Long-term impact of biochar on the immobilisation of nickel (II) and zinc (II) and the revegetation of a contaminated site

Zhengtao Shen [a,]*, Amelia Md Som [b], Fei Wang [a], Fei Jin [a], Oliver McMillan [a], Abir Al-Tabbaa [a]

[a] (Geotechnical and Environmental Research Group, Department of Engineering, University of Cambridge, Cambridge, CB2 1PZ, United Kingdom)

[b] (UniKL MICET, Lot 1988 Bandar Vandor Taboh Naning, Melaka, 78000 Alor Gajah, Malaysia)

* Corresponding author: Email: ztshennju@gmail.com; zs281@cam.ac.uk. Phone number: 0044+7541935253. Fax: 0044+7541935253

Abstract: A field remediation treatment was carried out to examine the long-term effect of biochar on the immobilisation of metals and the revegetation of a contaminated site in Castleford, UK. The extracted concentrations of nickel (Ni) (II) and zinc (Zn) (II) in the carbonic acid leaching tests were reduced by 83 - 98% over three years. The extracted Ni (II) and Zn (II) concentrations three years after the treatment were comparable to a cement-based treatment study carried out parallelly on the same site. The sequential extraction results indicated that biochar addition (0.5 - 2%) increased the residue fractions of Ni (II) (from 51% to 61 - 66%) and Zn (II) (from 7% to 27 - 35%) in the soils through competitive sorption, which may have resulted in the reduction of leachabilities of Ni (II) (from 0.35% to 0.12 - 0.15%) and Zn (II) (from 0.12% to 0.01%) in the plots with biochar compared with that without biochar three years after the treatment. The germination of grass in the plots on site was failed. Further laboratory pot study suggested that larger amounts of biochar (5% or more) and compost (5% or more) were needed for the success of revegetation on this site. This study suggests the effectiveness and potential of biochar application in immobilising heavy metals in contaminated site in the long term.

Keywords: Biochar, Heavy metal, Leaching, Sequential extraction, Revegetation, Soil remediation

1 Introduction

Biochar is the solid and carbon-rich product of heating biomass in a low oxygen environment (pyrolysis) and is used to store carbon in a more recalcitrant form (Lehmann et al., 2008; Sohi, 2012). Its feedstock usually comes from agriculture green wastes (manure, crop residues, trees, grasses etc.), industrial green wastes and urban sludge (Beesley et al., 2011). Its co-products (bio-oil and syn-gas) during pyrolysis can be used as green energy (Lehmann et al., 2008). Moreover, due to its highly porous micro-structure, active functional groups, high pH, surface area and cation exchange capacity (CEC), biochar can effectively immobilise contaminants by adsorption, ion exchange, surface complexation and precipitation (Beesley et al., 2011; Bian et al., 2014; Zhang et al., 2013). Compared with conventional remediation materials (e.g. cement, lime and clay) (Du et al., 2012; Jiang et al., 2014), biochar also assists in revegetation and restoration of the treated contaminated land (Beesley et al., 2011). These are critical processes for the stabilization and sustainable development of the land and reducing further risk to humans and the surrounding ecosystem (Arienzo et al., 2004; Ruttens et al., 2006). Therefore, biochar is a promising material with the potential to be applied in soil remediation for its multiple environmental benefits.

A number of studies have highlighted biochar's role in removing contaminants in aqueous solution (Inyang et al., 2012; Kołodyńska et al., 2012; Meng et al., 2014). Recent studies have also reported the successful applications of biochar in soil remediation in the short term. For instance, Rees et al. (2014) observed a reduction of extractable cadmium (Cd) (II), lead (Pb) (II), copper (Cu) (II), nickel (Ni) (II) and zinc (Zn) (II) in soils after the addition of a 80% coniferous and 20% hardwood biochar in one week. Likewise, Uchimiya et al. (2012) observed a reduction of Pb (II), Cu (II) and Zn (II) after undertaking the Toxicity Characteristic Leaching Procedure (TCLP) extraction after adding cottonseed hull biochar to the contaminated soil within one week. Beesley and Marmiroli (2011) also observed a reduction of metals in column leachate 8 weeks after hardwood biochar treatment. Houben et al. (2013) found a reduction of Cd (II), Pb (II) and Zn (II) in $CaCl_2$ extraction from soil 56 days after Miscanthus straw biochar amendment. These short-term findings demonstrate that the application of biochar in soil remediation is feasible, however limited long-term studties have been carried out to date. Bian et al. (2014) used wheat straw biochar to treat an agriculture land which was lightly contaminated by Cd (II) (0.2 mg/kg) and Pb (II) (12.9 mg/kg) and observed reductions of Cd (II) and Pb (II) concentrations in $CaCl_2$ and Diethylenetriaminepentaacetic acid (DTPA) extractions as well as crop biomass. While Lucchini et al. (2014a) did not observe any significant changes of total metal concentrations in soil or plant three years after wood biochar treatment on a lightly contaminated agriculture land (8-9 mg/kg of Ni (II), and 33-38 mg/kg of Zn (II)). Therefore, the long-term stability of the immobilisation of heavy metals in contaminated land treated by biochar, which is crucial for verifying the feasibility of biochar application in practical remediation projects, remains unclear and needs further investigation.

