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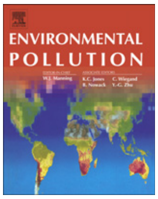

Review

A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils

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ABSTRACT

Biochars are biological residues combusted under low oxygen conditions, resulting in a porous, low density carbon rich material. Their large surface areas and cation exchange capacities, determined to a large extent by source materials and pyrolysis temperatures, enables enhanced sorption of both organic and inorganic contaminants to their surfaces, reducing pollutant mobility when amending contaminated soils. Liming effects or release of carbon into soil solution may increase arsenic mobility, whilst low capital but enhanced retention of plant nutrients can restrict revegetation on degraded soils amended only with biochars; the combination of composts, manures and other amendments with biochars could be their most effective deployment to soils requiring stabilisation by revegetation. Specific mechanisms of contaminant-biochar retention and release over time and the environmental impact of biochar amendments on soil organisms remain somewhat unclear but must be investigated to ensure that the management of environmental pollution coincides with ecological sustainability.

1. Introduction

Soil contamination is an excess of any element or compound, through direct or secondary exposure, which causes a toxic response to biota or humans, resulting in unacceptable environmental risks (Adriano, 2001; Abrahams, 2002; Vangronsveld et al., 2009). Contamination of soils with both organic and inorganic toxins occurs worldwide (Mench et al., 2010) and more environmentally acceptable alternatives to unsustainable waste disposal techniques for dealing with this problem have been sought. As the modern agenda seeks to engineer natural processes to meet remediation needs in the most cost-effective ways possible, the *in situ* application of amendments to contaminated soils to bind pollutants whilst providing material conditions that promote plant growth and stimulate ecological restoration have become more popular (Adriano et al., 2004; Bernal et al., 2006; Vangronsveld et al., 2009). Regulators are now starting to recognise the influence of contaminant bioavailability and mobility on environmental risk and consequently there is an increasing adoption of a risk-based approach when assessing soil quality (Swartjes, 1999; Fernández et al., 2005). Such risk-based regulatory systems are concerned with the *effect* of the contaminant, rather than just the total *concentration* in the soil so measures addressing onward consequences of pollution rather than merely reducing total soil concentrations will be the focus of subsequent remediation strategies.

The amendment of soils for their remediation is a long standing procedure, with the aim of reducing the risk of pollutant transfer to proximal waters or receptor organisms. Organic materials are a popular choice for this as they are derived from biological matter and often require little pre-treatment before they may be directly applied to soils. Additionally the practice of soil amendment may also be a convenient route to the disposal of organic residues surplus to requirement. Carbon rich amendments, such as activated carbons, have been deployed for soil and sediment remediation purposes due to their ability to reduce contaminant bioavailability (Brändli et al., 2008; Cho et al., 2009) and hence risk. Activated carbons are a strongly sorbing carbonaceous charcoal material produced from the incomplete combustion of organic materials (e.g. coal or coconut shells), followed by activation to increase surface area (Brändli et al., 2008). Organic contaminants have been

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shown to sorb strongly to carbonaceous fractions, which are often present in soils at contaminated sites, such as coal (Cornelissen and Gustafsson, 2005), coke (Ghosh et al., 2003) or soot (Jonker and Koelmans, 2002). The sorption of organic contaminants to soils and sediments can be up to two orders of magnitude higher than expected on the basis of sorption to natural organic matter due to the presence of these additional carbonaceous fractions (Cornelissen et al., 2005). This greater sorption is responsible for the lower accumulation of organic pollutants than otherwise expected in organisms exposed to contaminated soils (Jonker et al., 2007; Kreitinger et al., 2007) and the limited potential for bioremediation of these soils due to the reduced microbial bioavailability (Hawthorne and Grabanski, 2000; Rhodes et al., 2008). The large sorption potential of carbonaceous fractions present in contaminated soils and sediments has led to the deliberate introduction of clean types of these fractions (e.g. activated carbon, biochar) into sediments, to reduce organic contaminant bioavailability (Zimmerman et al., 2004). More recent studies have also explored this possibility in soils (Brändli et al., 2008; Beesley et al., 2010; Fagervold et al., 2010). For inorganic contaminants, which cannot be degraded by microbial action, such as heavy metals, the labile loading in soils are of greatest ecological relevance because they have the greatest immediate environmental impact (Temminghoff et al., 1998; Madejón et al., 2009; Moreno-Jiménez et al., 2009, 2011; Beesley and Dickinson, 2010). In this respect materials for reducing the bioavailability of metals/metalloids can immobilise contaminants within the soil matrix (Bolan et al., 2003; Clemente et al., 2006) and reduce risk. In multi-polluted sites, such as those where organic and inorganic toxins breach safe levels, duality of amendments, that can reduce organic and inorganic contaminant mobility, could offer strategic and cost-effective advantages.

Like activated carbons, biochars are also produced by combustion processes (pyrolysis), but the source materials are generally limited to biological residues (e.g. wood, poultry litter, crop residues etc) and not commonly activated or further treated before application to soils. Some biochars, unlike activated carbons, are not fully carbonised, and are therefore composed of different proportions of carbonised to amorphous organic matter (Chun et al., 2004) and may react to contaminants in soils more like native soil organic matter. Symmetries may be drawn between activated carbons and biochars, with more and more studies being published solely documenting the use of non-activated charcoals, or biochars, to reduce organic contaminant bioavailability in soils with potential added benefits of increasing carbon sequestration and soil fertility (Cao et al., 2009; Spokas et al., 2009; Yu et al., 2009; Beesley et al., 2010; Zhang et al., 2010; Gomez-Eyles et al., 2011). In the recent literature the benefits associated with applying biochars to soils beyond their high C content, such as their soil conditioning properties have been reported (Novak et al., 2009; Yin Chan and Xu, 2009; Blackwell et al., 2009; Atkinson et al., 2010 and Sohi et al., 2010). It has also recently been demonstrated that biochar addition to grass pasture soil can reduce ruminant urine-derived N_2O emissions (Taghizadeh-Toosi et al., 2011). However, despite the increasingly diverse documented benefits of biochars to a variety of soil parameters, the implications of interactions between biochars, soils, microbes and plant roots are not well understood (Joseph et al., 2010) nor consistently reported because their application for soil remediation has been studied less than for other organic materials such as composts or manures (Namgay et al., 2010). Therefore, whilst biochars' properties may be potentially attractive for contaminated soils' deployment, their ecological efficacy must be determined and their field-based potential explored. Biochars may provide an important sink for dissolved contaminants at sites where leachates and runoff are collected and irrigated onto the soil surface (e.g. Robinson et al., 2007), but the ultimate success of such measures depends on the amount of contaminant that the biochar can retain before saturation, as well as the durability of the biochar–contaminant complex which may be related to the production parameters (for example the source material and temperature; Gell et al., 2011). When mixed with soils the degradation of biochar by the usual soil processes may also adjust the balance of element-organic matter complexation with time. It is such compounding factors that may render biochars unsuitable for the application to some contaminated soils whilst perfectly suitable in other situations.

With an increasing amount of literature on both trace element dynamics in the presence of biochars and the effects of biochars on ecological parameters, in this review we aim to:

i) Discuss agreements and conflicts regarding the effects of biochar on the mobility and availability of soil contaminants.
ii) Review the existing knowledge on the effects of biochar on plant growth and soil flora and fauna in the context of revegetation and ecological restoration of contaminated soils.
iii) Identify immediate research needs arising and suggest future directions for research.

