Solid Earth Discuss., 5, 2155–2179, 2013
www.solid-earth-discuss.net/5/2155/2013/
doi:10.5194/sed-5-2155-2013

Solid Earth
Discussions
Open Access

Use of phytoremediation and biochar to remediate heavy metal polluted soils: a review

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Received: 12 November 2013 – Accepted: 15 November 2013
– Published: 25 November 2013

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Anthropogenic activities are resulting in an increase on the use and extraction of heavy metals. Heavy metals cannot be degraded and hence accumulate in the environment having the potential to contaminate the food chain. This pollution threatens soil quality, plant survival and human health. The remediation of heavy metals deserves attention, but it is impaired by the cost of these processes. Phytoremediation and biochar are two sound environmental technologies which could be at the forefront to mitigate soil pollution. This review provides an overview of the current state of knowledge phytoremediation and biochar application to remediate heavy metal contaminated soils, discussing the advantages and disadvantages of both individual approaches. Research to date has attempted only in a limited number of occasions to combine both techniques, however we discuss the potential advantages of combining both remediation techniques and the potential mechanisms involved in the interaction between phytoremediators and biochar. We identified specific research needs to ensure a sustainable use of phytoremediation and biochar as remediation tools.

1 Introduction

Industrialisation and technical advances have led to an increase in the use of heavy metals and heavy metal pollution. Contrary to organic substances, heavy metals are non degradable and accumulate in the environment. While some soils can have a high background level of heavy metals due to volcanic activity or weathering of parent materials, in other soils anthropogenic activities, including smelting, mining, use of pesticides, fertilisers and sludges are responsible for these high levels of heavy metals.

Soil heavy metal pollution has a pernicious effect on soil microbial properties (Yang et al., 2012) and on the taxonomic and functional diversity of soils (Vacca et al., 2012). Soil heavy metal pollution poses a risk to the environment and to human health (Roy and McDonald, 2013) due to biomagnification (increases in metal concentration as the element passes from lower to higher trophic levels). Some of these elements can be essential for living organisms while some others are non-essential. Even concentrations of essential elements beyond a certain threshold will have pernicious health effect as they interfere with the normal metabolism of living systems. It is not the purpose of this article to review the adverse effects of heavy metals on human or plant health. Kabata-Pendias and Pendias (2001) provide a list of toxic effects of heavy metals on plants and the mechanism involved, while a summary of adverse effects of heavy metals on human health was provided by Ali (2013). We would like to remind to the reader that studies on heavy metal pollution are focused on As, Cd, Cr, Hg and Pb as they are toxic, non-essential heavy metals, and on Cu, Ni and Zn which, although essential, can cause health problems in humans or can result in phytotoxicity at high concentrations.

With an increasing amount of literature on heavy metal remediation, we aim to summarise the state of art of two of these techniques situated at the forefront of remediation practices (phytoremediation, with a focus on phytoextraction and biochar soil amendment) and to discuss their mechanism and how we could combine them to improve remediation efforts.

2 Phytoremediation

Phytoremediation is an umbrella term for a series of techniques that combine the disciplines of soil microbiology and chemistry and plant physiology (Cunningham and Ow, 1996). Currently the most extended practice for soil heavy metal remediation does not address the problem of contamination as it consists on encapsulation or digging and dumping. Immobilisation or extraction can be expensive and, as a consequence, phytoremediation can be considered relatively attractive as it can be used at a relatively low cost to restore or partially decontaminate a site compared to other options, as the cost is 5 % of other alternative methods (Prasad, 2003). Other advantages would include its good perception as a remediation technique among the general public and being more environmental friendly than other options, as the introduction of vegetation in the pol-

luted area can also help to prevent erosion or contaminant leaching. Phytoremediation consists in the use of plants to remove contaminants from the environment or to transform them into less harmless forms (see Table 1 for a summary of phytoremediation techniques). Phytoremediation is a relatively new technology as research studies have been mostly conducted from 1990 onwards.