In the present stduy, Salisbury biochar produced from British broadleaf hardwood was applied to a contaminated site in the UK in 2011. In order to aid revegetation, a small amount of compost was also added to supply nutrients for grass growth. The effects of the treatment on the leaching performances and geochemical phases of Ni (II) and Zn (II) in the site soils were investigated three years after the treatment. Finally, as the extent of revegetation on-site over this period was negligible, the influences of the treatment levels of biochar and compost on the revegetation of the site soils were investigated in laboratory.

2 Materials and methods

2.1 Site information

A site of approximately 2 hectares and located in Castleford, West Yorkshire, UK was adopted for this study. According to the national weather service, the annual average rainfall amount in this area is 600-700 mm. The information of the soil layers and the contamination of the site have been presented elsewhere (Wang et al., 2015). In general, the site exhibited a high degree of heterogeneity in both soil textures and contamination levels due to various chemical industries that took place on the site during World War 1 and before World War 2. In the biochar application area, one borehole and one trial pit investigation revealed the presence of mainly Ni (II) (200 - 740 mg/kg) and Zn (II) (150 - 810 mg/kg) (the main focuses of this study) and several other contaminants (Cu (II), Pb (II), chromium (Cr) (III or XI) and petroleum hydrocarbons).

2.2 Biochar, compost and treatment

Salisbury biochar derived from British broadleaf hardwood was used in this study due to the reliable availability and sustainability of hardwood in the UK (Shen et al., 2015). Salisbury biochar was obtained from Southern Woodland products (Salisbury, UK). It was produced at a pyrolysis temperature of 600 ºC in a retort with a residence time of 13.5 hours. The lid of the retort was on but no additional protective gas was added during the production. 600 kg of raw hardwood was taken for one burn. The physicochemical properties and adsorption characterisation of this biochar have been presented elsewhere (Shen et al., 2015). In summary, the biochar sample revealed a pH of 6.96, BET surface area of 5.30 m^2/g, cation exchange capacity of 7.20 cmol/kg, carbon content of 79.91%, nitrogen content of 0.73% and Ni (II) and Zn (II) contents each less than 0.01%. Compost was purchased from Biogran Natural in Bath, UK. The typical composition provided by the supplier indicates that the compost comprises approximately 50% organic matter with a pH of 7.2. Its typical elements include 3.4% nitrogen, 4.4% phosphorus and 0.3% potassium.

The treatment was employed at the site in May 2011. The field trial design consists of four trial plots with a plan area of 1 m^2 each, 2 m in depth and spaced approximately 0.5 m from each other. After considering the contamination level of the site, the adsorption capacity of the biochar and the engineering costs (Shen et al., 2015), the biochar dosages were selected as 0%, 0.5%, 1% and 2% (w/w) in trial plots labelled TP0, TP1, TP2 and TP3 respectively (Table A1). Additionally 0.5% compost (w/w) was added to each plot to supply nutrients for revegetation as suggested by Beesley et al. (2011). The trial plots were firstly excavated and the soil, biochar and compost were thoroughly mixed in them by a mixer. Grass seeds were then sown at a dosage of 100 g per trial plot and the trial plots were watered twice a day for 15 days before being left open to the environment. The grass was named fast acting lawn seed purchased from Westland Garden Health, UK and comprised a mixture of 50% *creeping red fescue* and 50% *perennial ryegrass*.