2. Organic pollutants

2.1. Principals and practices affecting sorption

Many of the initial studies on the use of carbonaceous sorbent amendments to reduce organic contaminant bioavailability focused on the application of activated carbon to sediments. For example, laboratory studies have found significant reductions in polychlorinated biphenyl (PCB) bioaccumulation by clams, polychaete worms and other benthic organisms exposed to sediments amended with activated carbon (Millward et al., 2005; Zimmerman et al., 2005; McLeod et al., 2007, 2008; Sun and Ghosh, 2008). This has led to the *in situ* field-scale application of activated carbon, with reported 90% reductions in aqueous equilibrium PCB concentrations 18 months after activated carbon application (Cho et al., 2009). These results are particularly encouraging as aqueous equilibrium partitioning concentrations have been shown to give a good indication of organic contaminant bioavailability in sediments (Oen et al., 2006; Van der Heijden and Jonker, 2009). Decreases in aqueous equilibrium concentrations after amending sediments with activated carbon have also been reported for other organic contaminants like dichloro-diphenyl-trichloroethane (DDT) (Tomaszewski et al., 2007) and polycyclic aromatic hydrocarbons (PAHs) (Zimmerman et al., 2004). Such results are encouraging for reducing risk, but whilst studies utilising biochars have found that application rates of $\leq$10% have reduced the rapidly desorbing PAH fraction ($\sum$PAH; Gomez-Eyles et al., 2011) the increased sorption of, for example diuron, has consequently reduced its microbial degradation (Table 1; Yang et al., 2006). This presents a challenge to managing organic contaminants; in one respect sorption can reduce short term risk but may not always ultimately be remedially beneficial. This depends on the sorption strength and factors inherent to the contaminant, char and soil which can influence retention over time.

For example, organic contaminant sorption to organic matter is usually described using the dual-mode sorption concept (Pignatello and Xing, 1995; Xing and Pignatello, 1997). Within this concept, organic matter is assumed to be composed of two domains, one displaying linear and non-competitive *ab*sorption or *partitioning* (non-carbonised organic matter) (Chun et al., 2004; Chen et al., 2008; Zhou et al., 2009), and the other showing non-linear, extensive and competitive surface adsorption (carbonised organic

Table 1
Summary of selected recently reported studies utilising biochars and their influences on organic and inorganic pollutants.

Amendment type	Contaminant	Endpoints	Effect	Reference
	Organic			
AC[a] (2 and 5%).	Polychlorinated dibenzo-p-dioxins/ dibenzofurans (PCDD/Fs)	Earthworm bioaccumulation assays Aqueous equilibrium concentrations	78–99% reduction of TEQ[b]. 70–99% reduction in aqueous concentrations.	(Fagervold et al., 2010)
Powdered AC[a] (2%).	PAHs	Aqueous equilibrium concentrations	63–99% median reduction.	(Brändli et al., 2008)
Granulated AC[a] (2%)	PAHs	Aqueous equilibrium concentrations	4–64% median reduction for granulated AC[a].	(Brändli et al., 2008)
Hardwood-derived biochar (450 °C) mixed at 30% v:v.	PAHs	Rapidly desorbing fraction	>40% reduction.	(Beesley et al., 2010)
Activated charcoal (0.1, 1 and 5%).	Phenanthrene	Microbial mineralisation	>99% reductions with 0.l% amendment.	(Rhodes et al., 2010)
Pinus radiata derived biochar (350 °C) 0.1 and 0.5% application rate.	Phenanthrene	Sorption coefficient (K_d)[c]	K_d[c] increased by a factor of 2–51.	(Zhang et al., 2010)
Pinus radiata derived biochar (700 °C) 0.1 and 0.5% application rate.	Phenanthrene	Sorption coefficient (K_d)[c]	K_d[c] increased by a factor of 6–700.	(Zhang et al., 2010)
Hardwood-derived biochar (10%).	PAHs	Earthworm bioaccumulation assays Rapidly desorbing fraction	45% reduction in accumulation. >30% reduction in rapidly desorbing fraction (ΣPAH).	(Gomez-Eyles et al., 2011)
Wheat ash (1%).	Diuron	Sorption	Sorption increased in amended soils by a factor of 4 on a unit mass basis.	(Yang and Sheng, 2003b)
Wheat derived char (0.05, 0.5 and 1%).	Diuron	Sorption	Sorption increased by a factor of 7–80 with 1% amendment.	(Yang et al., 2006)
		Microbial degradation	Diuron degradation reduced by >10% with 0.5% amendment.	
Eucalyptus spp derived biochar (450 °C) 0.1, 0.5, 1.0, 2.0 and 5.0% application rates.	Diuron	Sorption	Sorption capacity increased in amended soils by a factor of 7–80.	(Yu et al., 2006)
Eucalyptus spp derived biochar (850 °C) 0.1, 0.2. 0.5. 0.8 and 1.0% application rates.	Diuron	Sorption	Sorption capacity increased in amended soils by a factor of 5–125.	(Yu et al., 2006)
Sawdust-derived biochar.	Atrazine and acetochlor	Sorption coefficient (K_d)[c]	K_d[c] increased by a factor of 1.5 for acetochlor. Atrazine sorption also increased, but increase cannot be quantified.	(Spokas et al., 2009)
Eucalyptus spp derived biochar.	Chlorpyrifos and carbofuran	Microbial degradation *Allium cepa* growth and accumulation	>40% reduction in degradation. Increase in *Allium cepa* fresh weights and 10 and 25% reductions of chlorpyrifos and carbofuran in total plant residues respectively.	(Yu et al., 2009)
Charcoal derived biochar (350 °C).	Terbuthylazine	Sorption	Sorption increased in amended soils by a factor of 2.7.	(Wang et al., 2010)
AC[a]	Heptachlor exo-epoxide	Growth and uptake into *Cucurbita maxima* and soil solution concentrations	No effect on growth but a reduction in soil solution concentrations and uptake into shoots.	(Murano et al., 2009)
Gossypium spp derived biochar (450 and 850 °C) 0, 0.1, 0.5. and 1.0% application rates.	Chlorpyrifos and fipronil	Half-lives of pesticides in sterilised and unsterilised soils. Growth and uptake into *Allium tuberosum*	Half life of chlorpyrifos and fipronil increased by up to 161% and 129% in unsterilised soil and up to 136% and 151% in sterilised soil respectively with 1% amendment with 850 °C biochar. Increase in the fresh weight of *Allium tuberosum* with 0.5 or 1% amendment with 850 °C biochar. Uptake of Chlorpyrifos and fipronil in *Allium tuberosum* significantly reduced with 1% amendment of both 450 °C biochars by 56% and 20% and 850 °C biochars by 81% and 52% respectively.	(Yang et al., 2010)
Powdered AC[a] (0, 200, 400, and 800 mg AC per kg soil).	Dieldrin	Tenax extractable (6 h) dieldrin concentrations. Uptake into *Cucumis sativus*	Decrease in tenax extractable dieldrin. No relationship between AC and uptake into *Cucumis sativus*.	(Hilber et al., 2009)
Sawdust-derived biochar (700 °C).	Terbuthylazine	Sorption	Sorption increased in amended soils by a factor of 63.	(Wang et al., 2010)

(*continued on next page*)

Table 1 (*continued*)