Phytoextraction is the main and most promising technique to remove soil heavy metals. It is based on the use of hyperaccumulators which uptake heavy metals and then translocate them to aboveground tissues (Table 1). One common way of defining a hyperaccumulator is as a plant that can store heavy metals at a level 100-fold greater than common plants without yield reduction (Chaney et al., 2007). On other occasions, these types of plants are defined on their basis to accumulate more than 100 $mg\,kg^{-1}$ dry weight of Cd, more than 1000 $mg\,kg^{-1}$ of Cu, Co, Cr, Ni or Pb, or more than 10 000 $mg\,kg^{-1}$ of Mn or Zn (Baker and Brooks, 1989). Some other authors have mentioned that these values are conservative and propose these criteria to be lowered (van der Ent et al., 2013). Species used for phytoextraction must not only accumulate high amounts of the target element but also have a high growth rate, tolerate the toxic effects of the heavy metals, be adapted to local environment and climate, be resistant to pathogen and pests, be easy to cultivate and repulse herbivores to avoid food chain contamination (Ali et al., 2013).

To date, more than 400 species have been identified as hyperaccumulators, including more than 300 Ni hyperaccumulators (Li et al., 2003). In contrast with Ni only a few plant species have demonstrated the potential to accumulate Cd, Cu, Pb, and Zn (Brooks, 1998). Many phytoremediators belong to the taxonomical order of Brassicales and phytoremediators are also abundant in Asterales, Solanales, Poales, Malpighiales, Fabales, Caryophyllales and Rosales (Shao et al., 2011). The amount of metal extracted from the soil depends not only of the plant species utilised but also on the type of soil and climate of the region (Shao et al., 2011).

The mechanism and reasons of phytoaccumulation remain unknown. Metal concentrations are higher in the shoots compared to the roots, suggesting that there could be an ecological role, leading to protection against insect, herbivore or fungal attack, by making the leaves toxic or unpalatable.

Phytoextraction has three main purposes: firstly, to remove the contaminant from the soil or contain it, secondly phytoextraction of elements that have market value and finally gradually improving soil quality to cultivate crops with higher market value (Vangrosweld et al., 2009).

There are a number of problems associated with the effectiveness of this remediation technique. Phytoremediation might not be suitable in areas were the heavy metal concentration is too elevated as plants could show symptoms of phytotoxicity. In addition, most of the phytoaccumulators have slow growth rate or produce few biomass, limiting the amount of metal uptaken.

Manipulation of soil pH, soil nutrient content or soil organic matter can also be undertaken to improve metal hyperaccumulation. In this sense, these additional agronomic practices can be carried out when heavy metal concentrations in the soil are too elevated to reduce plant stress (Adriano et al., 2004; Gabos et al., 2011; de Abreu et al., 2012). Thus, liming can allow the decrease of the heavy metal available fraction, thus enabling vegetative growth, while fertilisers can improve phytoextractor growth. On the other hand, both liming and fertiliser addition can alter the mobility and speciation of soil heavy metals. As an example, Li et al. (2012) found that Cd removal from soil was enhanced by the phytoaccumulator *Amaranthus hypocondriacus* after NPK or NP fertilisation due to an increase on plant biomass. However, they found that N alone did not increase plant biomass and led to a limited increment in phytoextraction. Other studies (Huang et al., 2013) have found that P fertilisers can decrease soil pH, enhancing the mobility of Cd and leading to increased phytoextraction by *Sedum alfredii*. When adding a phosphate fertiliser to promote phytoremediation, the choice of amendment should be carefully chose as cations (K^+, Na^+, Ca^{+2} or NH_4^+) associated with the phosphate could affect the mobility of heavy metals (Bolan et al., 2003; Huang et al., 2013). Indeed, plant growth (Oo et al., 2013) and the mobility of different elements in the soil (Ahmad et al., 2013) can be related with soil salinity. For example, Stevens et al. (2003)

observed that Zn^{2+} and Pb^{2+} mobility increased with the increment of electrical conductivity. Differences in soil pH caused by the addition of different phosphate fertilisers can also lead to differences in phytoextraction (Mandal et al., 2012). Urea has also been used to alleviate plant stress and improve B phytoextraction by the plant species *Brassica juncea* (Giansoldati et al., 2012).