2.3 Chemical analysis of the site soils

Soil samples were collected three years after the treatment to verify the long-term effect of the treatment. Three samples (taken from between 0 and 10 cm in depth) were collected at different locations of each plot. The soils were dried at 40 °C in an oven for 48 h and homogenised to form one representative sample for each plot.

Then the soils were sieved to less than 2 mm and sealed in sample bags for further analysis. According to the particle size analysis (< 2 mm) using an AccuSizer 780 Optical Particle Sizer (Particle Sizing Systems, California, USA), 97% of the particles of the plot soils fall within 0.05 - 2 mm.

2.3.1 Carbonic acid leaching of the site soils

Standard leaching tests are widely used as indicators to estimate the release potential of hazardous and toxic elements from solid waste (Wang et al., 2014). The carbonic acid leaching (based on BS EN 12457-2 and Lewin et al. (1994)) was used in this study. Firstly 10 g dry soil was mixed with 100 mL carbonic acid (pH = 5.6) and rolled at 20 rpm for 24 h. Then the mixture was filtered with 0.45 µm filter and the metal concentrations in the leachates were tested by inductively coupled plasma/optical emission spectrometry (ICP-OES) (Perkin-Elmer, 7000DV).

2.3.2 Sequential extraction of the site soils

The soil samples were further investigated using a 5-step sequential extraction (based on Li et al. (1995, 2001), Tessier et al (1979) and Wang et al., (2014)) to determine the different geochemical phases of heavy metals present in the soils three years after the treatment. The metals were partitioned into five operationally defined fractions through the following steps:

Step 1 - exchangeable fraction (non-specific adsorption): Soil sample (1 g) was extracted with 8 ml of 0.5 M $MgCl_2$ at pH of 7 with continuous agitation for 20 min at room temperature;

Step 2 - fraction bound to CO_3^{2-}/PO_4^{2-} (specific adsorption): The residue from Step 1 was extracted with 8 mL of 1 M NaOAc (adjusted to pH 5.0 with HOAc). Continuous agitation was maintained for 5 h at room temperature;

Step 3 - fraction bound to Fe/Mn oxides: The residue from Step 2 was extracted with 20 mL of 0.04 M $NH_2 \cdot OH \cdot HCl$ in 25% (v/v) HOAc followed with occasional agitation for 6 h at 96 °C;

Step 4 - fraction bound to organic matter: The residue from Step 3 was extracted with 3 mL of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 (adjusted to pH 2.0 with 70% HNO_3). The mixture was then heated at 85 °C with occasional agitation for 2 h. After cooling, 3 mL of 30% H_2O_2 (adjusted to pH 2.0 with 70% HNO_3) was added and the extraction was heated at 85 °C with occasional agitation for 3 h. After cooling, 5 mL of 3.2 M NH_4OAc in 20% HNO_3 was added and the mixture was continuously agitated for 30 min;

Step 5 - residue fraction: The residue from step 4 was digested with 9 mL of 36% HCl and 3 mL of 70% HNO_3 for 16 h at room temperature and then heated at 95 °C for 2h.

Continuous agitation was performed using a shaker at 200 rpm. Following each step, the samples were centrifuged at 3000 rpm for 10 min at room temperature. The supernatant was then collected and filtered through a 0.45 µm filter and acidified or diluted when necessary before analysed by ICP-OES. The remained solid samples were washed with 8 ml deionized water prior to the next extraction step, and the washing solution was discarded after centrifugation at 3000 rpm for 10 min.

Combining the amount of the heavy metals extracted from each step of the sequential extraction gives the total amount of the heavy metals in the soil. All laboratory analysis in this study was conducted in a temperature controlled lab at 20 ± 1 °C and 50 ± 2% humidity based on the department lab standard.

2.4 Grass growth test

The visual assessment indicated no grass growth in any of the four trial plots. Further lab tests using a range of biochar and compost additions to soil samples collected from the site were conducted. The mixtures (50 g) containing 0 - 20% biochar and 0 - 40% compost were placed into germination pots. The pots were covered to prevent the soil drying out and left to incubate overnight. Each pot was then sown with 1 g of grass seeds (the same as that applied on site) and watered daily with 10 mL water. The pots were kept on bench tops under fluorescent light, and the temperature and relative humidity were maintained at 20 ± 1 °C and 50 ± 2% respectively. The grass was harvested after 4 weeks and placed in a fan-assisted oven at 80 °C for 3 days before being weighed.