Amendment type	Contaminant	Endpoints	Effect	Reference
	Inorganic			
Hardwood-derived biochar (400 °C) at 20% v/v application.	As	Pore water concentrations and growth and uptake into *Miscanthus* × *giganteus*.	Increase in pore water concentrations in 2 out of 3 soils. No significant difference in growth or uptake of As into foliage.	(Hartley et al., 2009)
Eucalyptus saligna derived activated biochar (550 °C) at 0, 5, and 15 g biochar per kg soil.	As, Cd, Cu, Pb, and Zn spiked at 0, 10, and 50 mg kg^{-1}.	Phosphate-extractable As and DTPA-extractable Cd, Cu, Pb and Zn. Growth and uptake into *Zea mays*.	17% increase in phosphate-extractable As. 51% decrease in DTPA-extractable Pb and 124% increase in DTPA-extractable Zn. No significant difference in maize shoot dry matter. Decrease in As, Cd, Cu and Pb in shoots.	(Namgay et al., 2010)
Orchard prune residue derived biochar (500 °C) mixed with mine tailings at 0–10% (dry wt).	Mine tailings with Cd, Cr, Cu, Ni, Pb and Zn.	Leachabilty testing (TCLP) and bioavailability (DTPA).	Highest biochar application rate reduced leachable Cd, Pb and Cr. Bioavailable Cd, Pb and Zn reduced significantly (compared to control) by all application rates. Greatest reduction for Cd.	(Fellet et al., 2011)
Hardwood-derived biochar (450 °C), mixed with soil (30% v:v) or leached in column tests.	Brownfield soil contaminated with As, Cd, Cu and Zn.	Extraction of pore water in 60 day field pot-trials. Extraction of column leachates weekly, for 8 weeks.	Reduction in Cd in field pore water (10 fold) compared to untreated control. Some mobilisation of As and Cu. In column tests, Cd and Zn concentrations reduced 300 and 45 fold respectively.	(Beesley et al., 2010; Beesley and Marmiroli, 2011)
Hardwood-derived biochar (450 °C), mixed with soil (30% v:v) or applied as surface mulch (to 30 cm).	Urban soil with moderately elevated levels of As, Cd, Cu, Pb and Zn.	Extraction of pore water in 6 month lysimeter (biochar mixed with and without addition of *Lumbricus terrestris*) and 1 year soil profile study (biochar surface mulch).	Biochar surface mulch enhanced As and Cu mobility in the profile, had little effect on Cd and Pb. In the lysimeters, biochar enhanced As, Cu and Pb mobility; earthworm inoculation muted this effect.	(Beesley and Dickinson, 2011)

[a] Activated carbon.

[b] Toxicity equivalent.

[c] Sorption coefficient estimated for Freundlich sorption isotherm.

matter) (Cornelissen et al., 2005). It is this extensive adsorption that is mainly responsible for the increased sorption capacity of soils containing carbonaceous sorbents, but introducing biochars may adjust the ratio of carbonised to amorphous organic matter.

2.2. *Material factors affecting biochars' performance*

Increasing the pyrolysis temperature of biochars increases their degree of carbonisation, which increases their surface area (Chen et al., 2008) but reduces the abundance of amorphous organic matter. This has been shown to increase biochars' capability to adsorb organic contaminants (Yu et al., 2006; Zhou et al., 2009; Kasozi et al., 2010; Wang et al., 2010; Zhang et al., 2010), reducing their uptake into soil organisms (Yu et al., 2009). Chen et al. (2008) measured the surface area of biochars at different pyrolysis temperatures and found biochars pyrolysed at 700 °C had half the surface area of activated carbon. This suggests that activating biochars pyrolysed at high temperatures will have the highest organic contaminant remediation potential, although pyrolysis temperatures of above 400 °C have been shown to decrease surface area in some cases, presumably due to the collapse of micropore walls (Sharma et al., 2004). Given that adsorption to biochars will be predominantly non-linear this suggests that even if biochars with high surface areas are produced sorption sites could become saturated. The blocking of sorption sites in activated carbons by organic matter has been extensively reported (Kilduff and Wigton, 1998; Cornelissen and Gustafsson, 2005; Rhodes et al., 2010), and several studies have hypothesised that this is the likely cause for the diminished capability of aged biochar to adsorb organic contaminants (Yang and Sheng, 2003a; Zhang et al., 2010). Reduced efficiency of carbonaceous sorbents due to competition between contaminants has also been reported (Yang and Sheng, 2003b; Cao et al., 2009). In a study comparing activated carbon to biochars produced at lower temperatures, the biochars were found to absorb atrazine linearly into their non-carbonised organic matter (Cao et al., 2009) suggesting advantages when remediating soils with organic and inorganic contaminants that compete for sorption sites. However, the sorption capacities of the low temperature biochars were an order of magnitude lower than that of the activated carbon for atrazine. It may be the case that the amorphous portion of additive biochars, which depends to an extent on its production, could compete with native organic matter in soils with compounds favouring different fractions of organic matter being preferentially retained by either soil or the additive char. A summary of selected recently reported studies on organics can be found in Table 1; selected studies using activated carbons are included for comparison.

2.3. *Conflicts and compromises arising*

Laboratory studies exploring the potential of various types of carbonaceous sorbents to reduce the bioavailability of polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs) (Fagervold et al., 2010), PAHs (Brändli et al., 2008; Yang et al., 2009; Beesley et al., 2010; Rhodes et al., 2010; Zhang et al., 2010; Gomez-Eyles et al., 2011), and organic pesticides (Yang and Sheng, 2003b; Yang et al., 2006; Yu et al., 2006; Cao et al., 2009; Spokas et al., 2009; Yu et al. 2009; Wang et al., 2010) in soils (Table 1) have demonstrated another possible compromise. From an agricultural perspective, the increased sorption of organic pesticides to soil can be beneficial in terms of reducing pesticide residues in crops (Yu et al., 2009), but it can also be detrimental in terms of reducing herbicide efficiency, resulting in the need for higher application rates of these chemicals (Yu et al., 2006; Spokas et al., 2009; Kookana, 2010). It would appear, therefore that there may be a balance to be reached somewhere between the complete immobilisation of organic compounds, in one respect removing risk, and the sorption strength, allowing microbial degradation of some organic contaminants. A compromise between the increased sorption capacities of high pyrolysis temperature activated chars and the benefits provided by low temperature chars in terms of reduced toxicity and linear absorption, is needed depending on contaminant remediation goals and the compound in question.

3. Inorganic pollutants

3.1. *Heavy metal mobility*

Unlike organic contaminants, whose sorption to biochar may ultimately increase their persistence in the environment because they will be protected from microbial degradation (Table 1), inorganic elements are not degraded. This presents its own challenges to utilising biochars. Biochars are able to complex metal ions on their surfaces and therefore reduce bioavailability (Fig. 1), which renders a reduced risk. However, by this mechanism essential plant nutrients may also be immobilised. If a purely quantitive reduction in heavy metal mobility is sought then the results of Uchimiya et al. (2010) are encouraging. In this study the effects of a broiler litter-derived biochar amendment were compared to a pecan shell-derived steam-activated carbon in synthetic rainwater leaching experiments to determine both the efficiency of biochar and activated carbon for immobilising Cu, Ni and Cd and the effects of ageing (oxidation) on metal retention. Here biochar was most effective at reducing Cu concentrations in leachate, while the activated carbon reduced Ni and Cd concentrations the furthest. However, in a sandy loam soil, with low intrinsic Cu retention capacity, it was suggested by Uchimiya et al. (2011a) that cation exchange capacity (CEC) was the primary mechanism by which biochar enhanced Cu retention whilst, in a clay-rich, alkaline soil with higher intrinsic Cu retention capability, sorption to mineral (ash) components of the char assisted retention (precipitation). Adding biochar increased the rate at which the soil solution came to equilibrium (sorption-desorption hysteresis) (Uchimiya et al., 2011b) which may increase the rate of sorption of any further contaminants added to the soil matrix. Clearly specific soil parameters influence complexation and competition between elements and consequences of biochar addition to soil chemistry.

