. phase (iv)) can be taken up
38 by organisms and, therefore, only the free ions are bioavailable (Di Toro et al., 2001; Thakali et al.,
39 2006). In soils and sediments there is often disequilibrium between these four phases but the system
40 always moves towards equilibrium. If the concentration of metal ions dissolved in solution decreases
41 (for example, due to uptake), then the system re-equilibrates by more metals desorbing from the
42 surfaces and complexes to increase the amount of metal ions in solution until a new equilibrium is
43 reached. Likewise, if the surface area on which the metals can bind increases, then the system re-
44 equilibrates and metals are removed from solution and sorbed on the surfaces. In order to cause a
45 toxic effect, heavy metals must dissolve into solution, be taken up by an organism and be transported
46 to cells where a toxic effect can occur. This complex interaction between organisms and contaminants
47 can be described by a simple model known as the source-pathway-receptor model (Hodson, 2010).
48 The source of the pollution is a heavy metal (e.g. Pb), the receptor is a biological organism (e.g. an
49 earthworm), and the pathway is the process that leads to the contaminant being taken up by the
50 organism (e.g. desorption of Pb from the soil surface into the soil solution and diffusion across the gut
51 wall of the earthworm) (Sneddon et al., 2009). Therefore remediation of heavy metal contaminated
52 sites can be performed by (i) removing all or part of the source, (ii) eliminating the pathway, or (iii)
53 the modifying exposure of the receptor (Nathanail and Bardos, 2004). Thus remediation is achieved in
54 heavy metal polluted environments by reducing the bioavailability of the metals to the receptor
55 organisms (Semple et al., 2004) as lower metal bioavailability in biochar amended soils can result in
56 reduced metal uptake by biological organisms and a lower probability of toxic effects (Park et al.,
57 2011). Since heavy metals cannot be degraded or broken down (i.e. the source cannot be removed
58 without also removing the substrate), and receptors often cannot be isolated in complex ecosystems,
59 the only viable option to break the source-pathway-receptor linkage is to disrupt the pathway between
60 the contaminant and the receptor. It is the manipulation of bioavailability, rendering them more or less

61 available or mobile during environmental exposure that increasingly forms the basis of risk
62 assessment and classification of polluted areas, rather than absolute concentrations in soils (Swarjes,
63 1999; Fernandez et al., 2005). As such, risk based regulatory systems concern themselves with the
64 effect rather than concentration of heavy metals in soils (Beesley et al., 2011). Importantly, in the
65 legislative context of most nations, it is this potential to cause harm to humans or ecosystems (the
66 effect) that defines polluted sites and not the presence (concentration) of the contaminant per se. As
67 we have identified that the effect is more important than the concentration, if biochars are to be
68 deployed to heavy metal contaminated systems then their ability to break the pathway from source to
69 receptor becomes a focal point (Figure 1).



70

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

73

74 *1.3 Biochar as a remedial amendment*

75 Biochars are organic materials and organic amendments can render heavy metals immobile and non-
76 bioavailable by various physico-chemical means (Bolan and Duraisamy, 2003; Bernal et al. 2006),
77 disrupting the pathway of exposure and reducing risk. The application of organic amendments to
78 soils, from a remedial point of view, has typically been justified by their relatively low cost, compared
79 to 'hard' engineering solutions as well as their prevalence as a waste, ordinarily requiring other forms

80 of disposal (burial in landfill, incineration etc). The pyrolysis of organic materials to produce biochar
81 increases the surface area and effective cation exchange capacity (CEC) compared to the un-charred
82 source, but has a lower decomposition rate than non-charred materials, theoretically requiring more
83 infrequent additions to maintain efficacy than other, more labile organic materials, such as composts,
84 manures etc. Therefore the justification for the addition of biochar to environmental matrices is that
85 can work as a sorbent for metals in solution by establishing a new equilibrium between the
86 concentrations sorbed to surfaces and that in solution and its greater resistance to degradation should
87 render longevity of the effect. Before this chapter embarks on the detail of the mechanistic,
88 advantageous and disadvantageous functions of biochar an important premise should be noted; the
89 same features of biochar that render it suitable for remediation of heavy metal contaminated substrates
90 may at once deem it unsuitable for application specifically where the desired effect is to increase
91 availability of metals. The obvious example is Zn, an essential plant nutrient and important element to
92 fortify food and feed but, in excess, a toxicant. Rather than considering absolute increases or
93 decreases in heavy metal concentrations in substrates receiving biochars the emphasis should be
94 placed on bioavailability, mobility and specific requirements related to land use.

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

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106 2.1 *Direct mechanisms*

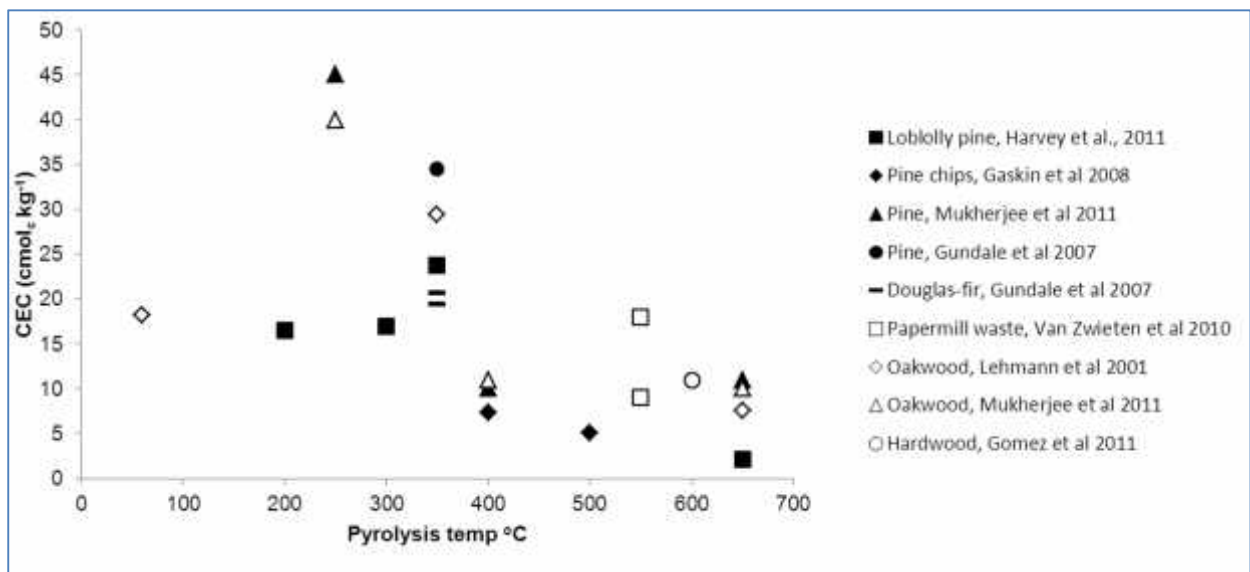
107 Direct mechanisms of heavy metal immobilisation by biochar include, but are not limited to,
108 fundamental chemical and largely ‘at-surface’ processes, such as adsorption and complexation. It is
109 widely acknowledged and discussed that biochars may both mobilise and immobilise heavy metals
110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

112

113 2.1.1 *Chemical sorption*

114 During exposure to the atmosphere, such as occurs during environmental weathering of freshly
115 produced biochars applied to soils, the oxygenation of biochar surfaces occurs (Cheng et al. 2006)
116 forming oxygen containing functional groups (e.g. carboxyl, hydroxyl, phenol and carbonyl groups)
117 on the massive internal surface area of the biochar (Liang et al. 2006, Lee et al. 2010, Uchimiya et al.
118 2010b, Uchimiya et al. 2011b). These functional groups induce a negative charge and a high cation
119 exchange capacity (CEC). CEC first increases, and then decreases, with increasing pyrolysis
120 temperatures (Gaskin et al. 2008, Lee et al. 2010, Harvey et al. 2011, Mukherjee et al. 2011); a peak
121 CEC of up to 45 cmol_c kg⁻¹ has been shown to occur between 250 and 350 °C, depending on source
122 material (Figure 2). The lower oxygen:carbon ratio and reduced abundance of oxygenated (acid)
123 functional groups lowers CEC after higher temperature pyrolysis (Cheng et al. 2006, Lee et al. 2010,
124 Harvey et al. 2011, Uchimiya et al. 2011a, Shen et al. 2012). The capacity for metal immobilisation
125 demonstrated by lower temperature (<500 °C), faster pyrolysis biochars (Beesley et al. 2010, Beesley
126 and Marmiroli 2011) is therefore, in part, a result of high CEC of these biochars; biochar with a
127 similar CEC to the soil it is applied to will not immobilise heavy metals as effectively as a biochar
128 with greater CEC than the soil (Gomez-Eyles et al (2011). Soils from tropical regions that are highly
129 weathered, acidic, low in organic carbon, and have their mineralogy dominated by kaolinite and Fe-

130 or Al-oxyhydroxides, yield a low cation exchange capacity (Fontes and Alleoni, 2006; Schaefer et al.,
131 2008). These soils are more readily phyto-toxic than soils from temperate regions due to their inherent
132 inability to retain heavy metals (Naidu et al., 1998; Melo et al., 2011). In such soils it is more likely
133 that adding biochar will increase CEC and be effective in immobilizing heavy metals. This was shown
134 by Jiang et al. (2012), where the addition of 3% and 5% of rice straw derived biochar to an Oxisol
135 (rich in Fe and Al-oxyhydroxides) increased the CEC, resulting a greater immobilization of Cu(II) and
136 Pb(II).



137

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

140

141 Surface sorption of metals corresponds directly with the release of H⁺ ions from the biochar
142 (Uchimiya et al. 2010b), but also of the release of Na, Ca, S, K and Mg (Uchimiya et al. 2011a) into
143 solution which indicates retention of metals on protonated (acidic) functional groups but also metal
144 exchange with other cations. In aqueous systems biochars usually show higher sorption capacity for a
145 single metal than for multiple metals, because there is competition for binding sites between metals.
146 Phosphorus- and sulphur-containing ligands influence the sorption of metal ions such as Pb and Hg
147 that have a stronger affinity for phosphates and sulphates, respectively (Cao et al. 2009, Uchimiya et

148 al. 2010b). Biochar surface oxygenated functional groups may impact on the oxidation of redox
149 sensitive metals whilst biochar application to soils also changes soil porosity and modifies soil
150 physical structure which may influence microscale redox condition. In these cases, redox sensitive
151 elements will change their speciation and geochemistry; for instance, As(III) is found in anoxic
152 environments (<100 mV) and is more mobile in soils and toxic than As(V) (Borch et al., 2010); Cr
153 can get oxidized in aerobic environments (>300-400 mV) and Cr(VI) is more toxic than Cr(III) (Kotas
154 and Stasika, 2000) whilst Cu(I) can also be found under anoxic conditions (Borch et al., 2010).
155 Elaborating on the case of Cr, the application of a low temperature (250 °C) coconut derived biochar
156 reduced Cr(VI) to Cr(III) completely after adsorption to biochar surface functional groups (Shen et al.
157 2012) whereas at higher pyrolysis temperature (350 °C and 600 °C) the same biochars removed less
158 Cr from solution and reduction occurred before adsorption.