Organic amendments such as chicken manure have also been shown to increase growth of the species *Rorippa globosa* (Wei et al., 2011). Chicken manure addition resulted in a decrease in soil extractable Cd and thus, the concentration of Cd in the shoots was lower in soils amended with chicken manure than in soils amended with urea or in the controls (soil + phytoremediator). However, the total concentration of metal extracted in the shoots was in both cases higher than in the control. Other materials such as pig manure vermicompost can also be used to improve plant yield and assist phytoremediation, as demonstrated by Wang et al. (2012) in an experiment using Cd as target heavy metal and *Sedum alfredii* as phytoremediator. Indeed, the use of organic amendments has numerous applications, for example, Siebielec and Chaney (2012) have demonstrated the effectiveness of biosolids compost in the rapid stabilization of Pb and Zn and revegetation of military range contaminated soils increasing tall fescue growth by more than 200 % while Clemente et al. (2012) recovered a land contaminated by mining activity with Cd, Cu, Pb, and Zn by combination of the halophytic shrub *Atriplex halimus* L. with pig slurry.

The use of chelators such as citric acid or EDTA has also been sometimes advised to assist phytoremediation, with the aim of increasing the mobility of soil heavy metals and thus plant extraction (Zhou et al., 2007; Freitas et al., 2013). However, we should bear in mind that the use of chelators can originate other environmental problems including toxicity for plants and metal leaching (Zhou et al., 2007).

In addition, experiments should be done to account for the potential impact of climate change on the capability of phytoextractors to accumulate heavy metals, which at the moment is uncertain (Rajkumar et al., 2013).

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Finally, we would like to remark that pot experiments are a good first approach to evaluate the potential of a phytoextractor, but they cannot substitute field experiments as the uptake of heavy metals is higher in pots than for the same soil in the field (see for example, Marschner, 1986). This can be due to differences in soil moisture or microclimate and to the fact that field-grown plants can reach down to less polluted soil.

3 Biochar

Biochar is a porous, carbonaceous product obtained from the pyrolysis of organic materials. Numerous materials can be used as feedstocks, including sludges, plant materials and manures. Although the use of charcoal (wood biochar) has been common since preterit times, the idea of using other feedstocks for biochar production is new and relatively unexplored. Typically biochars have high cation exchange capacity and are alkaline. Biochar has many potential benefits on soil properties as an increase in soil biological activity (Lehmann et al., 2011; Paz-Ferreiro et al., 2012), diminishing soil greenhouse gas emissions from agricultural sources and thus enhancing soil carbon sequestration due to its elevated content of recalcitrant forms of carbon (Gascó et al., 2012). The changes brought about by biochar addition to the soil will cause alterations in soil quality (Paz-Ferreiro and Fu, 2013) with the potential to increase agricultural yields (Jeffery et al., 2011; Liu et al., 2013). The multiple benefits of biochar for soil have been compiled recently in the book by Joseph and Lehmann (2009). However, little information was available in this book about the effect of biochar on soil heavy metals.

4 Studies on the effect of biochar on soil heavy metals

Table 2 shows a brief summary of the latest papers about the effect of biochar on soil heavy metals. Fellet et al. (2011) tried to use biochar to remediate a multicontaminated

mine soil. Biochar addition did not result in the decrease of the total heavy metal content of the soil, however, biochar addition reduced the bioavailability of Cd, Pb and Zn and the mobility (measured using a leaching experiment) of Cd, Cr and Pb.