In the case of phyto-toxic concentrations of metals, studies utilising a sediment-derived canal bank soil heavily contaminated with Cd and Zn, amended with a hardwood-derived biochar showed significant reductions in concentrations of both metals in pore water collected during 60 days field exposure (Beesley et al., 2010). In a column tests using the same soil as the field-exposure experiment, biochar similarly reduced concentrations of Cd and Zn in leachate with evidence of surface sorption of both Cd and Zn to biochar (Beesley and Marmiroli, 2011), examined by scanning electron microscopy (SEM). Fig. 1 shows the relative increase in surface concentration of Cd and Zn on a piece of biochar, shown by the image's brightness, after contaminated leachate from soil was passed over it in that experiment. Notice the network of interior pores in the SEM images which may differentially affect element retention, providing an uncertainly as to the location of the greatest sorption. Novak et al. (2009) also reported a decrease in Zn concentrations in leachate after 0–2% (wt:wt) pecan-shell biochar addition to an acidic agricultural soil, possibly related to an increase in pH whilst Laird et al. (2010) similarly discovered that leachate recovery of Zn, added via dried swine manure to leaching lysimeters with loamy soil and biochar, decreased with increasing biochar application rates (from 0 to 20 g biochar per kg^{-1} soil). In that particular study Cu, as well as P, K, Mg and also Ca decreased after

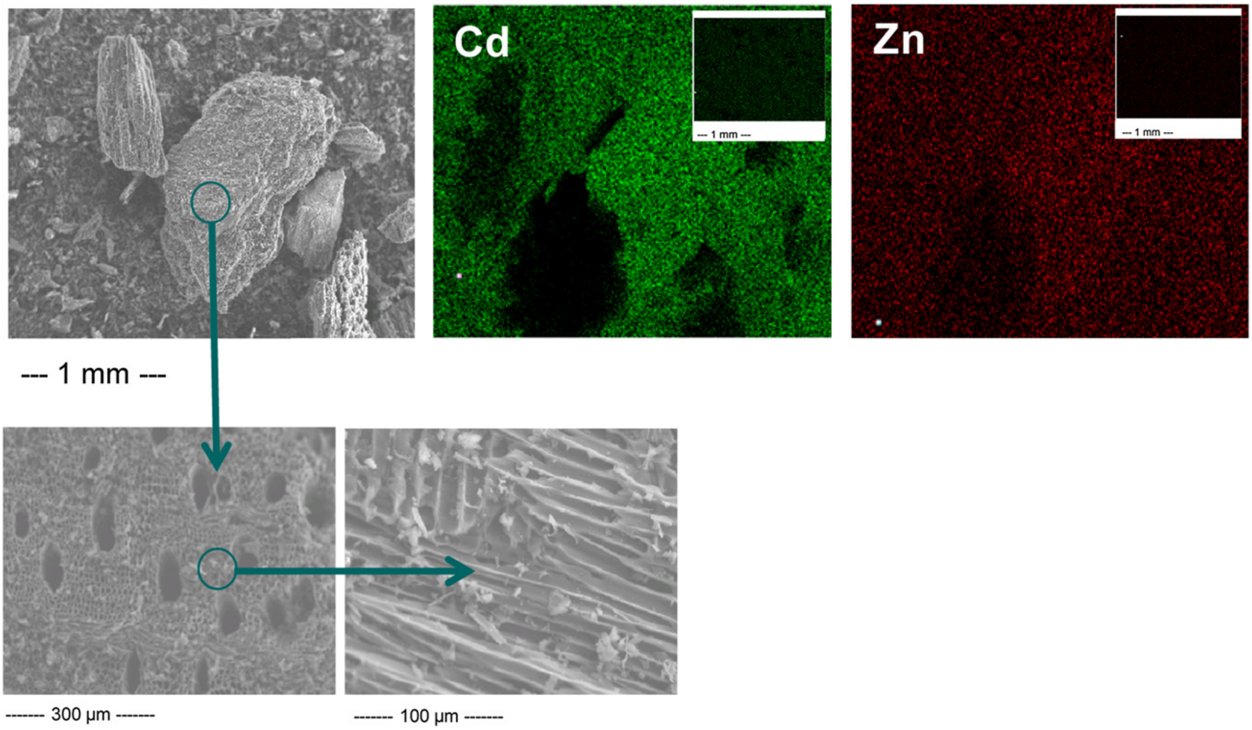

Fig. 1. Scanning Electron Microscope (SEM) images of a hardwood biochar's surface at increasing magnifications and element dot-maps demonstrating the retention, by surface sorption, of soluble Cd and Zn from a polluted soil after a column leaching test. Inset dot-maps are biochar's surface metal retention before passing Cd/Zn contaminated leachate through biochar filled columns whilst the main dot-maps are after leaching (after Beesley and Marmiroli, 2011) demonstrating, by the lighter shade, surface retention.

biochar addition. Fellet et al. (2011) amended mine tailings with 0–10% orchard prune derived biochar, finding that, as well as increasing pH and CEC, biochar reduced bioavailable (DTPA-extractable) concentrations of Cd, Pb and Zn. The results of various studies examining heavy metals and As are summarised in Table 1.

With specific regard to lead, Cao et al. (2009) conducted batch sorption tests on dairy-manure biochars produced at different temperatures compared to a commercially available wood-derived activated carbon. Biochar had a greater capacity for Pb sorption than activated carbon, despite its lower surface area, retaining up to 6 times more Pb. One of the mechanisms suggested by the authors was that the biochar may reduce Pb mobility by the precipitation of insoluble Pb-phosphates. Biochar was found to be rich in P, and unlike C and N, an increase in the temperature at which biochar is produced has been found to increase P, Mg and Ca (Cao and Harris, 2010). Due to the fact that biochars' properties are more aligned to soils than activated carbons' are, its mechanisms of chemical rather than solely physical behaviour in soils may be further in focus, which somewhat complicated the interpretation of some results but may allow bespoke biochars to be produced. The study conducted by Cao et al. (2009) revealed that the biochar produced at 200 °C was more effective in sorbing Pb than biochar produced at 350 °C because despite greater total P concentrations, the 200 °C biochar had the greatest soluble P. Karami et al. (2011) added hardwood-derived biochar to a heavily contaminated mine soil, also suggesting that P may influence Pb retention in biochar amended contaminated mine soil (psuedo-total lead; 2%). In that study biochar addition reduced pore water Pb concentrations from ~ 80 mg l^{-1} to less than half of that value. However, combining biochar with greenwaste compost was found to reduce Pb in soil pore water even further (<5 mg l^{-1}), suggesting combined effects and supporting experimentation not only on physical retention of contaminants but chemical and biological drivers.