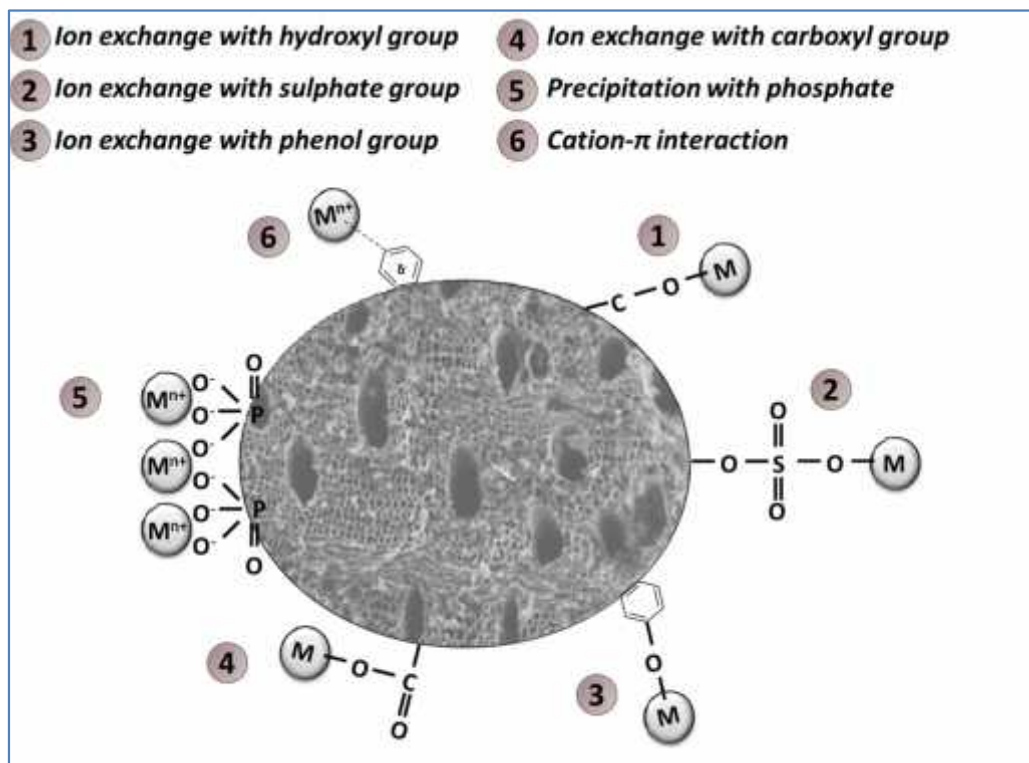
159

160 *2.1.2 Physical sorption*

161 Aside from a pure ion exchange between biochar surface and metal, a non-stoichiometric release of
162 protons and other cations from the surface of biochars has been found (Uchimiya et al. 2010b, Harvey
163 et al. 2011); more metals are adsorbed than protons or cations are released and sorption can occur at
164 pH below the point of zero net charge (Sanchez-Polo and Rivera-Utrilla 2002). The immobilisation of
165 metals by biochar cannot, in these instances, be purely attributed to ion exchange alone. Metal
166 sorption to biochars is an endothermic physical process (Kannan and Rengasamy 2005, Liu and
167 Zhang 2009, Harvey et al. 2011) and an electrostatic interaction between the positively charged metal
168 cations and π -electrons associated with either C=O ligands or C=C of a shared electron 'cloud' on
169 aromatic structures of biochars occurs (Swiatkowski et al. 2004, Cao et al. 2009, Uchimiya et al.
170 2010b, Harvey et al. 2011). Each carbon from a benzene ring donates an electron to the structure
171 which is then 'delocalized' resulting in an 'electron cloud' or a π -cloud above and below the planar
172 surface of that benzene ring. Metal cations are positively charged due to 'missing' electron(s) from
173 their d-orbitals so when a positively charged cation approaches the benzene ring, the electron cloud

174 becomes polarized and there is a weak electrostatic interaction between the negatively charged planar
175 surface of the benzene ring and the positively charged metal cation. A representation is given in
176 **Figure 3**. The bond energies of cation- π interactions are in the range 1 to 30 kcal mol⁻¹(Zarić 2003),
177 while the bond energies of transition metal-carbon bonds are typically an order of magnitude higher
178 (>100 kcal mol⁻¹) (Simoes and Beauchamp 1990).

179



180

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

182

183 An increase in pyrolysis temperature of biochars increases their aromaticity whilst the abundance of
184 oxygenated functional groups decreases (Harvey et al. 2011, McBeath et al. 2011). So, increasing
185 pyrolysis temperature increases the proportion of cations sorbed due to ‘weak’ electrostatic bonding
186 (i.e. cation- π interactions) and decreases the proportion due to stronger chemisorption (i.e. by cation
187 exchange). Therefore, lower temperature pyrolysis should result in effective short term metal
188 immobilisation due to the formation of inner and outer sphere complexes with oxygenated (acid)

189 functional groups, but with time these may diminish in the soil environment (within the first 90 days
190 after application; Zimmerman et al. 2011). Thereafter there may be a release of metals back into
191 solution. Higher pyrolysis temperatures result in a negative surface charge that should remain stable
192 for longer but metals will be weakly (physically) adsorbed to biochar surfaces and immobilisation
193 easily reversed. Melo et al. (un-published data) determined, in aqueous batch experiments, that biochar
194 derived from sugar cane pyrolysed at 700 °C increased Cd and Zn sorption nearly 4-fold, compared to
195 that produced at 400 °C. When the same biochar was applied to soil the effect of temperature on metal
196 sorption was only observed in a sandy soil, and no difference was shown in a clay rich Oxisol.

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

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

200

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. <u>Dairy manure biochars showed strong Pb retention capacity.</u>	(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 sorptive capacity than soil without biochar. <u>High oxygen-containing functional groups associated with lower temperature biochars enhanced the heavy metal sequestration ability of biochar when added to soil.</u>	(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). <u>Adding more biochar to heavy metal contaminated solutions can increase metal removal, but aggregation of biochar particles can reduce efficiency.</u>	(Chen et al., 2011)

201

202 *2.1.3 Precipitation*

203 Biochar source materials are unlikely to be 100% organic in nature and contain minerals which
204 remain entrained in the biochar matrix after pyrolysis resulting in a non-organic (or ash) fraction in
205 biochar. Source material mineral contents can range from <1% for woody biomass, up to ~25% for
206 manure or crop residues. Following high temperature pyrolysis the ash content of biochars can be
207 upto 50% for manure-derived, or 85% for bonemeal-derived biochars (Amonette and Joseph 2009).
208 Thus mineral salts of Na, K, Ca, Mg, P, S, Si and C are found in abundance in the ash fraction, usually
209 in an oxidised form, their concentrations of which increase with pyrolysis temperature (Gaskin et al.
210 2008). Uchimiya et al. (2010b) found lead phosphate precipitates effective in immobilising Pb in a
211 broiler litter-derived biochar whilst precipitation of Pb with phosphates contributed to as much as
212 87% of total Pb sorption to a dairy manure-derived biochar (Cao et al. 2009). Lead-phosphate
213 minerals contributing to sorption in biochars include hydrocerussite and hydroxypyromorphite (Cao et
214 al. 2011), lead phosphate, and lead hydroxyapatite (Chen et al. 2006). Lead-phosphate minerals have a
215 very low solubility so their formation could result in increased capability of biochars to adsorb higher
216 concentrations of Pb, compared to other divalent cations (Namgay et al. 2010, Uchimiya et al. 2010b,
217 Trakal et al. 2011). Precipitation may also occur with other metals such as Cu, Cd, or Zn which
218 precipitate as insoluble phosphate and carbonate salts, mainly at high pH (Lindsay, 1979) (Figure 3).

219

220 *2.2 Indirect mechanisms [effects]*

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

226

227 2.2.1 pH changes

228 It is widely reported that addition of biochars to soils has resulted in pH increases (Yamato et al.,
229 2006; Chan et al., 2007; Uchimiya et al., 2010a; Van Zweiten et al., 2010; Bell and Worrall, 2011);
230 metal solubility changes according to pH, generally being lower at higher pH. For metalloids the
231 geochemistry is somewhat opposing, with higher pH conditions reducing retention (Adriano, 2001).
232 Arsenic solubility and availability increases when pH in soils rises, in most cases, since arsenic binds
233 to positively charged surfaces such as Fe and Mn oxides in soils and anion exchange capacity (AEC)
234 is inversely related to pH (Moreno-Jiménez et al., 2012). Cationic metals (e.g. Cu, Zn, Pb), which are
235 bound to the negatively charged surfaces of soils such as clay minerals and organic matter, increase in
236 solubility as pH decreases because CEC is positively related to pH. When the soil pH is increased
237 metals are increasingly bound to negatively charged surfaces. Contrary to cationic metals, As is
238 released from positively charged soil surfaces when the soil pH is increased; an increase of soil pH
239 has thus been reported to increase As mobility and uptake by organisms (Fitz and Wenzel 2002,
240 Moreno-Jiménez et al. 2012). Antimony (Sb) and molybdenum (Mo) geochemistry is more similar to
241 As than to metals (showing anionic and uncharged species in soils), so we might expect similar pH
242 effects, although to date there is not enough information to draw conclusions regarding the effect of
243 biochar on Sb and Mo.

244 Studies have reported that soil pore water pH increases after biochar application to circumneutral and
245 acidic contaminated substrates (Beesley et al. 2010, Beesley et al. 2011; Beesley and Dickinson,
246 2011; Karami et al, 2011; Zheng et al, 2012; Beesley et al. 2013), explaining changes in metal and As
247 mobility in pore water. Various other studies report a soil liming effect of biochars, often resulting
248 from alkaline biochars (Namgay et al, 2010; Fellet et al, 2011; Sizmur et al, 2011). Sizmur et al
249 (2011) noted an especially beneficial increase in soil pH of more than 4 units when a nettle-derived
250 biochar was added to a mine soil (pH 2.7). Jones et al (2012) report a liming effect of adding woody
251 biochar (450 °C) to a rotational maize/grass planted agricultural soil (pH increased from 6.86 to 7.18
252 after 2 years, but back to 6.6 after 3 years). The pH of biochar recovered from the soil (aged)
253 decreased by 2 units over the 3 year experimental duration, showing that biochars liming effect may

254 be transient, thus the effects on metals and metalloids may also be transient. A summary of pH effects
255 of biochars on heavy metal extractability, by different methods, following biochar amendment to
256 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. <u>Biochar most effective for reducing Cd bioavailability and leachability.</u>	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. <u>Biochar can rapidly immobilise and retain Cd and Zn leached from soil.</u>	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. <u>Biochar effective for sustained reductions in pore water Cu and Pb concentrations.</u>	Karami et al. (2011)

258 2.2.2 Organic matter/soluble carbon

259 Biochar applied to soils can increase concentrations of organic matter, especially water-extractable
260 fractions (Lin et al. in-press). Increases in stable organic matter, priming effects (where the input of
261 new organic matter stimulates degradation of existing organic matter in soils) both positive and
262 negative and increased or decreased dissolved organic carbon (DOC) concentrations have been noted
263 as results of biochar application to soils (Cheng et al, 2008; Hartley et al, 2009; Novak et al, 2009;
264 Gomez-Eyles et al, 2011; Bell and Worrall, 2011; Zimmerman et al, 2011; Zheng et al, 2012). Since
265 several metals (eg Cu) form stable complexes with organic matter, adding biochars especially to soils
266 low in organic matter, such as those in arid or semi-arid regions, could result in the occurrence of
267 stabilised organo-metal complexes. However, mineralisation of organic matter in soils results in the
268 often considerable generation of dissolved organic matter/carbon; even in short term column leaching
269 experiments high concentrations of DOC have been leached from biochars (Beesley and Marmiroli,
270 2011), although it is debatable whether this is the result of mineralisation *in-situ* or leaching of
271 unstable surface organic fractions on biochar surfaces, possibly complexed to mineral fractions in the
272 ash. In biochar amended soils co-mobilisation of DOC and metals, especially Cu and As, have been
273 noted both in pot trials (Beesley et al, 2010) and in the field (Beesley and Dickinson, 2011). In the
274 case of Beesley and Dickinson (2011), a hardwood biochar (400°C) was applied both as a surface
275 mulch (depth of 30 cm top dressing) and mixed (in lysimeters) into an urban soil. Both application
276 methods induced increases in DOC concentrations in soil pore waters (<100 to >300 mg l⁻¹) with the
277 surface application affecting pore water DOC concentrations at up to 25 cm soil depth below the
278 biochar application. In other field (Jones et al, 2012) and pot (Karami et al. 2011) studies there were
279 no significant difference in DOC concentrations attributed to biochar application.

280 The mechanisms for the co-mobilization of As and soluble organic matter are less clear than for
281 metals, although Mikutta and Kretzschmar (2011) observed ternary complex formation between
282 arsenate and ferric iron complexes of humic substances which could be responsible for the increasing
283 As mobility with increasing DOC. Alternatively, DOC may compete with arsenic directly for
284 retention sites on soil surfaces (Fitz and Wenzel 2002), resulting in an increase in soluble As with

285 increasing concentrations of DOC (Hartley et al. 2009). Arsenic is methylated in soil in the presence
286 of (non-charred) organic matter (Oremland and Stolz 2003) and methylated As species are less toxic
287 than inorganic ones (Hughes 2002), but As speciation in biochar amended soils is yet to be reported.

288

289 *2.2.3 Availability of phosphorus*

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

304 Phosphate is chemically analogous to As (V), so increases in P availability result in the release of As
305 from soil surfaces, into solution and uptake into plants via phosphate ion channels (Meharg and
306 Macnair 1992). Although arsenate is desorbed from soil surfaces by phosphate (Cao et al., 2003), it is
307 not always available for plant uptake since P and As will compete again for the same root transporter
308 (Meharg et al. 1992). Therefore, As (V) uptake into plants can be avoided by high concentrations of
309 soluble P (Moreno-Jiménez et al. 2012) but if the soluble fraction of As is not taken up by plants,
310 there is a risk it may leach to surface and groundwaters (Fitz and Wenzel 2002). Phosphate rich

311 compounds applied to Pb contaminated soils have also been found to reduce Pb bioavailability
312 (Brown et al, 2003). In contaminated mine soils Karami et al (2011) noted a decrease in available P
313 after biochar amendment to a mine soil in a pot experiment, suggesting that phosphate precipitation
314 was responsible for large reduction in soluble Pb measured in pore water. Fellet et al (2011) noted that
315 an orchard prune residue biochar (550°C) increased total P when amended into a mine soil as this
316 biochar's total P concentration was ~45 times greater than that of the soil. Beesley et al (2013) also
317 found pore water P concentrations of the same biochar to be ~14 times greater than the contaminated
318 mine soil it was applied to in a pot trial, suggesting biochar as source of soluble P.