2.5 Quality assurance and quality control

An advanced quality assurance (QA) and quality control (QC) system was developed and conducted according to Perera et al., (2005). The details of QA/QC in this project were presented in the SMiRT project final report (Al-Tabbaa and Liska, 2012). In general, prior to the application, the commercially available and quality controlled additives (biochar and compost) were purchased from Southern Woodland products (Salisbury, UK) and Biogran Natural (Bath, UK) as described in section 2.2, and stored and transported by professional industrial partners. During the application, the in-situ mixing was conducted and controlled by professional industrial partners. After the application, the sampling was also conducted and controlled by professional industrial partners. The procedures and methods of the chemical tests in lab were controlled according to existing standards or published papers. The QA/QC checks of the testing instruments (ICP-OES and pH meter etc.) in lab were conducted during and after installation by the suppliers. The testing instruments were also calibrated in lab before the chemical analysis.

2.6 Statistical analysis

All the experiments in this study were carried out in triplicates. The means and standard deviations were calculated and presented for each experiment. The significance of differences between two groups were evaluated by a one-way analysis of variance (ANOVA) at the significance level of 0.05 using SPSS 16.0 when necessary.

3 Results and discussion

3.1 Carbonic acid leaching performance of the site soil

The dissolved Ni (II) and Zn (II) concentrations in the leachates significantly ($P < 0.001$) reduced three years after the treatment for all the four plots (Fig. 1). Specifically, the Ni (II) concentrations in leachates from TP0, TP1, TP2 and TP3 soils reduced with respect to the pre-treatment measurements by 98%, 93%, 90% and 92% respectively. Likewise, the Zn (II) concentrations in the leachate from TP0, TP1, TP2 and TP3 soils reduced 83%, 97%, 97% and 95% from the original concentrations. The soil pH values of the four plots were consistently between 7.9 and 8.1 and show no significant trends ($P > 0.05$) indicating a change over time (Fig. 1), which was probably due to the low contents of biochar and compost addition.

Leaching performance indicates the release potential of hazardous elements from the contaminated soils (Wang et al., 2014). The reduction of Ni (II) and Zn (II) concentrations in the leachates (Fig. 1) suggested the hazards associated with soils had been successfully decreased by the treatment compared with that before treatment. Bian et al. (2014) also conducted a three-year study applying wheat straw biochar in a contaminated paddy field and observed a similar reduction of extracted metal concentrations. The Ni (II) and Zn (II) concentrations in the leachates three years after the treatment in this study were comparable to conventional cement-based stabilisation/solidification trials carried out in parallel on the same site (Wang et al., 2015), suggesting that the field performance of biochar may be similar to technologies currently being used. Wang et al., (2014) conducted another cement-based remediation on a similar site in the UK. The 17-year data confirms the long-term effectiveness of the immobilisation of metals after the treatment. However, as biochar's potential in soil remediation was only addressed recently (Beesley et al., 2011), it is difficult to find existing studies over such a long term and make a relevant comparison. The dark earth in Amazon revealed the high stability of biochar in soils over 800 years (Lehmann, 2007), therefore its effectiveness in immobilising metals in soils over decades or even centuries can be expected.

3.2 Fractions of Ni (II) and Zn (II) in the site soils three years after the treatment

The fractions of Ni (II) and Zn (II) in the site soils three years after the treatment were investigated by sequential extraction tests and the results are shown in Fig. 2 and Table A2. The results indicated that Ni (II) exists primarily in residue form although to a lesser extent in TP0 (51%) compared with TP1, TP2 and TP3 (61 - 66%). Conversely, the fractions bound to Fe/Mn oxides and to organics were greater in TP0 than the other trial plots. Exchangeable and CO_3^{2-}/PO_4^{3-} bound fractions were negligible in all trial plots.

The sequential extraction also indicated that Zn (II) exists primarily bound to Fe/Mn oxides (59 - 66%). The proportion bound to organics was higher in TP0 than in TP1, TP2 and TP3 while the residue in TP0 (7%) was much lower than the other plots (27 - 35%). As with Ni (II), the amounts bound to CO_3^{2-}/PO_4^{3-} were low (< 8%) in all trial plots and exchangeable fraction was negligible.