3.2. Arsenic behaviour and implication to other elements

Arsenic is a common soil contaminant that is given special attention due to its toxicity. Unlike cationic metals (Cu, Zn, Pb, Cd etc), it is present as an oxy-anion in solution and presents some specific challenges to remediation because, unlike metals, arsenic mobility in soil is increased with increasing soil pH and binds to anion exchange sites on soils such as Fe, Al and Mn oxides and oxyhydroxides (Masscheleyn et al., 1991). This may also mean that those material conditions induced by biochar addition to soils, which may not necessarily impact on metal mobility, could control As mobility, regardless of the capacity of biochar as a sorbent. Biochars may have demonstrated effectiveness for As removal from wastewaters (Mohan and Pittman, 2007) but some concerns surround their application to As contaminated soils due to the potential increases in soil pH (Hartley et al., 2009) and soluble C (Beesley et al., 2010). Parameters such as pH and C may need to be controlled for maintenance of soil fertility which may not be conducive to reducing As mobility given that mobilisation and co-mobilisation could be respective consequences of increased pH and soluble C.

In terms of documented studies, increased concentrations of As in the pore water of a moderately contaminated urban soil were recorded after it had been amended with 30% (v:v) hardwood-derived biochar in both surface mulch or mixed application (Beesley and Dickinson, 2011) whilst Beesley and Marmiroli (2011) found that biochar had a negligible influence on As concentrations in contaminated effluent leached from a multi-element polluted soil in column tests, despite some surface sorption. Namgay et al. (2010) noted increases in phosphate-extractable As after biochar addition whilst Hartley et al. (2009) found that an increase in pore water As did not translate to increased foliar concentrations of this metalloid in *Miscanthus* × *giganteus* (Table 1). It can reasonably be expected that other anionic elements, such as antimony, chromium, molybdenum, selenium or tungsten, may be influenced similarly to As when biochar is applied to soil.

3.3. Side effects and their mitigation

To overcome such limitations associated with some biochars relating to mobilisation of arsenic for example, their impregnation with other solid amendments to aid in the immobilisation or degradation of soil contaminants has been tried. The combination of biochar with iron-oxides may be a good option to achieve mutual benefit as iron-oxides can reduce As mobility in soil by anion exchange (Warren et al., 2003; Tighe et al., 2005). Nguyen et al. (2008) found that ageing black carbon, often used as a proxy for biochar, retained Fe on particle surfaces after exposure to soils. Mench et al. (2003) found good synergisms between compost and iron-rich materials to decrease available fractions of metals and As in soils, so biochar in combination with compost and iron-rich amendments may provide As-retention capability, enhanced retention of phyto-toxic metals, enhanced degradation and sorption of organics (compost) and reduced C to N/P/K ratios (compost). Furthermore the preparation of biochars with magnetised Fe^{3+}/Fe^{2+} has been demonstrated to enhance organic pollutant and phosphate sorption, compared to non-magnetic char and no competitive effects were observed between organic pollutants and phosphate (Chen et al., 2011). For wastewater applications this is valuable because the sorbent can be removed by a magnet, but the applications to soils have yet to be explored. Although potentially beneficial, such modifications raise the production cost of the biochar, which may place practical limitations on its use in the field.

Adding biochars, which typically have a pH of 7–9, to acidic soils will result in an increase in the soil pH and a concurrent decrease in the mobility of cationic metals in soils due to reduced competition between H^+ ions and metal ions for cation exchange sites either directly on the surface of biochar or as a general liming effect on the soil matrix. But, the addition of biochars to neutral or alkaline soils may not result in as dramatic decreases in metal mobility (e.g. Gomez-Eyles et al., 2011), indicating that many of the reductions in metal mobility observed are due to the liming effect of biochar to acidic soils and not necessarily to biochar *per se* as an immobilising agent.

Yuan and Xu (2011) incubated 9 biochars (pH 6.4–10.4) of leguminous and non-leguminous origins, for 60 days, in an acid soil (pH 4.3). Non-legume biochars raised pH by <0.7 units whereas legume biochars raised pH by >1 unit. In this study the liming effect was positively correlated with the biochar pH, so it was possible to predict the pH increases of adding biochar to the soil and thus consequent likely effects to pollutant mobility. Beesley and Marmiroli (2011) also noted sharp increases of ~ 2 units in solute pH after de-ionised water was passed through columns containing biochar. Karami et al. (2011) measured soil and soil pore water pH after an acid mine soil was amended with a hardwood biochar noting no difference in the pH of the amended soil but significant differences in the pH of the soil pore water of ~ 2 units between different sample collections (1, 2 and 3 months). It may not always translate that soil pH and soil solution pH respond in the same way to biochars and this may mean that, even if biochar were added as a surface mulch without mixing with soils, their liming of percolating waters could mobilise some elements in soils to which there was no physical contact. The same could be true of the effects of soluble C for, whilst the application of organic materials to soils has resulted frequently in an immobilisation of metals in soils (Adriano et al., 2004; Madejón et al., 2009; Mench et al., 2010), they can also enhance solubility by co-mobilisation with dissolved organic carbon (DOC) (Bernal et al., 2006). Considerable differences in concentrations of water soluble carbon (WSC) have been recorded from different biochars with Gell et al. (2011) measuring concentrations of 0.1–109 g kg^{-1} WSC in biochars with a range of source materials and production temperatures. Beesley and Marmiroli (2011) found that WSC concentrations were reduced rapidly as biochar was leached in a column system, suggesting considerable rapid outputs of C in solution from biochar to amended soil systems upon initial application or environmental exposure. Beesley et al. (2010) found that Cu mobility increased after a hardwood biochar amendment because biochar increased DOC in soil pore water whilst Gomez-Eyles et al. (2011) showed a decrease in water soluble carbon and a concurrent decrease in Cu mobility after amendment of a hardwood-derived biochar, so the linkages are far from straightforward and will depend on local soil conditions.

4. Ecological and biological remediation

4.1. Plant-based approaches

We have discussed how biochars may immobilise or mobilise some soil contaminants, and examined evidence of both cases. However, in terms of remediation of soils there are supplementary ecological aspects to consider, which might be borne on greatly by the properties and peculiarities of different biochars. Given that contaminated land often contains young, poorly developed soils with little or no vegetation cover (Bellamy et al., 2005; Mench et al., 2010) the revegetation of contaminated soils is key to its stabilisation (Arienzo et al., 2004; Ruttens et al., 2006) and the presence of a vegetative cover over bare soil reduces the potential for migration of contaminants to watercourses or being inhaled by receptor organisms (Tordoff et al., 2000). The goal of plant-based approaches to minimising the risk posed by contaminated soils (phytomanagement) is to limit the transfer of the contaminants to ecosystems or humans (Robinson et al., 2009). In the case of organics, this is achieved through the degradation of a contaminant or making it inert and environmentally immobile and biochar may achieve the latter but not necessarily via the former mechanism. For inorganic pollutants, degradation does not occur and therefore reducing mobility and bioavailability is desirable. These factors present challenges to multi-contaminant polluted sites.

The pure benefits of biochar to plant-based remediation may be related to enhanced plant growth as liming effects, increased water holding capacity and improved soil structure have been reported after the amendment of agricultural soils with biochars (Blackwell et al., 2009; Atkinson et al., 2010; Sohi et al., 2010), all of which are material conditions conducive to plant success. However, many of these benefits are only seen when an organic or inorganic fertiliser is added along with the biochar amendment, suggesting that biochar alone is often unsuitable as a soil amendment to stimulate revegetation (Yamato et al., 2006; Chan et al., 2007; Steiner et al., 2008; Asai et al., 2009; Van Zwieten et al., 2010a). Some studies report a decrease in plant growth after amendment of soils with biochars (Kishimoto and Sugiura, 1985; Mikan and Abrams, 1995), although others report agronomic benefits when biochar is exclusively added to soils (Novak et al., 2009). Table 2 summarises the results of several recent studies utilising plants and measuring plant growth parameters. One reason for the apparent contradictions is that some biochars can increase nutrient retention which may prevent leaching and increase nutrient use efficiency (Major et al., 2009) but may also decrease the availability of nutrients in unfertilised soils. For example, sugar beet tailings biochar has been shown to adsorb phosphate (Yao et al., 2011). Ultimately, adjusting the balance of available nutrients in unfertilised plots could be both beneficial, in nutrient excessive conditions and damaging in nutrient limited soils, causing deficiency. The evidence therefore

Table 2
Summary of selected recently reported studies utilising biochars and their influences on plant growth and success.