319

320 *2.2.4 Reduction/oxidation (Redox)*

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

330

331 *2.2.5 Modification of biochars*

332 Biochars have heavy metals inherent within their structure, derived from their source material, which
333 may be accumulated and concentrated in ash fractions during pyrolysis. These may contribute to a
334 heavy metal loading in soils they are applied to as well as reducing their metal sorption capacity. One
335 of the most comprehensive screening exercise to determine heavy metal concentrations of biochars

336 was reported by Freddo et al. (2012) who analysed heavy metal concentrations in nine dissimilar
337 biochars (rice straw, maize, bamboo, redwood and an unspecified softwood produced at 300-600 °C);
338 other studies are summarised in Table 3, with comparison to typically measured soil heavy metal
339 concentrations across Europe. In all cases some biochars exceed the median European topsoil total
340 concentrations suggesting that they may contribute heavy metal loadings to soils, but reported
341 aqueous concentrations are typically very low implying low leaching risk from entrained heavy
342 metals. Quilliam et al (un-published data) amended agricultural pasture soils with biochar derived
343 from Norway spruce (*Picea albies* (L.)) which had been pressure treated with a Cu based wood
344 preservative several years prior to pyrolysis, comparing it to the same biochar that had not been Cu
345 treated. Treated wood biochar had greater pseudo-total Cu and bioavailable (CaCl₂ extraction) Cu
346 concentrations than untreated wood biochar. Debela et al. (2012) experimented with manipulation of
347 source material, co-pyrolysing sawdust and a metal contaminated soil, thereafter determined metal
348 leachability. Their results showed that leaching of Cd and Zn could be reduced by up to 93%, and Pb
349 leaching by up to 43%, the latter without added sawdust. Contrastingly As leaching was enhanced up
350 to 10 fold by the co-pyrolysis process. Mendez et al. (2012) produced biochar from sewage sludge to
351 determine whether the pyrolysis process could render reduced leachability and bioavailability of heavy
352 metals from the sludge, for application to agricultural soils. The pseudo-total concentrations of metals
353 increased after pyrolysis, attributed to their accumulation in the ash fraction, but plant-available
354 concentrations of Cu, Ni, Pb and Zn and the mobility of Cd additionally decreased. A degree of
355 caution should therefore be exercised when applying biochars made from source materials
356 contaminated with heavy metals, to soils to avoid introducing toxicity issues.

357 Biochars may be modify either during production or when applying them to soils using inorganic
358 amendments, a common practice when napplying other organic amendments to soils to produce better
359 results than applying the amendments individually (Mench et al. 2003). Iron oxides (FeOx) and other
360 metal oxides (Al, Mn etc) are effective binding surfaces for metals and metalloids such as As, Hg, Se,
361 Cr, Pb, etc, and are used in remediation of heavy metal contaminated substrates (Warren et al. 2003,
362 Waychunas et al. 2005). The formation of chemical bonds with surface atoms (chemisorption),

363 forming covalent, ionic or hydrogen bonds by inner and outer sphere complexation retains metals
364 (Waychunas et al. 2005). Iron-oxides effectively immobilise As (Dixit and Hering 2003). Iron-oxide
365 impregnated sorbents have been used in waters and activated carbons have been impregnated with
366 iron-oxide to enhanced the iron-oxides effectiveness (ie an increase surface area) (Reed 2000,
367 Vaughan and Reed 2005). Soaking the source material with iron chloride solution before pyrolysis
368 entrains the iron-oxide into the biochar structure (Chen et al. 2011a). Alternatively, the biochar may
369 be soaked in an iron solution after pyrolysis (Muñiz et al. 2009, Chang et al. 2010). The cost of
370 producing these biochars will be greater than unmodified biochar, so they may only be suitable for
371 specific small scale applications. Lin et al. (2012) experimented with the incubation (aging) of an Fe
372 rich soil (ferrosol) with biochars, suggesting the observed retention of Al and Fe during the ‘aging’
373 indicated the formation of mineral-biochar (organic) complexes related to decreasing surface C and
374 corresponding increasing surface oxidation of the biochars. Arsenic is widely known to be
375 immobilised by Fe rich materials as they provide anion exchange sites (Masscheleyn et al. 1991), so
376 optimising biochar for metal and As retention may be possible by modifying its characteristics during
377 production or pre-application.

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

Heavy metal/metalloid	<i>Background European topsoil concentrations (mg kg⁻¹)^a</i>	Range of concentrations measured in biochars (mg kg ⁻¹)	Extractant	As reported in reference
As	6	0.01-8.8 <100 (µg l ⁻¹) <0.1 (µg g ⁻¹)	Acid Aqueous	Hossain et al. (2010); Freddo et al. (2012); Bird et al. (2012) Beesley & Marmiroli (2011); Beesley et al. (2013) Zheng et al (2012)
Cd	0.2	<0.01-8.1 <100 (µg l ⁻¹) 0.01 (µg g ⁻¹)	Acid Aqueous	He et al. (2010); Hossain et al. (2010); Freddo et al. (2012); Bird et al. (2012); Gasco et al. (2012); Knowles et al. (2011) 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 <0.01- 0.18 70	Acid/Base Aqueous XRF	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) Graber et al. (2010); Chen et al. (in-press) 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 <0.01-0.95 <300 (µg l ⁻¹) 6.3-6.5 (µg g ⁻¹) 70	Acid/Base Aqueous XRF	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) Graber et al. (2010); Chen et al. (in press) Zheng et al. (2012) Beesley & Marmiroli (2011) Hartley et al. (2009)

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

384 **3. Toxicity**

385 *3.1 Phytotoxicity*

386 *3.1.1 Metals*

387 Experiments involving plants and biochars can be grouped according to those concerned with
388 enhancing biomass only (i.e. biochar as a fertiliser or growth medium) or also managing trace
389 element/nutrient bioavailability. Enhanced plant growth due to liming effects, increased water holding
390 capacity and improved soil structure have been reported after the amendment of agricultural soils with
391 biochars (Chan and Xu 2009; Blackwell et al., 2009; Atkinson et al., 2010 and Sohi et al., 2010) but
392 such benefits are often only seen when fertiliser is added together with the biochar soil amendment,
393 suggesting that biochar alone is not able to stimulate re-vegetation (Yamato et al., 2006; Chan et al.,
394 2007; Steiner et al., 2007; Asai et al., 2009; van Zwieten et al., 2010). In a review of the suitability of
395 biochars for remediating contaminated soils Beesley et al. (2011) suggest that the combination of
396 biochars with composts, manures and other amendments may be the most effective way to revegetate
397 bare soils.

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

410 to remediation attempts (Beesley et al. 2011). The results of selected studies reporting heavy metal
411 uptake to plants in soils amended with biochars are reported in Table 4.

412 The possibility exists that, depending on source material composition, biochars themselves are phyto-
413 toxic. In this case, even if their effects were to immobilise large concentrations of heavy metals, seed
414 germination would still be inhibited. Gell et al. (2011) screened 8 biochars for their phytotoxicity to
415 lettuce (*Lactuca sativa L.*), raddish (*Raphanus sativus L.*) and wheat (*Triticum aestivum L.*)
416 (germination shoot and root elongation measurements) finding that only one biochar, produced from
417 pig co-digestate, was significantly phytotoxic due to a high soluble salt content or water-soluble
418 phytotoxic organic compounds . Beesley et al. (2013) took another approach, loading a nutrient
419 solution with various proportions of an orchard prune residue biochar and measuring germination and
420 shoot elongation of tomato (*Solanum lycopersicum L.*), with the aim of discovering if there was a
421 toxic threshold after which adding more biochar adversely affected germination. They found that
422 germination success was decreased relative to the amount of biochar added to nutrient solution.
423 Biochar added at 0, 1, 30, 50 and 100% resulted in 100, 80, 60. 60 and 0% germination rates
424 respectively. This suggests that biochar may itself be phytotoxic if added in high doses, although the
425 effect of nutrient immobilisation by biochar may also explain this effect. Brennan and Moreno (*un-*
426 *published data*) tested the effect of two biochars (produced at 350°C) applied to Hg-polluted soil
427 (>1000 mg kg⁻¹) by assessing germination success of *Lolium. perenne*. Pine-derived biochar slightly
428 increased plant germination whereas olive-derived biochar (with greater ash fraction than pine)
429 doubled the germination, but neither had an effect on pH or electrical conductivity of soil. Biochar
430 therefore may decrease phytoavailability and phytotoxicity in Hg-polluted soils, but the evidence base
431 is as yet small to draw any conclusions to this effect.

432

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434

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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 350°C applied by mixing into soil at 20% (vol:vol) and 11 crops grown; beetroot (<i>Beta vulgaris</i>), spinach (<i>Spinacia oleracea</i>), radish (<i>Raphanus sativus</i>), broccoli (<i>Brassica oleracea</i>), carrot (<i>Daucus carota</i>), leek (<i>Allium ampeloprasum</i>), onion (<i>Allium cepa</i>), lettuce (<i>Lactuca sativa</i>), corn (<i>Zea mays</i>), tomato (<i>Solanum lycopersicum</i>), and courgette (<i>Cucurbita pepo</i>).	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). <u>Biochar alone ineffective at increasing biomass and heavy metal uptake.</u>	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°C mixed into Cd spiked soil at 0.5 and 5% (w:w) and wetland rush species (<i>Juncus subsecundus</i>) 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. <u>Biochars effective for Cd immobilisation, and to reduce uptake, but not promote growth of this wetland species.</u>	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' <i>Chenopodium quinoa</i> 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 °C, 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. <u>Biochar effective to reduce bioavailable Cu and mitigate Cu toxicity, alleviating plant stress symptoms.</u>	Buss et al. (2012)

437 3.1.2 Metalloids

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

456

457 3.2 Toxicity to soil organisms

458 Earthworms are important soil organisms because of their role in (i) increasing microbial biomass and
459 diversity, (ii) creating drainage channels in the soil, (iii) accelerating the rate of organic matter
460 decomposition, and (iv) increasing nutrient availability to plants. Earthworms are therefore often
461 referred to as soil ecosystem engineers (Jones et al., 1994; Jouquet et al., 2006) and key species
462 (Jordán, 2009) in the soil environment. Special attention to earthworms and their behaviour in

463 contaminated soils has been paid because ecosystem functioning is adversely affected by their
464 absence (Smith et al., 2005). Therefore, the majority of studies carried out to assess the effect of
465 biochar on the toxicity of heavy metals to soil organisms have focused on earthworms, in particular
466 the soil ecotoxicology model earthworm species *Eisenia fetida*. Gomez-Eyles et al. (2011) report that
467 the uptake of Cu by *E. fetida* was decreased by the amendment of a hardwood biochar because the
468 biochar decreased the concentration of soluble organic carbon. Cao et al. (2011) report that the
469 addition of a dairy manure biochar decreased Pb bioaccumulation in *E. fetida* by up to 79% because
470 the phosphate minerals in the biochar precipitated the Pb as insoluble hydroxyapatite.

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

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

482

483 3.2.1 Do soil organisms ingest biochar?

484 The ingestion of biochar by soil organisms is dependent upon the size of the biochar particles. Many
485 laboratory experiments investigating either the effect of biochar on soil organisms or investigating the
486 use of biochar as a remedial treatment grind the biochar to a fine powder (e.g. sieved to <2 mm;
487 Gomez-Eyles et al. (2011)) before addition to experimental vessels. However, grinding biochar to a
488 fine powder is unlikely to be replicated during field studies because of (i) the energy required to grind

489 the biochar into a powder, (ii) the loss of biochar from the surface of the soil upon application due to
490 wind, and (iii) the increased risk that airborne biochar powder may cause irritation by inhalation or
491 dermal contact.

492 There is considerable evidence that the geophagous tropical earthworm *Pontoscolex corethrurus*
493 consumes biochar particles in soils mixed with char (Ponge et al., 2006; Topoliantz and Ponge, 2003,
494 2005). Rather than ingesting the biochar particles alone, the earthworm ingests a mixture of biochar
495 and mineral soil particles. This is achieved by pushing aside the lighter biochar particles and
496 selectively ingesting the soil (Topoliantz and Ponge, 2003). The earthworm favoured the mixture of
497 biochar and soil to either biochar alone or soil alone (Ponge et al., 2006). There is no evidence that the
498 earthworm uses biochar as a source of nutrition (Topoliantz and Ponge, 2003). Conversely,
499 Collembola can consume carbonised materials and complete their life cycle using biochar as their sole
500 food source (Salem et al., 2013).