The fraction of Ni (II) (29 - 40%) and Zn (II) (59 - 66%) bound to Fe/Mn oxides formed a significant proportion of the total amounts in all four trial plots. The biochar and compost each contained very small amounts of Fe and Mn (Shen, 2015) and therefore metals were most likely bound to Fe/Mn oxides in the site soils. This finding is in line with Wang et al. (2014) who observed that the fraction bound to Fe/Mn oxides was the most significant constituent when sequentially extracting the contaminated soil in a similar site after the treatment with cement-based binders.

The fraction bound to organics in TP0, which may probably transferred from weaker Fe/Mn oxides fraction after compost addition, was larger than in the trial plots both containing biochar and compost (TP1, TP2 and TP3) and is most likely due to the surface complexation of metals with carboxyl and acidic groups in the compost. For the trial plots with biochar addition as well as compost, this fraction decreased and transferred to the more stable residue fraction. This suggests that competitive sorption took place and that the biochar addition resulted in the preferential formation of more stable bonds between metals and biochar than those resulting from complexation with organics. Likewise, this competitive effect may have also caused the reduction of Ni (II) bound to Fe/Mn oxides and Zn (II) bound to CO_3^{2-}/PO_4^{2-} in TP1, TP2 and TP3 compared with TP0. The absence of an exchangeable fraction may also be due to the competition after the addition of compost and biochar with the soil. Similar competitive effects were observed by Ahmad et al. (2014) and Beesley and Marmiroli (2011). No significant relationship between the fractions and biochar dosage was found, suggesting that more addition of biochar did not necessarily result in significant change in metal fractions when biochar was adequate.

3.3 Leachabilities of Ni (II) and Zn (II) in the sites soils three years after the treatment

The leachabilities of Ni (II) and Zn (II) in soils were obtained by dividing its extracted amount by its total amount in the soil. The extracted amounts from the carbonic acid leaching test are shown in Fig. 1 and the total amounts were obtained by calculating the sum of the five fractions in the sequential extraction tests (Table A2). Table 1 presents the leachabilities of Ni (II) and Zn (II) in the site soils three years after the treatment. The soils in TP0 exhibited higher leachabilities for Ni (II) (0.35%) and Zn (II) (0.12%) compared with TP1, TP2 and TP3 (0.12 - 0.15% for Ni (II) and 0.01% for Zn (II)).

This project was initially focused on reducing the concentrations of metals leached by rainfall and groundwater, therefore only leaching tests on the four plot soils were investigated before treatment to form a comparison with those after treatment. As the industrial site investigation, which contains 13 boreholes and 9 trial pits, only provide an overview of the contamination level of the site and did not exactly involve the four trial plots in this research, the initial total metal amounts in the four plot soils were unclear. Therefore, although the concentrations of Ni (II) and Zn (II) in the four plot soils significantly reduced three years after the treatment. It is hard to make a similar comparison on their leachabilities over time.

After three years, the plots with both biochar and compost additions exhibited much lower leachabilities of Ni (II) and Zn (II) than the plot with compost only (Table 1), which suggests that although all the treatments for the four plots reduced the concentrations of Ni (II) and Zn (II) in the carbonic acid leachate, the leachabilities of them were different and the addition of biochar reduced the leachabilities of Ni (II) and Zn (II) in the plot soils. This finding agrees with Liang et al. (2014) who also observed a significant reduction of leachability of Cd (II) for a contaminated soil 56 days after the treatment by dairy manure biochar. As suggested by the sequential extraction results in this study, the reduction of the leachabilities of Ni (II) (from 0.35% to 0.12 - 0.15%) and Zn (II) (from 0.12% to 0.01%) in TP1, TP2 and TP3 compared with TP0 was likely caused by the competitive effect resulting in stronger bonds (residue fraction, increase from 51% to 61 - 66% for Ni (II) and from 7% to 27 - 35% for Zn (II)) being formed due to the addition of biochar.

The low leachabilities of metals in the four plot soils probably resulted from the relatively high equilibrium pH (7.64 - 7.71) of the leachates (Table A3), which is due to the buffering capacities of the alkaline soil and biochar (Fig. 1). Ni (II) and Zn (II) were unlikely to largely dissociate from the binding sites (complexes and precipitates formed between metals and biochar and compost) at such high pH (Christensen and Christensen, 2000; Kongdee and Bechtold, 2009).