Earthworms can be added to soil at some stages of ecological restoration due to their well established positive effects on soil properties as organic matter content, soil formation, soil aeration and nutrient cycling. Sizmur et al. (2011) tested a polluted soil collected in the vicinity of a Cu mine using biochar in combination with compost and earthworms (*Lumbricus terrestris*). They found all treatments (biochar alone, biochar + compost and biochar + compost + earthworms) to reduce the amount of heavy metals compared to the control soils. A limiting aspect when using earthworm with remediation purposes is that their addition to soil could lead to the mobilization of heavy metals and hence to an increase of plant heavy metal concentrations. Interestingly, Sizmur et al. (2011) found that the treatments containing biochar and earthworms did not result in higher heavy metal mobility or plant availability.

Park et al. (2011) studied the effect of two biochars in a heavy metal spiked soil and a naturally strongly polluted soil. They performed a sequential extraction of some heavy metals. They found chicken manure biochar effective to reduce extractable concentrations of Cd and Pb, but not Cu concentration, while green waste biochar was more effective to diminish all of the heavy metals studied. Heavy metal fractions bonded to organic matter increased after biochar addition. Both biochars also decreased Cd and Pb presence in soil pore water.

Uchimiya et al. (2012a) analysed the effects on soil heavy metals concentrations of 10 biochars prepared from 5 feedstocks at two different temperatures. They observed that manures with a high or low proportion of ash or P were less effective to immobilize heavy metals. In contrast, biochars prepared at 700 °C were more effective, which could be attributed to transformations in the material, including the removal of nitrogen containing heteroaromatic and leachable aliphatic functional groups. They found Cu and Pb relatively easily to stabilize in soil, while Cd and Ni response depended strongly on the type of biochar added to the soil.

Beesley and Marmiroli (2011) detected a retention on biochar surface of As, Cd and Zn. These authors proved that sorption of the metal was produced at the biochar surface and that this process was not immediately reversible. Leachate concentrations of Cd and Zn were reduced 300 and 45 folds, respectively. However, leachate concentrations of As did not diminish.

Namgay et al. (2010) reported that the concentrations of Cd, As and Pb in maize shoots decreased after biochar application. Beesley et al. (2013) reported interesting results, finding that As can increase in soil pore water after biochar addition, but transfer to the plant be reduced. This would imply that, at least some biochars, could pose no risk of increasing heavy metals in plants and hence are safe in terms of food chain transfer, but leaching of As to nearby waters must be considered. Karami et al. (2011) added biochar to a mine soil polluted with Pb and Cu. They found that biochar addition reduced pore water Pb concentrations to half their values in the mine soil. When biochar was combined with greenwaste compost the levels of Pb concentrations in the pore water were 20 times lower than in the control. Jiang et al. (2012) found that the acid soluble fractions of Pb(II) and Cu(II) diminished by 18.8–77.0 % and 19.7–100.0 %, respectively, depending on biochar concentration. However, only 5.6–14.1 % of acid soluble Cd(II) was immobilised. Hartley et al. (2009) observed no increase on As transfer to plants in three soils planted with Miscanthus. They warned, however, that alkalyne biochars could mobilise As. It is a well know fact that As behaves differently to other metals with respect to pH, as As mobility is reduced in acid soils due to adsorption on iron oxide surfaces. Zheng et al. (2012) studied the effect of three biochars on different heavy metals (see Table 2) using a multi-polluted soil planted which they planted with rice. They found Cd, Pb and Zn to be reduced on rice shoots, in particular when using straw-derived biochar. However, As in rice shoots was increased by biochar addition. More importantly, we believe that this is the first study considering the effect of particle size of biochar on plant heavy metals. The authors found that decreases in particle size resulted in less Cd, Zn and Pb accumulating in the rice plants.