501

502 3.2.2 *Effect of earthworms on the bioavailability of metals*

503 The passage of soil through the gut of an earthworm increases the mobility (and thus the
504 bioavailability) of heavy metals in contaminated soils (Sizmur et al., 2011a). This increase is achieved
505 largely due to an increase in the solubility of organic carbon (Sizmur et al., 2011a; Sizmur et al.,
506 2011b); **Figure 4**. Therefore, considering the evidence presented above suggesting that earthworms
507 ingest biochar particles, one can speculate that the activity of earthworms in contaminated soil
508 remediated with biochar may either mix the biochar with the mineral soil and promote the sorption of
509 heavy metals on the surface of the biochar, or change the chemistry of the soil-biochar mixture and
510 cause the desorption of heavy metals from the biochar surfaces. Each of these possibilities may be
511 assisted by fragmentation of the biochar, which can increase effective surface area either for
512 adsorption of heavy metals or [microbial activity and] generation of DOC.

513 Beesley and Dickinson (2011) found that the addition of *Lumbricus terrestris* earthworms to soil
514 contaminated with heavy metals decreased the concentration of dissolved organic carbon and, thus

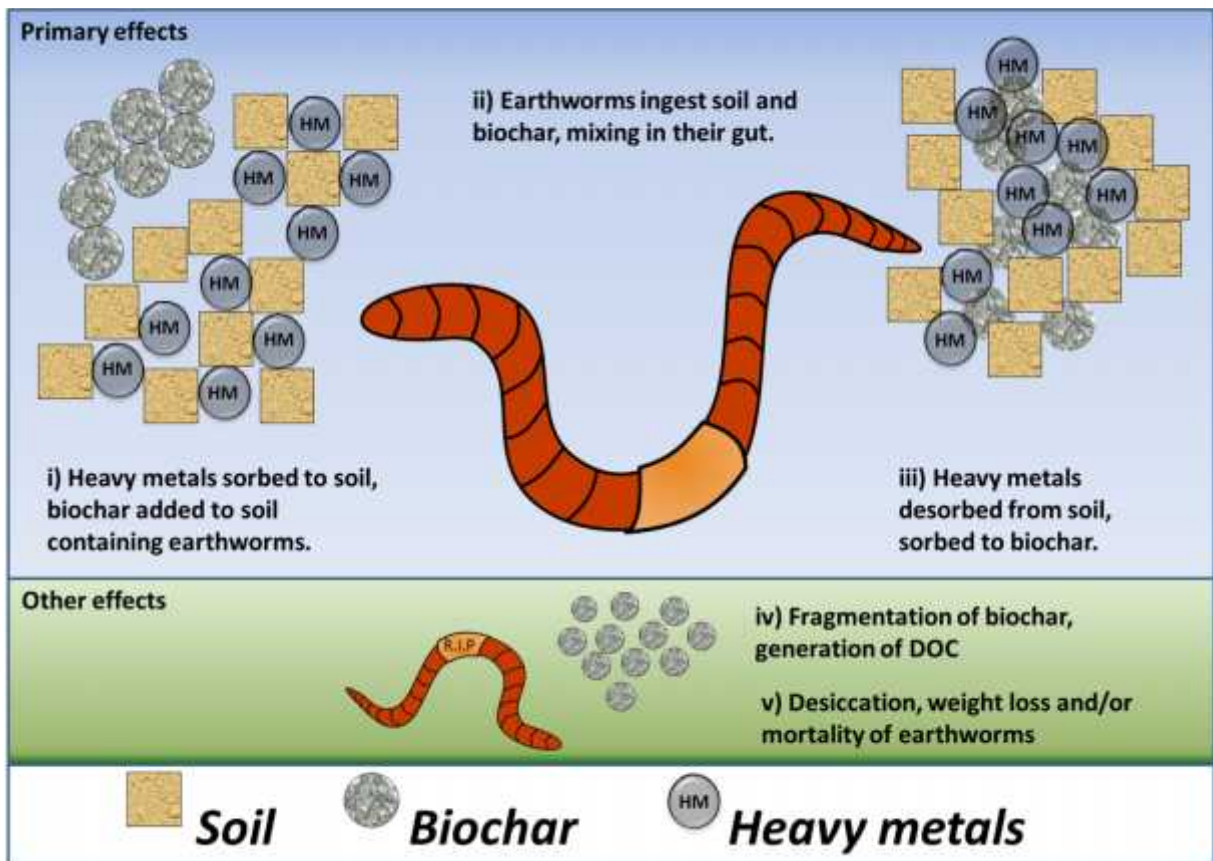
515 decreased the mobility of As, Cu, and Pb in biochar amended soil. Using the same species of
516 earthworm, Sizmur et al. (2011d) found that the addition of earthworms to contaminated soil
517 remediated with biochar had no effect on the mobility or bioavailability of Cu, Pb or Zn. The effect of
518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

528

529 3.2.3 Effects of biochar on earthworm activity

530 Manures applied to agricultural soils often contain elevated concentrations of heavy metals that
531 accumulate in the soil (Nicholson et al., 2003). By pyrolysing the manure to biochar the organic
532 content is decreased and the concentration of the (non-volatile) heavy metals is greater in the resulting
533 biochar compared to the feedstock (Cantrell et al., 2012). Liesch et al. (2010) investigated the toxicity
534 of two different biochars to the earthworm *E. fetida*. While the concentrations of heavy metals (As,
535 Cu, Zn) in the poultry litter derived biochar were high (52, 177 and 1080 mg kg⁻¹ respectively) it was
536 concluded that these were sub-lethal concentrations. Instead, mortality occurred after high application
537 rates of poultry litter derived biochar because of the presence of ammonia gas and an elevated soil pH.
538 Both Li et al. (2011) and Gomez-Eyles et al. (2011) report weight loss by *E. fetida* in soil amended
539 with wood chips, while Liesch et al. (2010) report no significant effect. There is evidence to suggest
540 that the reason for weight loss and avoidance of biochar amended soils by *E. fetida* is due to

541 desiccation and that desiccation can be overcome by pre-wetting biochar prior to application (Li et al.,
542 2011). These short term experiments reveal that although some types of biochar (particularly biochars
543 derived from manures) may be toxic immediately after application, the long term effect of biochar on
544 the earthworm populations and activity is rather negligible (Weyers and Spokas, 2011).



545

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

547 **4. Remediation**

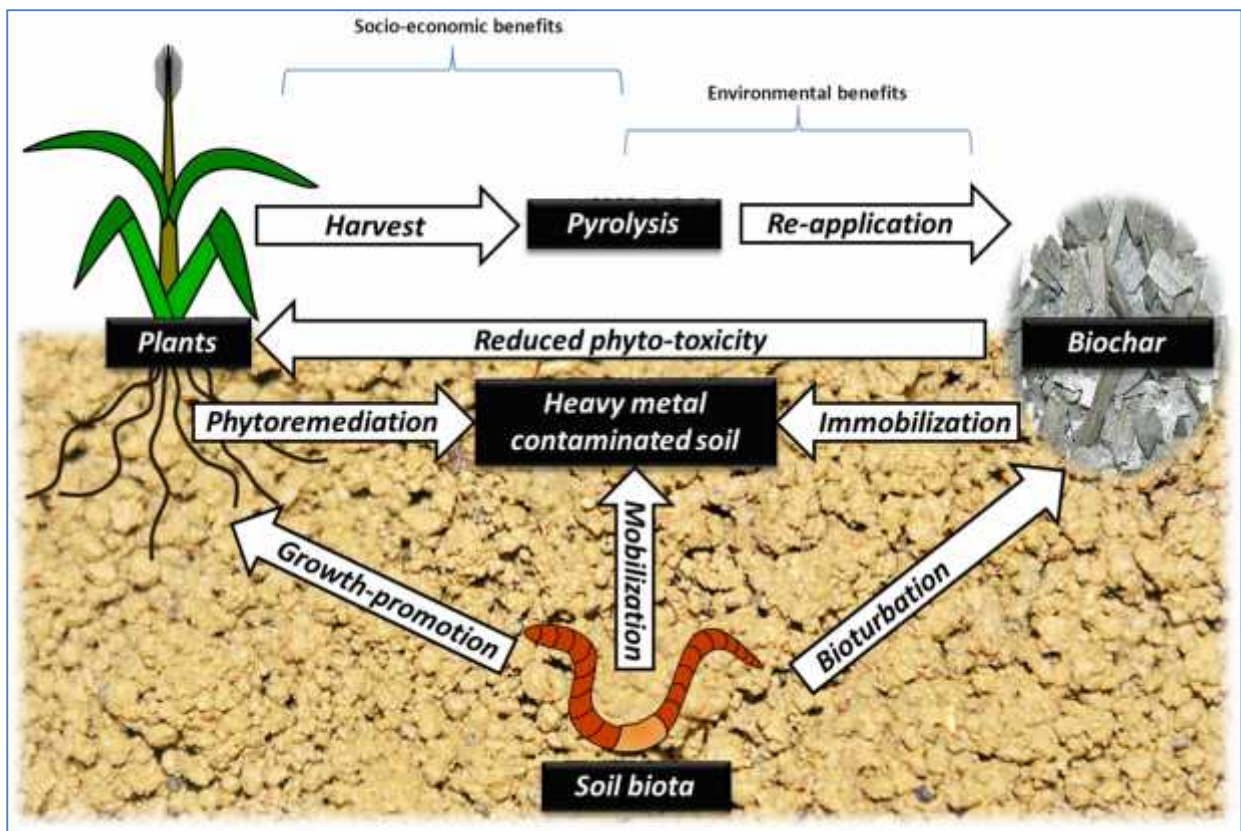
548

549 *4.1 Degraded lands and their functionality*

550 Technosols are soils containing or covered by a large quantity of man-made products and are now a
551 recognised soil type (World Reference Base classification (WRB); Rossiter, 2007), thus afforded the
552 same importance for their functionality as other soils. These soils vary widely in their levels of
553 disturbance and heterogeneity because of human intervention and their profiles are so strongly
554 impacted by direct human action that the original horizon sequences may be all but completely
555 destroyed (Hollis, 1991) often resulting in a characteristic lack of topsoil (Ennis et al. 2012). This is
556 the case where soils have been deepened historically through waste disposal (Davidson et al., 2006;
557 He and Zhang, 2006) and/or contain a predominance of artefacts of anthropogenic origin, not all of
558 them benign. Contaminated, industrially impacted, mining and urban lands are not only characterised
559 by young, poorly developed soils but by their sparse or absence of vegetation cover (Mench et al.
560 2010) often associated with a pollution legacy. Re-vegetation of contaminated soils is key to its
561 stabilisation and remediation (Arienzo et al. 2004; Ruttens et al. 2006), as the presence of a vegetative
562 cover over bare soil reduces the potential for migration of contaminants to proximal watercourses or
563 inhalation by receptor organisms (Tordoff et al. 2000), as well the restoration of natural cycling of
564 organic matter and nutrients. Barriers to re-vegetation and thus remediation are phyto-toxic
565 concentrations of heavy metals-in this context those which plants may not be able to immobilise at the
566 root level (Pulford and Watson, 2003)-and poor functionality (organic matter [cycling], nutrient
567 status, structure of soils, water-holding capacity).