No significant relation between the leachabilities of Ni (II) and Zn (II) and biochar dosage was found in the present study. The suitable dosage of biochar addition is dependent on various factors such as the contamination level of the site, the soil characteristics and the adsorption capacity of biochar (Bian et al., 2014; Lucchini et al., 2014b). As the addition of 0.5% biochar was sufficient to immobilise the metals in the soils for this site and more biochar addition did not result in better performances, considering the costs of the materials and the transportation, 0.5% addition of biochar is believed to be a suitable dosage for immobilising the metals on this site.

3.4 Effect of the treatment on plant growth

The visual assessment revealed that the grass germination on site was failed during the three years, suggesting that the site soil is in a poor condition for grass growth, which could result from various factors. First, the sandy soil can lead to a low retention of organic matter and nutrients that are necessary for plant germination and growth. Further, the presence of organic pollutants (total petroleum hydrocarbons: 0 - 8400 mg/kg) in this site (Wang et al., 2015) can also inhibit plant growth (Beesley et al., 2011). Moreover, the high concentrations of metals in the soil can bind to the soil organic matter (SOM) and limit its biodegradation, reducing the uptake of nutrients from SOM by grass roots (Bolan et al., 2014). However, the added compost could supply the nutrients (nitrogen and phosphorus) and meanwhile the high adsorption capacity of biochar could help retain the nutrients in the soils. The biochar can also adsorb the organic pollutants and therefore cut the access of grass roots to them. Likewise, the biochar can adsorb and immobilise the metals and help provide a suitable habitat for soil microbes to decompose SOM. Therefore, the addition of biochar and compost was expected to successfully aid the revegetation on site.

The failure of revegetation was very likely due to the insufficient dosage of biochar addition. Further laboratory tests focusing on exploring the reason why the revegetation was failed were carried out. The amounts of grass growth as a result of biochar and compost treatments are given in Fig. 3. Only 7 of 19 treatment ratios resulted in successful germination of grasses. The pots with 10% biochar + 10% compost, 10% biochar + 20% compost and 20% biochar + 40% compost exhibited relatively more grass growth (7.06 - 12.32 mg). While small amounts of grass (1.50 - 2.13 mg) were observed from the pots with 10% biochar + 0% compost and 20% biochar + 20% compost and less amount (0.20 mg) was observed from the pots with 5% biochar + 5% compost and 5% biochar + 10 % compost.

It can be found that in order to aid the germination and growth of grass, higher additions of both biochar and compost (Fig. 3) were needed to adsorb the contaminants, keep the plant roots away from pollutants and supply sufficient nutrients. However, high dosages of biochar can also lead to the immobilisation of available nutrients in the soils due to the adsorption and subsequently lead to failure of germination when the compost was not sufficient (Bolan et al., 2014). Therefore, only when the biochar addition level was adequate to adsorb the organic pollutants and heavy metals and the compost addition was equal to or higher than the biochar addition to supply sufficient nutrients was germination and plant growth successful in the lab trials carried out in this study (Fig.3). The results from this study suggest that 5% biochar + 5% compost addition is the minimum requirement for a successful revegetation on this site, however this will be dependent on site characteristics, contamination levels and the type of biochar being applied for other sites. The pot with 10% biochar + 0% compost germinated despite not fitting the above criteria; this is most likely a reflection of the high degree of heterogeneity of the site soil.

5 Conclusions

In this paper, a field remediation study was carried out on a contaminated site using biochar and compost mixed into four trial plots. The extracted concentrations of Ni (II) and Zn (II) in the carbonic acid leaching tests were successfully reduced three years after the treatment. The leachabilities of Ni (II) and Zn (II) in the plots with biochar addition exhibited much lower than that without biochar addition. Biochar is believed to play a key role in reducing the leachability of soils. This was confirmed by sequential extraction tests which indicated that biochar addition enhances the residue fractions of Ni (II) and Zn (II) in the soils through competitive sorption and consequently reduces their mobility. The laboratory pot study on plant growth suggested that larger amounts of biochar and compost were needed for successful revegetation on this site. The specific mechanisms between the soil and amendments of biochar and compost that govern plant germination have not been investigated in this study and are essential for further understanding the suitability of biochar for revegetating a contaminated site. This study suggests the effectiveness of biochar in immobilising metals in contaminated site in the long term.