Hydrochars could also be used for soil heavy metal inmobilization, however there is a lack of studies on the topic. Hydrochars are produced after pyrolysis of organic matter rich materials in the presence of subcritical liquid water. This technique can be applied to obtain pyrolysed products from wet feedstocks. In principle the adsorption capacity of hydrochars seems to be reduced compared to biochars or other adsorbents due to the fewer functional groups containing oxygen present on hydrochar surfaces. However, Xue et al. (2012) have demonstrated experiments that the use of activated hydrochars could overcome these problems. They performed a series of batch and columns experiments to show how this type of hydrochar could reduce Pb on water. The potential applicability of hydrochar to address soil heavy metal pollution remains untested. However, hydrochars tend to be acidic and could possess phytotoxic or genotoxic risks (Busch et al., 2013), which would deem them unsuitable in restoration projects.

There is a lack of studies concerning how pyrolysis conditions affect biochar properties as heavy metal sorbent. To fill this gap, Uchimiya et al. (2011b) performed an experiment using wood and grass biochars prepared at 5 different temperatures and another one (Uchimiya et al., 2012b) used poultry litter prepared at 4 different temperatures to study lead retention. From the first experiment they suggested using biochars prepared at high temperature (650° to 800 °C) for remediation purposes. In addition they recommended to perform acid or other oxidant post-treatment in order to increase oxygen-containing surface functional groups (carboxyl, carbonyl and hydroxyl) which have a great importance in relation to heavy metal sorption into biochar. In the case of the chicken litter biochar they found that lower production temperatures were more suitable than higher ones due to the stabilizing effect. Higher rates of amendment were necessary in their experiments for chicken manure biochar to get the same remediation effect than plant derived biochars.

It is expected that as biochar is in contact with soil for a prolonged period of time, oxidation, both biotic and abiotic, would result in the alteration of biochar, a process known as aging. This process, which would result in the formation of carboxylic, phenolic, carbonyl, quinones and hydroxyl functional groups and which can be emulated under laboratory conditions was studied by Uchimiya et al. (2010). These authors found that the immobilization of heavy metals related to their lability, i.e. it followed the order Cu(II) > Cd(II) > Ni(II). Aging did not impact heavy metal immobilisation, except for a small increase in Ni.

All of the above experiments have been conducted under laboratory conditions. We would urge scientist to design experiments to help to demonstrate the benefits of biochar against heavy metal pollution under field conditions. The only field study available (Cui et al., 2011), to our knowledge, shows that biochar can be used to reduce Cd uptake in paddy fields. The study consisted on two annual measurements, so it remains to explore the need to reapply biochar after more extended periods of time.

5 Mechanism of interaction between biochar and heavy metals

Biochar characteristics are a function of several factors, including the type of feedstock, the particle size of the feedstock and temperature and conditions of pyrolysis. The wide range of characteristics that biochar might posses makes some particular materials more suitable than others to remediate different heavy metals. Therefore, when selecting a biochar for remediation purposes scientists should be aware not only of soil type and characteristics but also on biochar properties.

Before reviewing the mechanisms implied in the interaction between biochar and heavy metal it is necessary to note that biochar act on the bioavailable fraction of soil heavy metals and that they can reduce also their leachability.

One of the characteristics of biochars is possessing large surface areas which imply a high capacity to complex heavy metals on their surface. Surface sorption of heavy metals on biochar has been demonstrated on multiple occasions using scanning electron microscopy (Beesley and Marmiroli, 2011; Lu et al., 2012). This sorption can be due to complexation of the heavy metals with different functional groups present in the biochar, due to the exchange of heavy metals with cations associated with biochar such as Ca^{+2} and Mg^{+2} (Lu et al., 2012) or other such as K^{+}, Na^{+} and S (Uchimiya et al.,

2011c) or due to physical adsorption (Lu et al., 2012). Also oxygen functional groups are known to stabilise heavy metals in the biochar surface, in particular (Uchimiya et al., 2011c) for softer acids like Pb(II) and Cu(II). In addition, Méndez et al. (2009) observed that Cu^{2+} sorption was related with the elevated oxygenated surface groups and also with high average pore diameter, elevated superficial charge density and Ca^{2+} and Mg^{2+} exchange content of biochar. Possibly, sorption mechanisms are highly dependent on soil type and the cations present in both biochar and soil. Some other compounds present in the ash, such as carbonates and phosphates (Cao et al., 2009; Karimi et al., 2011) can also help to stabilise heavy metals by precipitation of this compounds with the pollutants.