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

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



585

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

589

590 4.2 Former industrial sites

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

596 *Case study 1: Northwest England (UK)*

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

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615 *Case study 2: North Midlands (UK)*

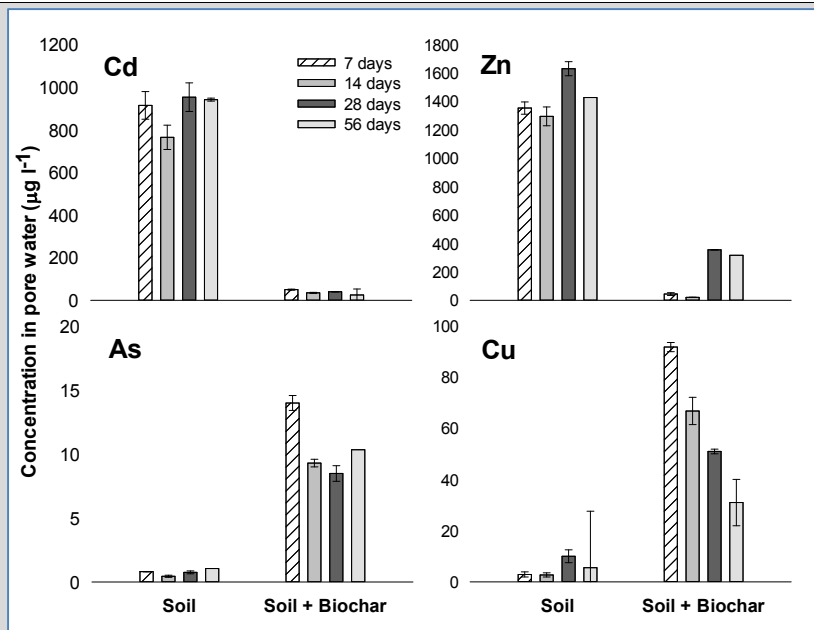
616 *A similar evaluation to that of Hartley et al (2009), albeit without plant uptake, was carried out with*
617 *acidic (pH 5.5) sediment derived soil from a canal bank site in the Midlands region of England*
618 *(Beesley et al, 2010). At this site suspected heavy metal rich effluent had been discharged into the*
619 *canal and concentrated Cd and Zn in the sediment. Soil was amended with hardwood derived biochar*
620 *(400°C) at 30% (vol:vol) and pore water concentrations of As, Cd, Cu and Zn measured over a 56*
621 *day period. In the case of this site it was hypothesised that biochar may arrest a leaching and toxicity*
622 *risk identified previously by considerable vertical mobility of Cd and Zn down the profile as a result*
623 *of a soluble or weakly surface sorbed fractions of metals. A Ryegrass (*Lolium perenne*) root*
624 *emergence toxicity test was used to indicate whether biochar could be effective in reducing*
625 *phytotoxicity and promoting re-vegetation of the soil (Moreno-Jimenez et al. 2011).*

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

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

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

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649 *Case study 3: South England (UK)*

650 *A facet of the assessment of remediation success, in terms of restoring soil functionality, is measuring*
651 *invertebrate populations' size and diversity; this can also be used as a proxy for relative resilience of*
652 *colonising populations to introduced, or non-native soil constituents, such as biochars. Functional*
653 *soils should be able to support diversity of microbial and invertebrate populations. However it is*
654 *necessarily difficult to develop universal biological indicators for this purpose (Harley et al, 2008).*
655 *Gomez-Eyles et al (2011) amended a multi-element contaminated soil (As, Cd, Co, Cu, Ni, Pb and Zn)*
656 *taken from a gasworks site in the south of England (UK) with a hardwood biochar (600oc) on a 10%*
657 *(w:w) basis. During the 56 day pot experiment pore water concentrations of heavy metals, arsenic,*
658 *and WSOC (water soluble organic carbon; DOC) were measured. Half of the treatments received 10*
659 *adult earthworms (E. fetida), and half did not. No additional organic material was added. It has been*
660 *suggested that adding biochar alone, without additional organic materials may not be able to*
661 *effectively meet the needs of gross pollutant immobilisation and net remediation goals (Beesley et al,*
662 *2011), including restoring and maintaining soil functionality. Gomez-Eyles et al (2011) found that the*
663 *earthworm weight loss after 28 days exposure to biochar was significantly greater than without*
664 *biochar. After 56 days exposure weight loss had further increased significantly. However, as*
665 *earthworms effectively mobilised Co, Cu and Ni, but adding biochar immobilised these metals, it*
666 *could be suggested that biochar's role in this situation was to mitigate the effects of earthworms on*
667 *pollutant mobility. Furthermore earthworm tissue concentrations of most measured metals were not*
668 *significantly increased by adding biochar. Thus, if biochar was added solely to this soil heavy metal*
669 *mobility could be mitigated, but this would make no attempt to restore soil functionality. Adding*
670 *earthworms alone mobilised heavy metals, so it is efficacious to combine earthworms and biochar.*

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674 *4.3 Former mine sites*

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

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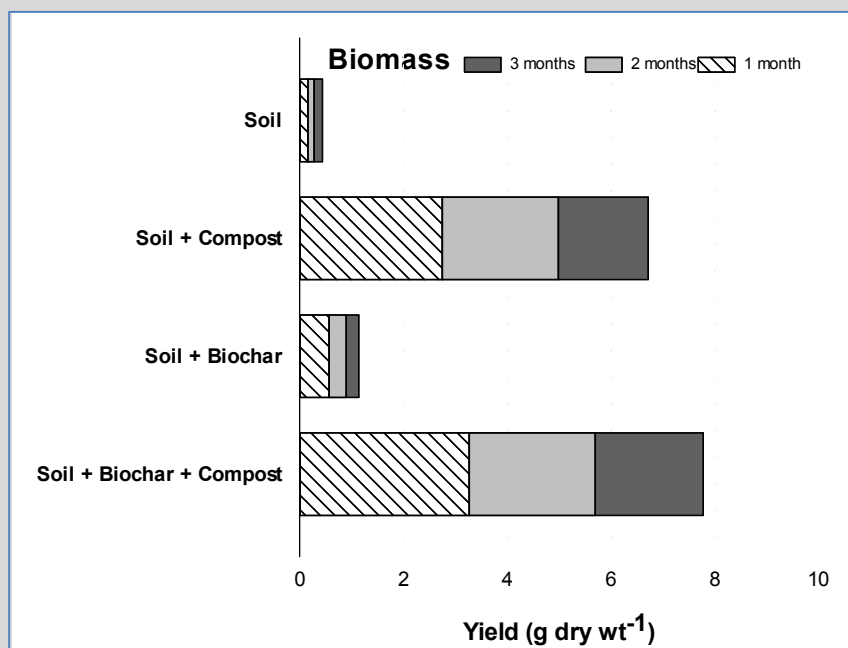
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699 Case study 4: Copper and Lead contaminated site (UK)

700 Karami et al (2011) investigated Cu and Pb mobility (by pore water collection) and uptake by
701 Ryegrass (*Lolium perenne*) in a pot experiment using a very heavily Pb contaminated (pseudo-total
702 >20000 mg kg⁻¹) soil from a former mine site in Cheshire, England (UK) mixed with 20% (vol:vol)
703 hardwood biochar (400°C), with and without the addition of 30% (vol:vol) green waste compost. The
704 investigation was focussed on determining i) biochar effects on metal mobility and ii) the impact of
705 biochar on ryegrass biomass and metal transfer to vegetation. All three treatments (biochar, compost,
706 and biochar plus compost) reduced Cu and Pb mobility (concentration measured in pore water
707 samples), but had differential effects on ryegrass biomass and uptake; in general biochar alone failed
708 to promote increased biomass yield compared to the control, whereas combining it with compost did
709 so to a greater extent than with only compost (Figure 7).



710

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

713

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

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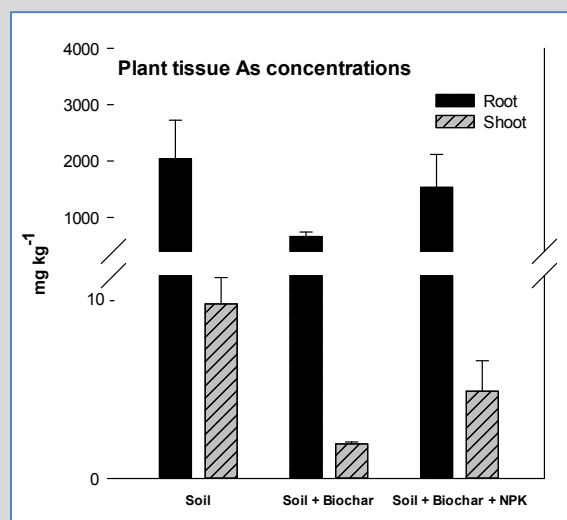
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735 Case study 5: Arsenic contaminated site (Spain)

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

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



749

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

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Fertilisation did, however significantly increase plant biomass yield to a greater extent than the unfertilised 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.

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

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

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

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797 *4.4 Urban sites*

798 Heavy metal in urban soils are more likely to have come from disperse sources, for example by aerial
799 deposition, originating a large distance from the site, than at industrial or mining sites, where
800 contamination is more likely to have originated on site. Such aerial deposition not only has an impact
801 on heavy metal concentrations in topsoils, but through leaching occurring over decadal timescales,
802 heavy metal concentrations in soils and pore waters can be elevated above background values at tens
803 of centimetres depth (Clemente et al., 2008). Surface additions of organic materials, such as composts,
804 can act as a source of DOC which may be leached through the urban soil profile acting as a carrier for
805 heavy metals and redistributing the DOC-metal complex at lower depths (Beesley and Dickinson,
806 2010).

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

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



837

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

842

843 *The addition of biochar to this urban soil, in common with compost and, to a lesser extent, non-*
 844 *pyrolysed wood chips, increased DOC concentrations in pore water collected from the upper 25 cm of*
 845 *the soil, but had little effect below that. At this depth a steady increase in As concentration was also*
 846 *recorded in pore water and a positive correlation between DOC and As concentrations in pore water*
 847 *statistically validated the trend; the same correlation was not seen after greenwaste compost*
 848 *amendment but was noted after amendment with non-pyrolysed wood chips. In the mesocosm*
 849 *experiment, after soil and amendments were mixed together, DOC concentrations were also greatly*
 850 *elevated compared to the control soil without amendment. For biochar, the concentration gradually*
 851 *decreased with time, but As concentrations increased. This would suggest that factors affecting the*
 852 *mobilisation of As after a surface applied biochar addition and a soil mixed application were*
 853 *different. After mixing there will be intimate soil-biochar contact whereas, after a surface amendment,*

854 *it is only the leachates from the biochar that impact on soil below and there is little soil-biochar*
855 *interaction beyond that where the two substrates contact. Thus DOC loaded leachates percolating*
856 *through the soil profile may redistribute contaminants, whereas pH effects may predominant after*
857 *soil-biochar mixing, taking account of the often high pH of biochar and lower pH of soils. There may*
858 *also be different hydrological effects of biochars mixed or surface applied to soils; after mixing*
859 *biochar pores may be blocked by soil derived mineral or organic materials, reducing water-biochar*
860 *contact. The same affect would not be seen if biochar was applied as a surface amendment and, in*
861 *this case, DOC may be desorbed from biochar more readily and leach to soils below rapidly. Such*
862 *practical factors require more investigation.*

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876 **5. Summary**

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

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880 1. Biochar has a very high surface area and some a high cation exchange capacity meaning they are
881 capable of sorbing high concentrations of heavy metals, such as Cd and Zn.

882 2. The surface chemistry of biochars can be manipulated to sorb certain contaminants more effectively

883 3. Biochars are more stable in soils for longer periods of time than other commonly applied soil
884 amendments, such as composts and sludges.

885 4. Biochar raises the pH of soils, making some nutrients more available to plants, immobilising some
886 heavy metals and liming acid soils.

887 5. Biochars can assist the re-vegetation of some contaminated soils and the vegetation grown on those
888 soils could be pyrolysed to produce more biochars to be returned to the soil.

889

890 Remediation strategy for industrial, mining impacted or urban soils could include biochars for
891 reducing leaching of heavy metals, decreasing phyto-toxicity of substrates and assisting revegetation.

892 In the case of arsenic contaminated sites, and especially where there is a potential that food crops may
893 be cultivated (for example urban allotment sites), a greater degree of caution should be exercised not

894 only in whether or not to apply biochar, but in what method of application and how much should be
895 applied. Some biochars also contain elevated concentrations of heavy metals due to their source

896 material; in these cases an evaluation would need to be made into the potential for introducing

897 contaminants to soils by biochar application. It must also be remembered that most biochars appear

898 inadequate as fertilisers if applied alone, so there may be a need to combine them with materials

899 containing labile nutrients. At very heavily contaminated and denuded sites, such as former mine

900 areas, particularly where there are surface leachates of heavy metals and unconsolidated soils and
901 wastes, biochars may be useful to restrict the wider impact of contamination beyond site boundaries.
902 Combination with other organic materials is likely to be required for affective phyto-
903 stabilisation/remediation. At old industrial sites there may be sufficient native soil remaining, and
904 recalcitrant nutrient capital that biochars can be applied alone to contamination hotspots to restart
905 natural processes. In all cases an intelligent approach should be taken to biochar application to land
906 after some data has been gleaned about the specific soil characteristics, heavy metals present in
907 elevated concentrations, preferably their bioavailability and their wider dispersal and posed risk.

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928 **References (non-formatted and in-press).**

929

930 Abrahams, P.W. 2002. Soils: their implications to human health. *Science of the Total Environment*
931 291, 1–32.

932

933 Adriano D.C. 2001. Trace elements in terrestrial environments. Biogeochemistry, bioavailability and
934 risks of metals. Springer-Verlag, New York.

935

936 Alloway, B.J. 1995. Heavy metals in soils. Blackie Academic & Professional, Glasgow.UK.

937

938 Amonette, J. and S. Joseph 2009. Characteristics of biochar: microchemical properties. *Biochar for*
939 *Environmental Management: Science and Technology*: 33.

940

941 Arienzo, M., Adamo, P., Cozzolino, V., 2004. The potential of *Lolium perenne* for revegetation of
942 contaminated soil from a metallurgical site. *Science of The Total Environment* 319, 13-25.

943

944 Asai, H., Samson, B.K., Stephan, H.M., Songyikhangsuthor, K., Homma, K., Kiyono, Y., Inoue, Y.,
945 Shiraiwa, T., Horie, T., 2009. Biochar amendment techniques for upland rice production in Northern
946 Laos: 1. Soil physical properties, leaf SPAD and grain yield. *Field Crops Research* 111, 81-84.