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Content of tables

Table 1 The leachabilities of Ni (II) and Zn (II) in the site soils three years after the treatment

Table 1 The leachabilities of Ni (II) and Zn (II) in the site soils three years after the treatment.

	TP0	TP1	TP2	TP3
Ni (II)	0.35%	0.15%	0.12%	0.13%
Zn (II)	0.12%	0.01%	0.01%	0.01%

Content of figures

Fig. 1. The dissolved concentrations of Ni (II) (a) and Zn (II) (b) in carbonic acid leachates as well as the pH values of the plot soils before and three years after the treatment.

Fig.2. Fractions of metals in each step of sequential extraction (a - Ni (II), b - Zn (II)).

Fig. 3. Plant growth (dry mass) in laboratory pot trials with different biochar and compost dosages (w/w).

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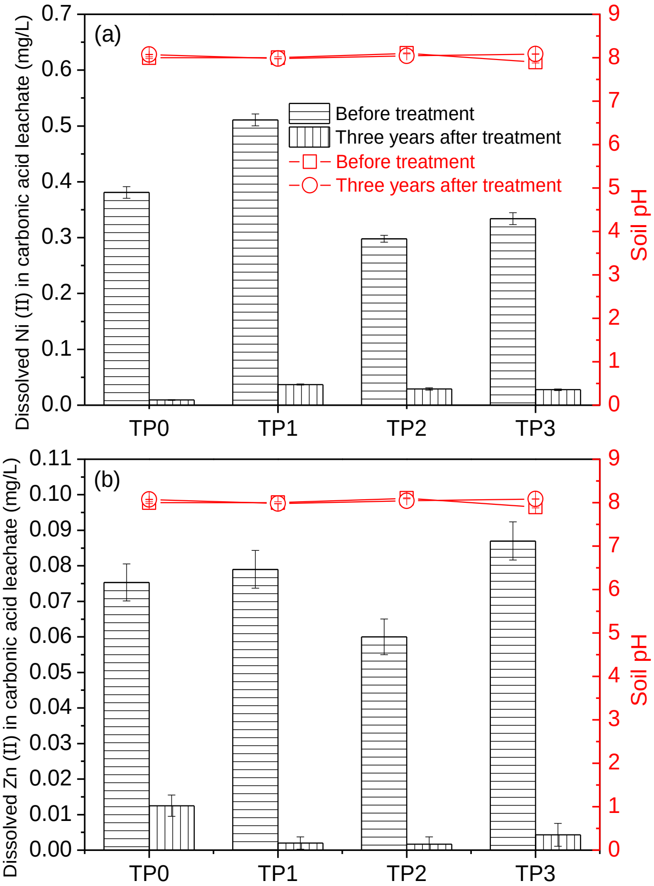


Fig.2. Fractions of metals in each step of sequential extraction (a - Ni (II), b (II) - Zn).