Alkalinity of biochar can also be partially responsible of the lower concentrations of available heavy metals found in biochar amended soils. Higher pH values after biochar addition can result in heavy metal precipitation in soils. Biochar pH value increases with pyrolysis temperature (Wu et al., 2012) which has been associated to a higher proportion of ash content.

Biochar can also reduce the mobility of heavy metals altering the redox state of those (Choppala et al., 2012). As an example biochar addition could lead to the transformation of Cr^{+6} to the less mobile Cr^{+3} (Choppala et al., 2012).

The relative contribution of the different mechanisms to heavy metal immobilisation by different biochar remains unknown, although some authors like Houben et al. (2013a) postulate that it is mostly a pH effect.

6 Combining biochar and phytoremediation

There is an abundance of reports in the literature about amendments such as lime and compost being used to reduce the bioavailability of heavy metals (Komárek et al., 2013) and thus, having the potential to be combined with phytoremediators (de Abreu et al., 2012). Biochar, as reviewed before, can also stabilise soil heavy metals in soils and thus reduce plant uptake. However, until recently there was a lack of experiments trying to combine both approaches to soil remediation.

Biochar is commonly reported in the literature to increase plant growth, hence there is a potential of biochar to increase the yield of phytoremediators. This increase in plant productivity is highly heterogeneous and has overall been quantified as 10 % (Jeffery et al., 2011; Liu et al., 2013). However, there are several factors that limit the accuracy of the figure provided by Jeffery et al. (2011) and Liu et al. (2013) and that could skew the data. To date most of the field experiments have been conducted in the short-term, being limited to a period of 1–2 yr and there are a high relative number of laboratory mesocosms incubations (with a duration of 1–2 months) included in the dataset. Also the dataset in this review comprises a higher number of experiments in tropical latitudes compared to temperate ones. Finally, we should bear in mind that a high heterogeneity in the response was detected, depending on the type of soil and plant utilised.

Improvements in plant yield after biochar addition are often attributed to increased water and nutrients retention, improved biological properties and CEC, effects on nutrient cycling and turnover and improvements in soil pH. Many of these effects are interrelated and potentially they could act synergistically. In general, acid soils with a coarse texture or a medium texture are more prone to produce increases in crop productivity (Jeffery et al., 2011; Liu et al., 2013). In the last years the scientific community has also raise awareness over the improvement of plant responses to disease as an additional benefit of biochar soil amendment (Graber et al., 2010). As said before, biochar can alter soil microbial community, possibly including an increase in beneficial organisms that produce antibiotics and can protect plants against pathogens. Another mechanism could be compounds included in biochar such as 2-phenoxyethanol, benzoic acid, hydroxy-propionic and butyric acids, ethylene glycol and quinones suppressing some of the pathogens present in the microbiota (Graber et al., 2010; Elad et al., 2011).

In principle, biochar prepared from any material would have the potential to increase plant yield and thus be used in combination with phytoremediation. However, the use of sewage sludge biochar would be unadvised due to its generally negative effect on crop

performance (Jeffery et al., 2011). Caution should also be taken with the presence of heavy metals in sewage sludge biochars, although some studies (Méndez et al., 2012; Hossain et al., 2010) show that the metals present in the biochar are not in mobile forms.