947

948 Atkinson, C., J. Fitzgerald and N. Higgs 2010. Potential mechanisms for achieving agricultural
949 benefits from biochar application to temperate soils: a review. *Plant Soil* 337: 1-18.

950

951 Beck, D.A., Johnson, G.R., Spolek, G.A. 2011. Amending greenroof soil with biochar to affect runoff
952 water quantity and quality. *Environmental Pollution* 159, 2111-2118

953

954 Beesley, L., E. Moreno-Jimenez, R. Clemente, N. Lepp and N. Dickinson 2010a. Mobility of arsenic,
955 cadmium and zinc in a multi-element contaminated soil profile assessed by in-situ soil pore water
956 sampling, column leaching and sequential extraction. *Environ. Pollut.* 158: 155-160.

957

958 Beesley, L., E. Moreno-Jiménez and J.L. Gomez-Eyles 2010b. Effects of biochar and greenwaste
959 compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants
960 in a multi-element polluted soil. *Environ. Pollut.* 158: 2282-2287.

961 Beesley, L. and N. Dickinson 2010. Carbon and trace element fluxes in the pore water of an urban soil
962 following greenwaste compost, woody and biochar amendments, inoculated with the earthworm
963 *Lumbricus terrestris*. *Soil Biol. Biochem.* 43: 188-196.

964

965 Beesley, L. and M. Marmiroli 2011. The immobilisation and retention of soluble arsenic, cadmium
966 and zinc by biochar. *Environ. Pollut.* 159: 474-480.

967

968 Beesley L, Moreno-Jimenez E, Gomez-Eyles JL, Harris E, Robinson B, Sizmur T. A review of
969 biochars' potential role in the remediation, revegetation and restoration of contaminated soils. *Environ*
970 *Pollut* 2011; 159: 474-480

971

972 Beesley, L., Marmiroli, M., Pagano, L., Pighi, V., Fellet, G., Fresno, T., Vamerali, T., Bandiera, M.,
973 Marmiroli, N. 2013. Biochar addition to an arsenic contaminated soil increases arsenic concentrations
974 in the pore water but reduces uptake to tomato plants (*Solanum lycopersicum* L.). *Science of the Total*
975 *Environment* 454, 498-608

976

977 Bell, M.J. and F. Worrall 2011. Charcoal addition to soils in NE England: A carbon sink with
978 environmental co-benefits? *Sci. Total Environ.* 409: 1704-1714.

979

980 Bernal, M.P., Clemente, R., Walker, D.J., 2006. The role of organic amendment in the bioremediation
981 of heavy metal-polluted soils. En: Gore, R.W. Ed, *Environmental Research at the Leading Edge*.
982 Nova Pub., New York. pp 2-58.

983

984 Bird, M.J., Wurster, C.M., De Paula Silva, P.H., Paul, N.A., De Nys, R. 2012. Algal biochar: effects
985 and applications. *GCB Bioenergy* 4, 61-69

986

987 Blackwell, P., Reithmuller, G., Collins, M., 2009. Biochar application to soil, in: Lehmann, J., Joseph,
988 S. (Eds.), *Biochar for Environmental Management: Science and Technology*. Earthscan, London

989

990 Bolan, N.S. and V. Duraisamy 2003. Role of inorganic and organic soil amendments on
991 immobilisation and phytoavailability of heavy metals: a review involving specific case studies. *Aust.*
992 *J. Soil Res.* 41: 533-555.

993

994 Borch T, Kretzschmar R, Kappler A, Van Cappellen P, Ginder-Vogel M, Voegelin A, Campbell K
995 (2010) Biogeochemical redox processes and their impact on contaminant dynamics. Environ. Sci.
996 Technol. 44:15-23.

997

998 Buss, W., Kammann, C., Koyro, H-W. 2012. Biochar reduces copper toxicity in *Chenopodium quinoa*
999 Willd. in sandy soil. Journal of Environmental Quality 41, 1157-1165

1000

1001 Cantrell, K.B., Hunt, P.G., Uchimiya, M., Novak, J.M., Ro, K.S., 2012. Impact of pyrolysis
1002 temperature and manure source on physicochemical characteristics of biochar. Bioresource
1003 Technology 107, 419-428.

1004

1005 Cao X, Ma LQ, Shiralipour A (2003) Effects of compost and phosphate amendments on arsenic
1006 mobility in soils and arsenic uptake by the hyperaccumulator *Pteris vittata* L. Environ Pollut
1007 126:157–167.

1008

1009 Cao, X.D., L.N. Ma, B. Gao and W. Harris 2009. Dairy-Manure Derived Biochar Effectively Sorbs
1010 Lead and Atrazine. Environ. Sci. Technol. 43: 3285-3291.

1011

1012 Cao, X., L. Ma, Y. Liang, B. Gao and W. Harris 2011. Simultaneous Immobilization of Lead and
1013 Atrazine in Contaminated Soils Using Dairy-Manure Biochar. Environ. Sci. Technol. 45: 4884-4889.

1014

1015 Chan, K., L. Van Zwieten, I. Meszaros, A. Downie and S. Joseph 2007. Agronomic values of
1016 greenwaste biochar as a soil amendment. Aust. J. Soil Res. 45: 629-634.

1017

1018 Chan, K. and Z. Xu. Biochar: nutrient properties and their enhancement. p. 67. In: J. Lehmann,
1019 Joseph, S., (eds.) 2009. Biochar for Environmental Management: Science and Technology. Earthscan.

1020

1021 Chang, Q., W. Lin and W.-c. Ying 2010. Preparation of iron-impregnated granular activated carbon
1022 for arsenic removal from drinking water. J. Hazard. Mater. 184: 515-522.

1023

1024 Chen, B.L., Z.M. Chen and S.F. Lv 2011a. A novel magnetic biochar efficiently sorbs organic
1025 pollutants and phosphate. Bioresour. Technol. 102: 716-723.

1026

- 1027 Chen, S.-B., Y.-G. Zhu, Y.-B. Ma and G. McKay 2006. Effect of bone char application on Pb
1028 bioavailability in a Pb-contaminated soil. *Environ. Pollut.* 139: 433-439.
- 1029
- 1030 **Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M.B., Hay, A.G. Adsorption of**
1031 **copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous**
1032 **solution. *Bioresource Technology* (in-press)**
- 1033
- 1034 Cheng, C.H., J. Lehmann, J.E. Thies, S.D. Burton and M.H. Engelhard 2006. Oxidation of black
1035 carbon by biotic and abiotic processes. *Org. Geochem.* 37: 1477-1488.
- 1036
- 1037 Cheng, C.H., J. Lehmann and M.H. Engelhard 2008. Natural oxidation of black carbon in soils:
1038 Changes in molecular form and surface charge along a climosequence. *Geochim. Cosmochim. Acta*
1039 72: 1598-1610.
- 1040
- 1041 Choppala, G.K., Bolan, N.S., Megharaj, M., Chen, Z., Naidu, R. 2012. The influence of biochar and
1042 black carbon on reduction and bioavailability of chromate in soils. *Journal of Environmental Quality*
1043 41, 1175-1184
- 1044
- 1045 Clemente, R., Dickinson, N.M., Lepp, N.W. 2008. Mobility of metals and metalloids in a multi-
1046 element contaminated soil 20 years after cessation of the pollution source activity. *Environmental*
1047 *Pollution* 155, 254-261
- 1048
- 1049 Cui HJ, Wang MK, Fu ML, Ci E. Enhancing phosphorous availability in phosphorous-fertilised zones
1050 by reducing phosphate adsorbed on ferrihydrite using rice straw-derived biochar. *J Soils Sediments*
1051 2011; 11: 1135-1141
- 1052
- 1053 Davidson D A, Dercon G, Stewart M, Watson F. 2006. The legacy of past urban waste disposal on
1054 local soils. *J Archaeol Sci.* 33, 778-783.
- 1055
- 1056 Debela, F., Thring, R.W., Arocena, J.M. 2012. Immobilization of heavy metals by co-pyrolysis of
1057 contaminated soil with woody biomass. *Water, Air and Soil Pollution* 223, 1161-1170
- 1058
- 1059 Di Toro, D.M., Allen, H.E., Bergman, H.L., Meyer, J.S., Paquin, P.R., Santore, R.C., 2001. Biotic
1060 ligand model of the acute toxicity of metals. 1. Technical basis. *Environmental toxicology and*
1061 *chemistry* 20, 2383-2396.

- 1062 Dixit, S. and J.G. Hering 2003. Comparison of Arsenic(V) and Arsenic(III) Sorption onto Iron Oxide
1063 Minerals: Implications for Arsenic Mobility. *Environ. Sci. Technol.* 37: 4182-4189.
- 1064
- 1065 Ennis, C.J., Evans, G.A., Islam, M., Ralebitso-Senior, T.K., Senior, E. 2012. Biochar: Carbon
1066 sequestration, land remediation, and impacts on soil microbiology. *Critical Reviews in Environmental
1067 Science and Technology* 42, 2311-2364
- 1068
- 1069 Fellet, G., L. Marchiol, G. Delle Vedove and A. Peressotti 2011. Application of biochar on mine
1070 tailings: Effects and perspectives for land reclamation. *Chemosphere* 83: 1262-1267.
- 1071
- 1072 Fernández, M.D., Cagigal, E., Vega, M.M., Urzelai, A., Babín, M., Pro, J., Tarazona, J.V. 2005.
1073 Ecological risk assessment of contaminated soils through direct toxicity assessment. *Ecotoxicological
1074 and Environmental Safety* 62, 174–184
- 1075
- 1076 Fitz, W.J. and W.W. Wenzel 2002. Arsenic transformations in the soil-rhizosphere-plant system:
1077 fundamentals and potential application to phytoremediation. *J. Biotechnol.* 99: 259-278.
- 1078
- 1079 Fontes, M., and L. Alleoni. 2006. Electrochemical attributes and availability of nutrients, toxic
1080 elements, and heavy metals in tropical soils. *Scientia Agricola* (December): 589–608
- 1081
- 1082 Freddo A, Cai C, Reid BJ. Environmental contextualisation of potential toxic elements in polycyclic
1083 aromatic hydrocarbons in biochar. *Environ Pollut* 2012; 171: 18-24
- 1084
- 1085 Gartler, J., Robinson, B., Burton, K., Clucas, L. Carbonaceous soil amendments to biofortify crop
1086 plants with zinc. *Science of the Total Environment* (in-press)
- 1087
- 1088 Gasco, G., Paz-Ferreiro, J., Mendez, A. 2012. Thermal analysis of soil amended with sewage sludge
1089 and biochar from sewage sludge pyrolysis. *Journal of Thermal Analysis and Calorimetry* 108, 769-
1090 775
- 1091
- 1092 Gaskin, J., C. Steiner, K. Harris, K. Das and B. Bibens 2008. Effect of low-temperature pyrolysis
1093 conditions on biochar for agricultural use. *Transactions of the American Society of Agricultural and
1094 Biological Engineers* 51: 2061-2069
- 1095

- 1096 Gell, K., van Groenigen, J.W., Cayuela, M.L. 2011. Residues of bioenergy production chains as soil
1097 amendments: Immediate and temporal phytotoxicity. *Journal of Hazardous Materials* 186, 2017-2025
1098
- 1099 Gomez-Eyles, J.L., T. Sizmur, C.D. Collins and M.E. Hodson 2011. Effects of biochar and the
1100 earthworm *Eisenia fetida* on the bioavailability of polycyclic aromatic hydrocarbons and potentially
1101 toxic elements. *Environ. Pollut.* 159: 616-622.
1102
- 1103 Gomez-Eyles, J.L., Beesley, L., Moreno-Jiménez, E., Ghosh U., and Sizmur, T. (2013). The potential
1104 of biochar amendments to remediate contaminated soils. In Ladygina N. & Rineau F. [eds.]. *Biochar
1105 and soil biota*. Science Publishers, Enfield, New Hampshire 03748, USA/Jersey, British Isles.
1106
- 1107 Graber, E.R., Harel, Y.M., Kolton, M., Cytryn, E., Silber, A., David, D.R., Tsechansky, L.,
1108 Borenshtein, M., Elad, Y. 2010. Biochar impact on development and productivity of pepper and
1109 tomato grown in fertigated soilless media. *Plant and Soil* 337, 481-496
1110
- 1111 Hartley, W., Uffindell, L., Plumb, A., Rawlinson, H.A., Putwain, P., Dickinson, N.M. 2008.
1112 Assessing biological indicators for remediated anthropogenic urban soils. *Science of the Total
1113 Environment* 405, 358-369
1114
- 1115 Hartley, W., N.M. Dickinson, P. Riby and N.W. Lepp 2009. Arsenic mobility in brownfield soils
1116 amended with green waste compost or biochar and planted with *Miscanthus*. *Environ. Pollut.* 157:
1117 2654-2662.
1118
- 1119 Harvey, O.R., B.E. Herbert, R.D. Rhue and L.-J. Kuo 2011. Metal Interactions at the Biochar-Water
1120 Interface: Energetics and Structure-Sorption Relationships Elucidated by Flow Adsorption
1121 Microcalorimetry. *Environ. Sci. Technol.* 45: 5550-5556.
1122
- 1123 Hass, A., Gonzalez, J.M., Lima, I.M., Godwin, H.W., Halvorson, J.J., Boyer, D.G. 2012. Chicken
1124 manure biochar as liming and nutrient source for acid appalachian soil. *Journal of Environmental
1125 Quality* 41, 1096-1106
1126
- 1127 He Y, Zhang G.-L. 2006. Comments on 'Biochemical characterization of urban soil profiles from
1128 Stuttgart, Germany' by Klaus Lorenz and Ellen Kandeler. *Soil Biol Biochem.* 38, 413-414.
1129