Culture system	Biochar characteristics	Primary effect	Reference
Hydroponically cultured pepper (*Capsicum annuum* L.) and tomato plants (*Lycopersicum esculentum* Mill) in coconut fibre and tuff with NPK fertilisation.	Citrus wood biochar (1–5% application rate, by weight).	Increased plant yield, microbial biomass in rhizosphere and hormesis response.	(Graber et al., 2010)
Field experiment with rice (*Oryza sativa* L.).	Commercially sourced rosewood biochar (0 or 8 t ha^{-1} application rate).	Biochar improved rice grain yields, especially in combination with additional N and P but depleted chlorophylls without fertilisation.	(Asai et al., 2009)
Greenhouse experiment with dandelion and clover (*Taraxacum* ssp. and *Trifolium* ssp.) in soil.	Beet root chips derived biochar (0–80%, v:v, application rate).	Positive effects on plant growth and symbionts at low rates of BC application (<20% v:v), but negative effects for higher rates.	(Rillig et al., 2010)
Pot trial with cherry tomato (*L. esculentum*) in soil under greenhouse conditions.	Wastewater sludge biochar (10 t ha^{-1}, in combination with NPK).	Biochar increased plant biomass and production (by 64%), especially when it was combined with fertilisation.	(Hossain et al., 2010)
Pot trial with miscanthus (*Miscanthus x giganteus*) in soil.	Native British hardwood biochar (20% v/v).	Biochar did not significantly increase plant growth, but raised alkalinity.	(Hartley et al., 2009)
Laboratory incubation of watercress (*Lepidium sativum*) germination in aqueous extracts from bauxite refinery residue sand mixed with biochar.	Municipal greenwaste biochar (40 and 80 g l^{-1} (volume equiv. 40 and 80 Mg ha^{-1})).	Small, but non-significant reduction in germination index (percent germination and root length compared to distilled water control).	(Jones et al., 2010)
Greenhouse pot trial in clay-loam soil with common beans of N-fixing and non N-fixing variety (*Phaseolus vulgaris* L.).	Eucalyptus derived biochar (0–90 g biochar to 1 kg soil) combined with N and P fertilisation.	Moderate biochar application rates significantly improved atmospheric N fixation (by 49% and 78% with 30 g kg^{-1} and 60 g kg^{-1} biochar application respectively), but applications above 60 g kg^{-1} reduced N-fixation because biomass reduced.	(Rondon et al., 2007)
Fieldtrial for 4 years with maize (*Zea mays* L.), soybean (*Glycine max* (L.) Merr.) rotation.	Wood biochar made for cooking, no further details were available (0, 8 and 20 t ha^{-1} disc harrow incorporated).	First year maize grain yield did not increase, but increased by 28, 39 and 140% (over control) in years 2, 3 and 4 respectively with 20 t ha^{-1} biochar. Effects attributed to 77–320% increases in available Ca and Mg.	(Major et al., 2010)

suggests that the use of biochar in nutrient limiting conditions combined with an organic amendment, such as compost, may be more suitable for the remediation and revegetation of contaminated land (Beesley et al., 2010; Peltz et al., 2010). As biochars have been shown to adjust both nutrient and contaminant availability, retaining the balance between deficiency of nutrients and exclusion or immobilisation of pollutants on contaminated soils requiring vegetation cover could be difficult. The combined application of other organic amendments with biochars could be especially attractive when considering biochars with high cation exchange capacities. Biochars with high cation exchange capacities are the most suited for use in the remediation of metal contaminated soils, but they are also likely to retain more plant nutrients by the same mechanism that they immobilise contaminants.

4.2. Contaminant transfer

Notwithstanding the ability of amendments to efficiently retain pollutants, where plant growth is encouraged on contaminated soils, high biomass of the edible parts of plants could increase the risk of transfer of contaminants to higher trophic levels. Biochar may be an effective amendment for reducing plant uptake of pollutants due to its strong capacity to decrease the available fraction of contaminants in the soil and decrease uptake of trace inorganic elements (Namgay et al., 2010) and organic compounds (Yu et al., 2009). If pollutant concentrations in soils and uptake to plants is low then growth of plants yielding a high biomass can be encouraged by the combination of biochar and amendments with high concentrations of available N, P, K. If pollutant concentrations are high, it would be recommended to favour a higher proportion of biochar, with lower concentrations of labile nutrients, for gently encouraging the re-starting of natural processes (Bradshaw, 1997) but discouraging rampant revegetation and high biomass, which could increase transfer of pollutants. In this context, and considering that the growth of short rotation coppice on contaminated land has previously been reported (French et al., 2006), biomass produced on such soils could be pyrolysed to produce energy and the resulting biochar returned to the soil as a beneficial amendment, if the contaminants are demonstrated to be retained by the biochar (Stals et al., 2010), maintaining as closed a system as possible. Hartley et al. (2009) suggested the feasibility of growing *Miscanthus* on an As-polluted soil because low soil-plant transfer was observed, but the results suggested that biochar alone could not enhance yields on this industrially polluted soil, which suggests a need to combine biochars with other amendments if a certain yield of biomass is required. Karami et al. (2011) found that transfer of Pb and Cu to ryegrass from a soil amended with hardwood-derived biochar, could be differentially interpreted either through transfer co-efficients or bioconcentration factors. Ultimately they concluded that plant biomass and uptake had to be combined to assess risk, and those two factors were opposingly influenced by biochar. In this respect it would depend on the end use of the biomass as to whether, regardless of pollutant uptake, high biomass was encouraged.

4.3. Challenges to plant survival and success

Considerations about the long term effectiveness of biochar for promoting plant growth and biomass render several important, more mechanistic questions about biochars' effects on plant survival and success. Spokas et al. (2010) showed that the biochar-derived plant hormone ethylene (C_2H_4) may be responsible for some of the beneficial effects to plants observed due to biochar amendment. However, there was decreasing ethylene measured with increasing pyrolysis temperature and surface area of biochars. There was also no detectable ethylene in an activated charcoal treatment which had, by an order of magnitude, the greatest surface area. This indicates that either less ethylene is produced during higher pyrolysis temperatures, or that it is sorbed by biochars and activated charcoals with a high surface area. It has also been suggested, due to its ability to sorb organic chemicals in soils, that activated carbon can affect allelopathy and symbiosis. Activated carbon has been used in experiments to study allelopathic interactions between plants as it is able to sorb allelopathic compounds and minimise allelopathy between plants (Lau et al., 2008). However, it has been shown that in addition to this, activated carbon can reduce mycorrhizal root colonisation due to its ability to sorb signalling compounds between plant roots and symbioants (Wurst et al., 2010), despite evidence that in the majority of cases biochar additions increase mycorrhizal root colonisation (Warnock et al., 2007). In addition, compounds such as flavonoids, secreted for the signalling of compatible rhizobia by a legume host, that have been shown to have similar log K_{oc} values to the PAH naphthalene (Shaw and Hooker, 2008), are likely to sorb strongly to biochars that sorb naphthalene rendering them unavailable. Whether this is beneficial or detrimental to plant growth and revegetation essentially depends on whether the sorption of plant signalling compounds to biochar is a temporary process which increases their longevity in the soil (Thies and Rillig, 2009), or a permanent process, as would be desirable for the sorption of organic contaminants, and therefore decreases the overall availability of these compounds (Warnock et al., 2007). The more effective a biochar is at sorbing organic chemicals, the more likely there will be a negative impact on the availability of plant signalling compounds to symbiotic microorganisms, which may have negative impacts on plant growth and the success of revegetation, or to the action of phytoalexins, which may reduce plant resistance to disease. Conversely biochar has been shown to induce systemic resistance to foliar fungal pathogens in tomato or pepper and to broad mite pest on pepper (Elad et al., 2010). In some cases biochar application may reduce the needed dose of biocides in soil to avoid plagues and plant illness. It might be the case that contaminated soils receiving biochar inputs may require less intensive management practices to supply sustainable vegetation cover than where other amendments or no amendments are used.