There has been a recent interest about the possibility of combining phytoremediation with other potential plant uses such as using plants that can be used to obtain bioenergy (de Abreu et al., 2012). While heavy metal contaminated areas are not suitable for food production, planting biocrops could promote soil organic matter stocks and reduce soil pollutants (Hartley et al., 2009). Willow and poplar, have been commonly used as biocrops and they can be utilised for phytoremediation purposes due to their high uptake of heavy metals and fast growing rates (Baum et al., 2009). And in fact, it has been shown recently that biochar can improve the grennhouse gas balance of other bioenergy crops such as Miscanthus (Case et al., 2013).

It is also worth to mention that for long phytoextractors were considered to be non-mycorrhizal. However, in the last year it has been demonstrated that hyperaccumulators can form symbiosis with arbuscular mycorrhizal fungi (AMF) and these enhance plant growth and lead to higher contents of metal extracted (Al Agely et al., 2005; Orlowska et al., 2011). Positive effects of biochar have been usually found in arbuscular mycorrhizal fungi, although exceptions can be found in nutrient rich soils (Lehmann et al., 2011).

Biochar and phytoremediation techniques have been used recently to target at Cd polluted soils (Houben et al., 2013b) using *Brassica napus* L. as Cd and Zn phytoextractor in combination with Miscanthus biochar and for the case of multicontaminated soils using different biochars and plant species (Fellet et al., 2014). The authors of this last study used three biochars, produced from pruning residues from orchards, fir tree pellets and fir tree pellets mixed with manure at two different doses. Fellet et al. (2014) observed higher concentrations of Pb in plants grown with the fir tree pellets biochar. However, no increase in yield was obtained with this treatment, and the value of the translocation index, although significantly higher than in the control, was insufficient for the purposes of phytoextraction.

It seems plausible that one of the best approaches to combine biochar and phytoextractors would be in multi-contaminated soils, where both can target at different elements. Biochar could also be used as a soil conditioner prior to plant colonization in acidic, polluted mine tailings.

7 Conclusions and research needs

Biochar and phytoremediation have the potential to be combined in the remediation on heavy metal polluted soils (see Fig. 1). Biochar can reduce the bioavailability and leachability of heavy metals in the soil. On the other hand phytoextractors can reduce the amount of soil heavy metals in polluted areas.

We anticipate that in the next years there will be a growing interest to study the interaction between phytoremediators and biochars and we identify the next areas as the ones warranting research:

Biochars have highly heterogeneous properties, which should be understood to maximise the efficacy of soil remediation. We should comprehend, firstly, how these properties are relevant for heavy metal adsorption and how they contribute to the different mechanism of heavy metal immobilisation and secondly how to optimise the choice of pyrolysis conditions and feedstocks in order to produce the desired products.

Most experiments utilising biochar or phytoremediators alone and not in combination have been carried under laboratory conditions. In the case of phytoremediators this can result in an overestimation of heavy metal extraction.

For biochar most of the experiments done (both in field and under laboratory conditions) have been done in the short term, which poses an interrogation on the long term fate of these heavy metals. In fact it could be expected that, due to aging processes, the ability of biochar to sequester heavy metals decreases with time. More research will be needed to understand aging process in biochar.

Thus, well designed large scale field trials will be essential to evaluate the feasibility on the approach proposed in this article. The economics of these new remediation processes should be assessed against other options.

Acknowledgements. J. Paz-Ferreiro thanks the Chinese Academy of Sciences for financial support (fellowship for young international scientists number 2012Y1SA0002).

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Table 1. Summary of the different techniques of phytoremediation.

Technique	Description
Phytoextraction	Plants accumulate contaminants in harvestable biomass i.e., shoots
Phytofiltration	Sequestration of pollutants from contaminated waters by plants
Phytostabilization	Limiting the mobility and bioavailability of polluting substances by prevention of migration or inmobilization
Phytovolatilization	Conversion of pollutants to volatile form followed by their release to the atmosphere
Phytodegradation	Degradation of organic xenobiotics by plant enzymes within plant tissues
Rhizodegradation	Degradation of organic xenobiotics in the rhizosphere by rhizospheric microorganisms
Phytodesalination	Removal of excess salts from saline soils by halophytes

Table 2. Effect of biochar application on soil heavy metals. Blank indicates not specified in the article.