- 1130 He, Y.D., Zhai, Y.B., Li, C.T., Yang, F., Chen, L., Fan, X.P., Peng, W.F., Fu, Z.M. 2010. The fate of
1131 Cu, Zn, Pb and Cd during the pyrolysis of sewage sludge at different temperatures. *Environmental*
1132 *Technology* 31, 567-574
- 1133
- 1134 Hodson, M.E., 2010. The need for sustainable soil remediation. *Elements* 6, 363-368.
- 1135
- 1136 Hollis J M. 1991. The classification of soils in urban areas, in: Bullock, P., Gregory, P.J. (Eds.), *Soils*
1137 *in the Urban Environment*. Blackwell, Oxford, pp. 527
- 1138
- 1139 Hossain, M.K., Strezov, V., Yin Chan, K., Nelson, P.F. 2010. Agronomic properties of wastewater
1140 sludge biochar and bioavailability of metals in production of cherry tomato (*Lycopersicon*
1141 *esculentum*). *Chemosphere* 78, 1167-1171
- 1142
- 1143 Hughes, M.F. 2002. Arsenic toxicity and potential mechanisms of action. *Toxicol. Lett.* 133: 1-16.
- 1144
- 1145 Ippolito, J.A., Laird, D.A., Busscher, W.J. 2012. Environmental benefits of biochar. *Journal of*
1146 *Environmental Quality* 41, 967-972
- 1147
- 1148 Jiang, J., Xu, R., Jiang, T., and Li, Z. (2012). "Immobilization of Cu(II), Pb(II) and Cd(II) by the
1149 addition of rice straw derived biochar to a simulated polluted Ultisol." *Journal of hazardous materials*,
1150 229-230, 145–50.
- 1151
- 1152 Jones, C.G., Lawton, J.H., Shachak, M., 1994. Organisms as ecosystem engineers. *Oikos*, 373-386
- 1153
- 1154 Jones DL, Rousk J, Edwards-Jones G, DeLuca TH, Murphy DV. Biochar-mediated changes in soil
1155 quality and plant growth in a three year field trial. *Soil Biol Biochem* 2012; 45: 112-124
- 1156
- 1157 Jordán, F., 2009. Keystone species and food webs. *Philosophical Transactions of the Royal Society B:*
1158 *Biological Sciences* 364, 1733-1741.
- 1159
- 1160 Joseph SD, Camps-Arbestain M, Lin Y, Munroe P, Chia CH, Hook J, van Zwieten L, Kimber S,
1161 Cowie A, Singh BP, Lehmann J, Foidl N, Smernik RJ, Amonette JE. An investigation into the
1162 reaction of biochar in soil. *Aust J Soil Res* 2010; 48: 501-515

- 1163 Jouquet, P., Dauber, J., Lagerlöf, J., Lavelle, P., Lepage, M., 2006. Soil invertebrates as ecosystem
1164 engineers: Intended and accidental effects on soil and feedback loops. *Applied Soil Ecology* 32, 153-
1165 164.
- 1166
- 1167 Kannan, N. and G. Rengasamy 2005. Comparison of Cadmium Ion Adsorption on Various
1168 ACTIVATED CARBONS. *Water, Air, Soil Pollut.* 163: 185-201.
- 1169
- 1170 Karami, N., Clemente, R., Moreno-Jimenez, E., Lepp, N.W., Beesley, L. 2011. Efficiency of
1171 greenwaste compost and biochar soil amendments for reducing lead and copper mobility and uptake
1172 to ryegrass. *Journal of Hazardous Materials* 191, 41-48
- 1173
- 1174 Kishimoto, S., Sugiura, G. 1985. Charcoal as a soil conditioner, Symposium on forest products
1175 research, International achievements for the future, Pretoria, South Africa, pp. 12-23.
- 1176
- 1177 Knowles, O.A., Robinson, B.H., Contangelo, A., Clucas, L. 2011. Biochar for the mitigation of nitrate
1178 leaching from soil amended with biosolids. *Science of the Total Environment* 409, 3206-3210
- 1179
- 1180 Lado, L.R., Hengl, T., Reuter, H.I. 2008. Heavy metals in European soils: A geostatistical analysis of
1181 the FOREGS geochemical database. *Geoderma* 148, 189-199
- 1182
- 1183 Lee, J.W., M. Kidder, B.R. Evans, S. Paik, A.C. Buchanan Iii, C.T. Garten and R.C. Brown 2010.
1184 Characterization of Biochars Produced from Cornstovers for Soil Amendment. *Environ. Sci. Technol.*
1185 44: 7970-7974.
- 1186
- 1187 Lehmann, J., M.C. Rillig, J. Thies, C.A. Masiello, W.C. Hockaday and D. Crowley 2011. Biochar
1188 effects on soil biota - A review. *Soil Biol. Biochem.* 43: 1812-1836.
- 1189
- 1190 Li, D., Hockaday, W.C., Masiello, C.A., Alvarez, P.J.J., 2011. Earthworm avoidance of biochar can
1191 be mitigated by wetting. *Soil Biology and Biochemistry* 43, 1732-1737.
- 1192
- 1193 Liang, B., J. Lehmann, D. Solomon, J. Kinyangi, J. Grossman, B. O'Neill, J.O. Skjemstad, J. Thies,
1194 F.J. Luizao, J. Petersen and E.G. Neves 2006. Black carbon increases cation exchange capacity in
1195 soils. *Soil Sci. Soc. Am. J.* 70: 1719-1730.
- 1196

- 1197 Liesch, A., Weyers, S., Gaskin, J., Das, K., 2010. Impact of two different biochars on earthworm
1198 growth and survival. *Annals of Environmental Science* 4, 1.
- 1199
- 1200 Lin Y, Munroe P, Joseph S, Kimber S, Van Zwieten L. Nanoscale organo-mineral retentions of
1201 biochars in ferrosol: and investigation using microscopy. *Plant and Soil* 2012; 357: 369-380
- 1202
- 1203 **Lin, Y., Munroe, P., Joseph, S., Henderson, R., Ziolkowski, A. Water extractable organic carbon in**
1204 **untreated and chemical treated biochars. *Chemosphere* (in-press)**
- 1205
- 1206 Liu, Z. and F.-S. Zhang 2009. Removal of lead from water using biochars prepared from
1207 hydrothermal liquefaction of biomass. *J. Hazard. Mater.* 167: 933-939.
- 1208
- 1209 Major, J., C. Steiner, A. Downie and J. Lehmann. Biochar effects on nutrient leaching. pp. 273-284.
1210 In: J. Lehmann, Joseph, S., (eds.) 2009. *Biochar for Environmental Management: Science and*
1211 *Technology*. Earthscan.
- 1212
- 1213 Mankansingh, U., Choi, P-C., Ragnarsdottir, V. 2011. Biochar application in a tropical, agricultural
1214 region: A plot scale study in Tamil Nadu, India. *Applied Geochemistry* 26, 218-221
- 1215
- 1216 Masscheleyn, P.H., Delaune, R.D., Patrick, W.H. 1991. Effect of redox potential and pH on arsenic
1217 speciation and solubility in a contaminated soil. *Environmental Science and Technology* 25, 1414-
1218 1419.
- 1219
- 1220 McBeath, A.V., R.J. Smernik, M.P.W. Schneider, M.W.I. Schmidt and E.L. Plant 2011.
1221 Determination of the aromaticity and the degree of aromatic condensation of a thermosequence of
1222 wood charcoal using NMR. *Org. Geochem.* 42: 1194-1202.
- 1223
- 1224 Meharg, A.A. and M.R. Macnair 1992. Suppression of the High Affinity Phosphate Uptake System: A
1225 Mechanism of Arsenate Tolerance in *Holcus lanatus* L. *J. Exp. Bot.* 43: 519-524.
- 1226
- 1227 Melo, L.C. a., L.R.F. Alleoni, and F. a. Swartjes. 2011. Derivation of Critical Soil Cadmium
1228 Concentrations for the State of São Paulo, Brazil, Based on Human Health Risks. *Human and*
1229 *Ecological Risk Assessment: An International Journal* 17(5): 1124–1141
- 1230

- 1231 Mench, M., S. Bussi re, J. Boisson, E. Castaing, J. Vangronsveld, A. Ruttens, T. De Koe, P. Bleeker,
1232 A. Assun o and A. Manceau 2003. Progress in remediation and revegetation of the barren Jales gold
1233 mine spoil after in situ treatments. *Plant Soil* 249: 187-202
- 1234
- 1235 Mendez, A., Gomez, A., Paz-Ferreiro, J., Gasco, G. 2012. Effects of sewage sludge biochar on plant
1236 metal availability after application to a Mediterranean soil. *Chemosphere* 89, 1354-1359
- 1237
- 1238 Mikan, C., Abrams, M. 1995. Altered forest composition and soil properties of historic charcoal
1239 hearths in Southeastern Pennsylvania. *Canadian Journal of Forest Research* 25, 687-696.
- 1240
- 1241 Mikutta, C. and R. Kretzschmar 2011. Spectroscopic Evidence for Ternary Complex Formation
1242 between Arsenate and Ferric Iron Complexes of Humic Substances. *Environ. Sci. Technol.* 45: 9550-
1243 9557.
- 1244
- 1245 Moreno-Jimenez, E., Beesley, L., Lepp, N.W., Dickinson, N.M., Hartley, W., Clemente, R. 2011.
1246 Field sampling of soil pore water to evaluate trace element mobility and associated environmental
1247 risk. *Environmental Pollution* 159, 3078-3085
- 1248
- 1249 Moreno-Jimenez E, Esteban E, Penalosa JM. The fate of Arsenic in the soil-plant system in: Whitacre,
1250 D.M (ed.), 2012. *Reviews of Environmental Contamination and Toxicology*. Springer, USA.
- 1251
- 1252 Mukherjee, A., A.R. Zimmerman and W. Harris 2011. Surface chemistry variations among a series of
1253 laboratory-produced biochars. *Geoderma* 163: 247-255.
- 1254
- 1255 Mu iz, G., V. Fierro, A. Celzard, G. Furdin, G. Gonzalez-Sanchez and M.L. Ballinas 2009. Synthesis,
1256 characterization and performance in arsenic removal of iron-doped activated carbons prepared by
1257 impregnation with Fe(III) and Fe(II). *J. Hazard. Mater.* 165: 893-902.
- 1258
- 1259 Naidu, R., M. Sumner, and R. Harter. 1998. Sorption of heavy metals in strongly weathered soils: an
1260 overview. *Environmental Geochemistry and Health*: 5-9
- 1261
- 1262 Namgay, T., B. Singh and B.P. Singh 2010. Influence of biochar application to soil on the availability
1263 of As, Cd, Cu, Pb, and Zn to maize (*Zea mays* L.). *Aust. J. Soil Res.* 48: 638-647.
- 1264

- 1265 Nathanail, C.P., Bardos, R.P., 2004. Reclamation of contaminated land. Wiley.
- 1266
- 1267 Nicholson, F.A., Smith, S.R., Alloway, B.J., Carlton-Smith, C., Chambers, B.J., 2003. An inventory
1268 of heavy metals inputs to agricultural soils in England and Wales. *Science of The Total Environment*
1269 311, 205-219.
- 1270
- 1271 Novak, J.M., W.J. Busscher, D.L. Laird, M. Ahmedna, D.W. Watts and M.A.S. Niandou 2009.
1272 Impact of Biochar Amendment on Fertility of a Southeastern Coastal Plain Soil. *Soil Sci.* 174: 105-
1273 112
- 1274
- 1275 Oremland, R.S. and J.F. Stolz 2003. The Ecology of Arsenic. *Science* 300: 939-944.
- 1276
- 1277 Park, J.H., Choppala, G.K., Bolan, N.S., Chung, J.W., Chuasavathi, T., 2011. Biochar reduces the
1278 bioavailability and phytotoxicity of heavy metals. *Plant and Soil* 348, 439-451.
- 1279
- 1280 Ponge, J.-F., Topoliantz, S., Ballof, S., Rossi, J.-P., Lavelle, P., Betsch, J.-M., Gaucher, P., 2006.
1281 Ingestion of charcoal by the Amazonian earthworm *Pontoscolex corethrurus*: A potential for tropical
1282 soil fertility. *Soil Biology and Biochemistry* 38, 2008-2009.
- 1283
- 1284 Pulford, I.D., Watson, C. 2003. Phytoremediation of heavy metal-contaminated land by trees-a
1285 review. *Environment International* 29, 529-540
- 1286
- 1287 Quilliam, R.S., Marsden, K.A., Gertler, C., Rousk, J., DeLuca, T.H., Jones, D.L. 2012. Nutrient
1288 dynamics, microbial growth and weed emergence in biochar amended soil are influenced by time
1289 since application and reapplication rate. *Agriculture, Ecosystems and Environment* 158, 192-199
- 1290
- 1291 Reed, B. 2000. Adsorption of heavy metals using iron impregnated activated carbon. *J. Environ. Eng.*
1292 126: 896-874.
- 1293
- 1294 Ross, S.M. 1994. Toxic metals in soil-plant systems. Wiley, Chichester.
- 1295
- 1296 Rossiter D G. 2007. Classification of urban and industrial soils in the World Reference Base for Soil
1297 Resources. *J Soils Sediments.* 7, 96-100.