4.4. Micro-biological communities

Sustainable remediation of a contaminated soil should be broadly interested in maintaining or ideally enhancing soil quality. This can be achieved by sequestering carbon, reducing soil erosion, preserving the quality of ground and surface water and increasing soil biodiversity. Soil biota are responsible for providing a range of ecosystem services such as the decomposition of organic matter (to which degradation of organic contaminants finds association), cycling of nutrients, bioturbation and suppression of soil-borne disease and pests (Brussaard, 1997). The soil microbial community can also be used as an indicator of the quality of a soil and the extent to which degradation has occurred or restoration has progressed (Harris, 2003). The porous nature of biochars and their ability to sorb soluble organic carbon provides habitats within which microbiota can feed on sorbed organic substrates protected from grazers such as collembola, nematodes or protozoa (Pietikäinen et al., 2000; Hamer et al., 2004; Atkinson et al., 2010). This may be the reason for reported increases in microbial biomass and activities of biochar amended soils (Wardle et al., 1998; Pietikäinen et al., 2000; Chan et al., 2008; Steiner et al., 2008; Kolb et al., 2009; Steinbeiss et al., 2009). Chan et al. (2008) found an increase in microbial biomass C with increasing rates of non-activated (450 °C pyrolysis) biochar amendment but no effect with increasing rates of steam-activated (550 °C pyrolysis) biochar amendment. This may be due to the underestimation of microbial biomass C in activated carbon amended soils using a K_2SO_4 extraction (Durenkamp et al., 2010), or an indication that activation of charcoal produces a habitat less suitable for microbial colonisation. Pietikäinen et al. (2000) also found that activated carbon did not increase microbial biomass or activity as much as non-activated biochars. In addition, reduced rates of microbial degradation of organic contaminants have been observed in the presence of activated carbon reportedly due to sorption of substrates onto the surface of the activated carbon and the concurrent reduction in bioavailability (Yang et al., 2009; Rhodes et al., 2010); reductions in the biodegradation of organic pesticides due to the presence of biochar have also been reported (Yang et al., 2006), as discussed earlier. The soil biodiversity of contaminated land is usually poor because the contaminants are toxic to soil communities at high concentrations (Zhang et al., 2004; Andreoni et al., 2004; Giller et al., 2009). Since biochar is a potentially diverse niche for microorganisms, the application of biochar to soils may assist the preservation and support of soil biodiversity and biotope for the micro and mesobiota in contaminated soils.

4.5. Soil animals

Earthworms are considered ecosystem engineers owing to the role that they play in organic matter degradation, nutrient cycling and hydrology (Jones et al., 1994), all of which facilitate the revegetation of degraded land after disturbance (Boyer and Wratten, 2010). Studies on the toxicity of biochar to earthworms in the literature are both scarce and contradictory. Most of the experiments that have been performed have utilised *Eisenia fetida*, commonly used in ecotoxicology for testing the toxicity of chemicals to earthworms. This species is chosen because it is reasonably tolerant to contaminants, widely available and responsive in laboratory assays but it may not be the most suitable because it is a litter dwelling compost species that does not inhabit the mineral soil and is not common in most contaminated or agricultural environments (Lowe and Butt, 2007). Both Fagervold et al. (2010) and Gomez-Eyles et al. (2011) found that addition of activated carbon and hardwood-derived biochar respectively reduced the weight of *E. fetida* during the remediation of contaminated soils. However, neither study found a reduction in the lipid content of earthworms, which indicates that the earthworms did not starve or completely avoid ingestion during the test period. Soluble organic carbon, from which earthworms derive nutrition, may be sorbed to biochar and made unavailable to the worms, as suggested by Jonker et al. (2009) in a study involving the use of polychaete worms in contaminated sediments. In contrast, no significant difference in the weight of the soil dwelling worm, *E. fetida* was observed when a 2% amendment of biochar was made to laboratory and field pentachlorophenol (PCP)-contaminated soils (Wen et al., 2009). Liesch et al. (2010) found that whilst pine chip biochar had no effect on mortality or weight of *E. fetida*, poultry litter biochar caused 100% mortality in treatments above 67.5 Mg ha^{-1}. This was reportedly due to greater pH, salinity and ammonia concentrations in the poultry litter biochar. Elevated concentrations of Na, Mg, Al, Cu, Fe, Zn and As were also observed but these were below those known to cause toxicity. Washing or leaching biochars that have high salinity, ammonia or toxic element contents is suggested as a method to prevent toxicity

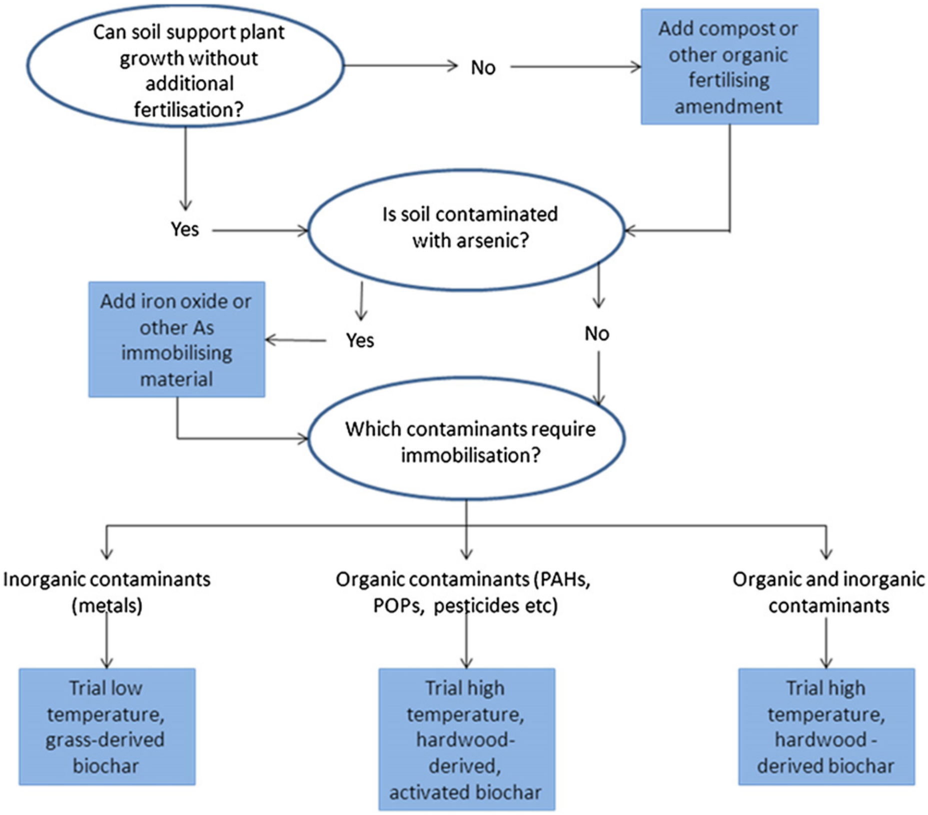

Fig. 2. Simplified schematic representation of scenarios in which various biochars could be trialled on polluted soils, relating to whether or not soil possesses sufficient nutrient capital to sustain vegetation, or whether additional fertilising organic materials are required.

to plants and animals but this may produce toxic leachate which will require disposal.