Feedstock (temperature)	Soil type	Pollutants	Reference
Mix of hardwoods (400 °C)	3 soils	As	Hartley et al. (2009)
Rice husk, rice straw and rice bran (400 °C)	Anthrosol	As, Cd, Pb, Zn	Zheng et al. (2012)
Wastewater sludge (550 °C)	Chromosol (Australian system)	As, Cd, Cr, Cu, Pb, Ni, Se, Zn, Sb, B, Ag, Ba, Be, Co, Sn, Sr	Hossain et al. (2010)
		Cu, Pb, Zn	Sizmur et al. (2011)
Broiler litter (350 and 700 °C), pecan shells (450 °C)	Abruptic Durixeralfs	Cu, Cd, Ni	Uchimiya et al. (2010)
Pecan shell (450 °C), broiler litter samples (700 °C)	Typic Kandiudult and Abruptic Durixeralfs	Cu	Uchimiya et al. (2011a)
Chicken manure (550 °C), green waste (550 °C)		Cd, Cu, Pb	Park et al. (2011)
Forest green waste (600–800 °C)	Peat	Cu	Buss et al. (2012)
dairy manure (350 and 700 °C), paved feedlot manure (350 and 700 °C), poultry litter (350 and 700 °C), turkey litter (350 and 700 °C), separated swine solids (350 and 700 °C)	Typic Kandiudult	Pb, Cu, Ni, Cd	Uchimiya et al. (2012a)
Mix of hardwoods (400 °C)		As, Cd, Zn	Beesley and Marmiroli (2011)
Mix of hardwoods (400 °C)	Anthrosol	Pb, Cu	Karami et al. (2011)
Orchard prune residue (500 °C)	Anthrosol	Cd, Cr, Cu, Ni, Pb, Tl, Zn	Fellet et al. (2011)
Eucalyptus		As, Cd, Cu, Pb, Zn	Namgay et al. (2010)
Wheat Straw (350–550 °C)	Anthrosol	Cd	Cui et al. (2011)
Rice Straw	Ultisol	Cu, Cd, Pb	Jiang et al. (2012)
Orchard prune residues (500 °C)	Anthrosol	As	Beesley et al. (2013)
Miscanthus (600 °C)		Cd, Zn, PB	Houben et al. (2013a)

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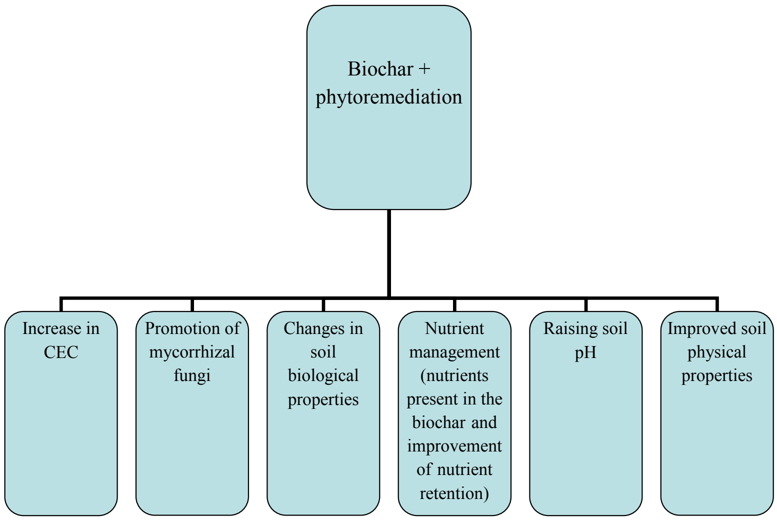

Fig. 1. An overview of the potential positive effects attained by combining phytoremediation and biochar in heavy metal pollution remediation.