1298 Ruttens, A., Mench, M., Colpaert, J.V., Boisson, J., Carleer, R., Vangronsveld, J. 2006.
1299 Phytostabilization of a metal contaminated sandy soil. I: Influence of compost and/or inorganic metal
1300 immobilizing soil amendments on phytotoxicity and plant availability of metals. Environmental
1301 Pollution 144, 524-532.

1302

1303 Salem, M., Kohler, J., Rillig, M.C., 2013. Palatability of carbonized materials to Collembola. Applied
1304 Soil Ecology 64, 63-69.

1305

1306 Sanchez-Polo, M. and J. Rivera-Utrilla 2002. Adsorbent-adsorbate interactions in the adsorption of
1307 Cd (II) and Hg (II) on ozonized activated carbons. Environ. Sci. Technol. 36: 3850-3854.

1308

1309 Semple, K.T., Doick, K.J., Jones, K.C., Burauel, P., Craven, A., Harms, H., 2004. Peer Reviewed:
1310 Defining Bioavailability and Bioaccessibility of Contaminated Soil and Sediment is Complicated.
1311 Environmental Science & Technology 38, 228A-231A.

1312

1313 Shen, Y.-S., S.-L. Wang, Y.-M. Tzou, Y.-Y. Yan and W.-H. Kuan 2012. Removal of hexavalent Cr
1314 by coconut coir and derived chars - The effect of surface functionality. Bioresour. Technol. 104: 165-
1315 172

1316

1317 Simoes, J.A.M. and J.L. Beauchamp 1990. Transition metal-hydrogen and metal-carbon bond
1318 strengths: the keys to catalysis. Chemical Reviews 90: 629-688.

1319

1320 Sizmur, T., Hodson, M.E., 2009. Do earthworms impact metal mobility and availability in soil?—A
1321 review. Environmental Pollution 157, 1981-1989.

1322

1323 Sizmur, T., Palumbo-Roe, B., Watts, M.J., Hodson, M.E., 2011a. Impact of the earthworm *Lumbricus*
1324 *terrestris* (L.) on As, Cu, Pb and Zn mobility and speciation in contaminated soils. Environmental
1325 Pollution 159, 742-748.

1326

1327 Sizmur, T., Tilston, E.L., Charnock, J., Palumbo-Roe, B., Watts, M.J., Hodson, M.E., 2011b. Impacts
1328 of epigeic, anecic and endogeic earthworms on metal and metalloid mobility and availability. Journal
1329 of Environmental Monitoring 13, 266-273.

1330

1331 Sizmur, T., Watts, M.J., Brown, G.D., Palumbo-Roe, B., Hodson, M.E., 2011c. Impact of gut passage
1332 and mucus secretion by the earthworm *Lumbricus terrestris* on mobility and speciation of arsenic in
1333 contaminated soil. *Journal of Hazardous Materials* 197, 169-175

1334

1335 Sizmur, T., Wingate, J., Hutchings, T., Hodson, M.E., 2011d. *Lumbricus terrestris* L. does not impact
1336 on the remediation efficiency of compost and biochar amendments. *Pedobiologia* 54, S211-S216.

1337 Smith, R., Pollard, S.J.T., Weeks, J.M., Nathanail, C.P., 2005. Assessing significant harm to terrestrial
1338 ecosystems from contaminated land. *Soil Use and Management* 21, 527-540.

1339

1340 Sneddon, J., Clemente, R., Riby, P., Lepp, N.W., 2009. Source-pathway-receptor investigation of the
1341 fate of trace elements derived from shotgun pellets discharged in terrestrial ecosystems managed for
1342 game shooting. *Environ. Pollut.* 157, 2663-2669.

1343

1344 Sohi, S., Krull, E., Lopez-Capel, E., Bol, R. 2010. A review of biochar and its use and function in soil.
1345 *Advances in Agronomy* 105, 47-82.

1346

1347 Steiner, C., Das, K.C., Garcia, M., Förster, B., Zech, W. 2008. Charcoal and smoke extract stimulate
1348 the soil microbial community in a highly weathered xanthic Ferralsol. *Pedobiologia* 51, 359-366.

1349

1350 Swartjes, F.A. 1999: Risk-based assessment of soil and groundwater quality in the Netherlands:
1351 standards and remediation urgency. *Risk Analysis* 19, 1235–1249.

1352

1353 Swiatkowski, A., M. Pakula, S. Biniak and M. Walczyk 2004. Influence of the surface chemistry of
1354 modified activated carbon on its electrochemical behaviour in the presence of lead(II) ions. *Carbon*
1355 42: 3057-3069.

1356

1357 Thakali, S., Allen, H.E., Di Toro, D.M., Ponizovsky, A.A., Rooney, C.P., Zhao, F.-J., McGrath, S.P.,
1358 Criel, P., Van Eeckhout, H., Janssen, C.R., Oorts, K., Smolders, E., 2006. Terrestrial biotic ligand
1359 model. 2. Application to Ni and Cu toxicities to plants, invertebrates, and microbes in soil.
1360 *Environmental Science & Technology* 40, 7094-7100.

1361

1362 Topoliantz, S., Ponge, J.-F., 2003. Burrowing activity of the geophagous earthworm *Pontoscolex*
1363 *corethrurus* (Oligochaeta: Glossoscolecidae) in the presence of charcoal. *Applied Soil Ecology* 23,
1364 267-271.

1365

- 1366 Topoliantz, S., Ponge, J.-F., 2005. Charcoal consumption and casting activity by *Pontoscolex*
1367 *corethrurus* (Glossoscolecidae). *Applied Soil Ecology* 28, 217-224.
- 1368
- 1369 Tordoff G, M., Baker A, J, M., Willis A, J. 2000. Current approaches to the revegetation
1370 and reclamation of metalliferous mine wastes, *Chemosphere* 41, 219–228.
- 1371
- 1372 Trakal, L., M. Komárek, J. Száková, V. Zemanová and P. Tlustoš 2011. Biochar application to metal-
1373 contaminated soil: Evaluating of Cd, Cu, Pb and Zn sorption behavior using single-and multi-element
1374 sorption experiment. *Plant, Soil and Environment* 57: 372-380.
- 1375
- 1376 Uchimiya, M., I.M. Lima, K.T. Klasson and L.H. Wartelle 2010a. Contaminant immobilization and
1377 nutrient release by biochar soil amendment: Roles of natural organic matter. *Chemosphere* 80: 935-
1378 940.
- 1379
- 1380 Uchimiya, M., I.M. Lima, K. Thomas Klasson, S. Chang, L.H. Wartelle and J.E. Rodgers 2010b.
1381 Immobilization of Heavy Metal Ions (CuII, CdII, NiII, and PbII) by Broiler Litter-Derived Biochars in
1382 Water and Soil. *J. Agric. Food Chem.* 58: 5538-5544.
- 1383
- 1384 Uchimiya, M., S. Chang and K.T. Klasson 2011a. Screening biochars for heavy metal retention in
1385 soil: Role of oxygen functional groups. *J. Hazard. Mater.* 190: 432-441.
- 1386
- 1387 Uchimiya, M., L.H. Wartelle, K.T. Klasson, C.A. Fortier and I.M. Lima 2011b. Influence of Pyrolysis
1388 Temperature on Biochar Property and Function as a Heavy Metal Sorbent in Soil. *J. Agric.*
1389 *Food Chem.* 59: 2501-2510.
- 1390 Vangronsveld, J., Herzig, R., Weyens, N., Boulet, J., Adriaensen, K., Ruttens, A., Thewys, T.,
1391 Vassilev, A., Meers, E., Nehnevajova, E., van der Lie, D., Mench, M. 2009. Phytoremediation of
1392 contaminated soils and groundwater: lessons from the field. *Environmental Science and Pollution*
1393 *Research* 16, 765-794.
- 1394
- 1395 Van Zwieten, L., S. Kimber, S. Morris, K. Chan, A. Downie, J. Rust, S. Joseph and A. Cowie 2010.
1396 Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil
1397 fertility. *Plant Soil* 327: 235-246.
- 1398

1399 Vaughan, R.L. and B.E. Reed 2005. Modeling As(V) removal by a iron oxide impregnated activated
1400 carbon using the surface complexation approach. *Water Res.* 39: 1005-1014.

1401

1402 Wang T, Camps-Arbestain M, Hedley M, Bishop P. Predicting phosphorous bioavailability from
1403 high-ash biochars. *Plant and Soil*; 2012: 357, 173-187

1404

1405 Warnock, D., J. Lehmann, T. Kuyper and M. Rillig 2007. Mycorrhizal responses to biochar in soil –
1406 concepts and mechanisms. *Plant Soil* 300: 9-20.

1407

1408 Warren, G.P., B.J. Alloway, N.W. Lepp, B. Singh, F.J.M. Bochereau and C. Penny 2003. Field trials
1409 to assess the uptake of arsenic by vegetables from contaminated soils and soil remediation with iron
1410 oxides. *Sci. Total Environ.* 311: 19-33.

1411

1412 Waychunas, G.A., C.S. Kim and J.F. Banfield 2005. Nanoparticulate Iron Oxide Minerals in Soils and
1413 Sediments: Unique Properties and Contaminant Scavenging Mechanisms. *Journal of Nanoparticle*
1414 *Research* 7: 409-433.

1415

1416 Wong, M.H. 2003. Ecological restoration of mine degraded soils, with emphasis on metal
1417 contaminated soils. *Chemosphere* 50, 775-780

1418

1419 Weyers, S.L., Spokas, K.A., 2011. Impact of Biochar on Earthworm Populations: A Review. *Applied*
1420 *and Environmental Soil Science* 2011.

1421

1422 Yamato, M., Y. Okimori, I.F. Wibowo, S. Anshori and M. Ogawa 2006. Effects of the application of
1423 charred bark of *Acacia mangium* on the yield of maize, cowpea and peanut, and soil chemical
1424 properties in South Sumatra, Indonesia. *Soil Sci. Plant Nutr.* 52: 489-495.

1425

1426 Yao, Y., Gao, B., Inyang, M., Zimmerman, A.R., Cao, X., Pullammanappallil, P., Yang, L. Biochar
1427 derived from anaerobically digested sugar beet tailings: Characterization and phosphate removal
1428 potential. *Bioresource Technology* 102, 6273-6278

1429

1430 Zarić, Snežana D. 2003. Metal Ligand Aromatic Cation- π Interactions. *European Journal of Inorganic*
1431 *Chemistry* 2003: 2197-2209.

1432

- 1433 Zhang, Z., Solaiman, Z.M., Meny, K., Murphy, D.V., Rengel, Z. 2013. Biochars immobilize soil
1434 cadmium, but do not improve growth of emergent wetland species *Juncus subsecundus* in cadmium-
1435 contaminated soil. *Journal of Soils and Sediments* 13, 140-151
- 1436
- 1437 Zheng RL, Cai C, Liang JH, Huang Q, Chen Z, Huang YZ, Arp HPH, Sun GX. The effects of
1438 biochars from rice residues on the formation of iron plaque and the accumulation of Cd, Zn, Pb, As in
1439 rice (*Oryza sativa* L.) seedlings. *Chemosphere* 2012; 89: 856-862
- 1440
- 1441 Zimmerman, A.R., B. Gao and M.-Y. Ahn 2011. Positive and negative carbon mineralization priming
1442 effects among a variety of biochar-amended soils. *Soil Biol. Biochem.* 43: 1169-1179.