The tropical earthworm, *Pontoscolex corethrurus*, is found in the Amazonian *terra preta* soils and whilst there is evidence that the earthworm ingests biochar particles (Topoliantz and Ponge, 2005), contributing to the fertility of these soils (Ponge et al., 2006), there is also evidence to suggest that these earthworms push aside the biochar particles to avoid ingesting them (Topoliantz and Ponge, 2003). The avoidance of biochar by earthworms has only been tested in the laboratory on biochar that has been previously sieved to <2 mm, resulting in conclusions that *E. fetida* do not avoid biochar amended soils compared to unamended controls (Chan et al., 2008) or that they actually favour biochar amended soils (Van Zwieten et al., 2010b). Chan et al. (2008) found that *E. fetida* preferred non-activated biochar produced at 450 °C to biochar activated with steam produced at 550 °C. However, using <2 mm sieved biochar for field-scale applications is unlikely, as this could generate excess dust, so the impact of larger (unsieved) biochar particles, which may be of an unfavourable texture, on earthworm toxicity needs to be tested. Beesley and Dickinson (2011) also discussed whether *Lumbricus terrestris* could ingest biochar, or whether their effects on metal mobility and DOC were due to soil disturbance only. In this study, on a moderately contaminated urban soil, earthworms reduced DOC concentrations in pore water, which concomitantly reduced concentrations of As, Cu and Pb. A number of mechanisms were proposed for these effects; biochar's liming effect on soil, co-mobilisation of metals and As with DOC and the ability, or inability of earthworms to ingest biochar. It was not clear whether their effect was by disturbance or ingestion of biochar and proximal soil. Such fundamental mechanisms require systematic experimentation to determine.

5. Conclusions, recommendations and research needs arising

Biochars have demonstrated clear potential for the reduction of a variety of organic and inorganic contaminants present in soils in their most mobile forms. Since modern environmental clean-up strategies increasingly focus on the effects of the most toxicologically relevant fractions of contaminants, biochars could represent suitable candidates for remediation trials. But pollutant immobilisation represents only one facet of contaminated land remediation. Combined with improvements to some soil physico-chemical limitations, biochars may be seen as highly suitable for the amendment of contaminated soils, but, in some cases this may require their combination with other amendments. For the phyto-toxic elements Cd and Zn, biochars have been found to possess retentive capabilities which may be further enhanced by manufacturing chars to increase CEC, surface area and pH. The same is true of other metals, although reports are contradictory depending on source material and production temperatures and those individual metals concerned. Reductions in organic pollutant mobility allow, theoretically, the same amendment to be deployed at multi-element polluted sites. This gives an attractive and cost-effective, versatile appeal to the continued trials of biochars on a wide variety of contaminated soils, keeping mindful of certain key caveats.

For example, the same virtuous properties that have been demonstrated to, in some cases so effectively reduce heavy metal mobility can immobilise essential macro-nutrients and, since the second facet of remediation requires maintenance of soil quality and ultimately material conditions conducive to plant growth, then biochars alone may be ineffective at sustainable remediation. Combined with wide C:N ratios and often very alkaline pH, the selection of a biochar to meet the needs of managing both gross pollutant mobility as well as net remediation goals could be difficult. Soil microbial communities may find protection within biochars' structure whilst soil animals might also favour some biochars, providing the material is palatable to them; these are factors to bolster the wider ecological argument for trials involving biochar on denuded soils. However, the long term impact of biochar on soil fauna has to be investigated further, as some negative effects on microorganisms and earthworms have been observed in laboratory studies. These issues are likely to be of greater concern when using high surface area biochars with high affinities for organic contaminants. In this respect a 'one biochar fits all' approach may be impossible so some decision criteria, such as those simplified by Fig. 2, could aid the choice of biochar given particular contamination scenarios; these require development based on the results of continued field trials.

One thing is certain, before applying biochar in the field, it is important to understand the degree to which the capacity of biochars to immobilise contaminants may be increased, reduced or modified with time as their sorption sites are occupied by native soil organic matter and competing contaminants. As long term field studies are lacking, which would inform our current muses and speculation, then practical considerations to account for several trade-offs should be taken into account before applying biochars to soil, as a cautionary measure. Higher rates of biochar addition will result in greater contaminant sorption and carbon sequestration but will be more expensive and may result in decreased soil fertility (Rondon et al., 2007) due to the sorption of plant nutrients. Toxicity to soil animals at high application rates may result from the abundance of unpalatable substrate, and at high application rates possible contaminants arising from the char itself, such as polycyclic aromatic hydrocarbons (Thies and Rillig, 2009) as well as contaminants present in the original feedstock may present their own introduced toxicity issues. As with any amendment, but especially given biochars' low density, we must be sure that the effects we observe cannot merely be attributable to dilution of the contaminated substrate. Whatever the application rate, supplementary nutrients, especially nitrogen may need to be added to maintain soil fertility, a factor exacerbated by soil dilution.

To maximise the benefits to soils, adding char to soil as finely divided particles increases the surface area and therefore the char's capacity for contaminant adsorption (Nocentini et al., 2010). Finely divided chars are denser and can therefore be transported more efficiently, or may be added to other substrates as bulking agents with greater success. The lifetime of small particles in soils is shorter than larger particles, however, it is still in the order of several centuries (Hammes and Schmidt, 2009) so finely divided chars may be added as a slurry, reducing losses by windblow and easing the incorporation of the char into the soil whilst usefully, and with longevity, providing material soil improvements. This type of physical modification may also ensure earthworms are able to palate and work biochars within soils; ecological sustainability will be the remaining question after our endevours have given us the answers to the routine chemical properties of this material. This could further be achieved via modifications to the production process to ensure a capital of amorphous organic matter remains within the end product. Of course, as with any amendment, the cost of biochar addition to contaminated soil will be one of the key determinant factors in its deployment, especially if it must be pretreated in some way. Utilising local waste materials will be less expensive than tailor-made chars but the chars may not be optimised for the particular contaminant reduction required, so there is a trade-off between cost and the effect. Since the incorporation costs of char are not likely to be dissimilar from the addition of other soil amendments, the low density of biochar means that, on a weight basis, greater transportation costs could be a deciding factor in the application of chars to some sites with large areas requiring remediation, regardless of the potential benefits.

During this review we have aimed to provide an overview into the current knowledge base surrounding the use of biochars for contaminated soil remediation and revegetation, as well as suggest directions for future work. In summary we would encourage the experimentally circumspect application of biochars to contaminated soils but suggest that such trials maintain sufficient ecological grounding in their approach.

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