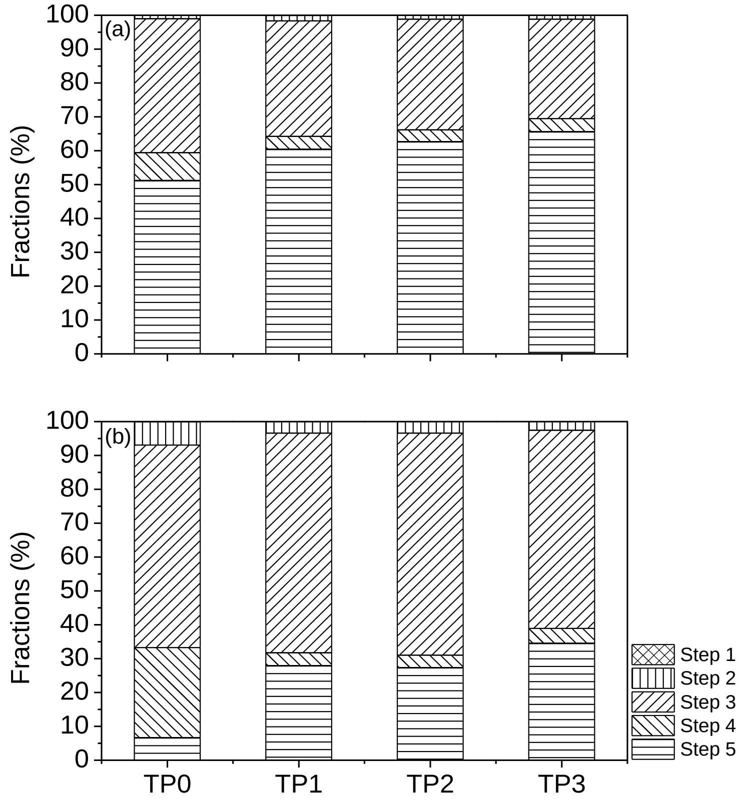
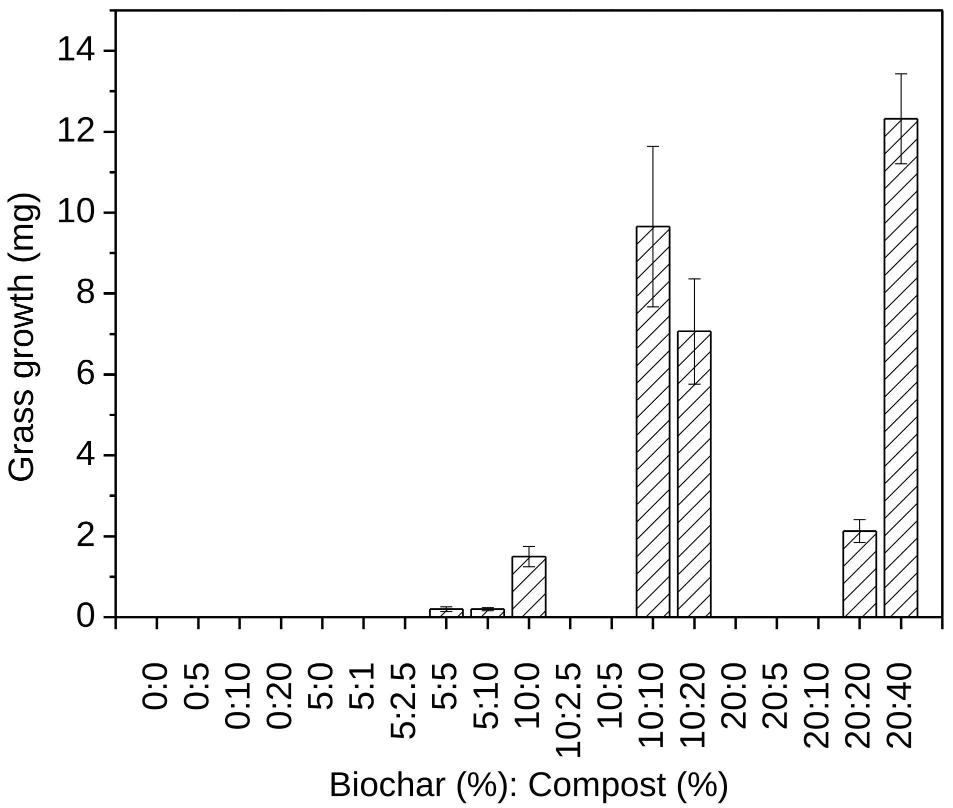


Fig. 3. Plant growth (dry mass) in laboratory pot trials with different biochar and compost dosages (w/w).



Grass growth (mg)
0
2
4
6
8
10
12
14
0:0
0:5
0:10
0:20
5:0
5:1
5:2.5
5:5
5:10
10:0
10:2.5
10:5
10:10
10:20
20:0
20:5
20:10
20:20
20:40
Biochar (%): Compost (%)

Long-term impact of biochar on the immobilisation of nickel (II) and zinc (II) and the revegetation of a contaminated site

Zhengtao Shen [a,*], Amelia Md Som [b], Fei Wang [a], Fei Jin [a], Oliver McMillan [a], Abir Al-Tabbaa [a]

[a] (Geotechnical and Environmental Research Group, Department of Engineering, University of Cambridge, Cambridge, CB2 1PZ, United Kingdom)

[b] (UniKL MICET, Lot 1988 Bandar Vandor Taboh Naning, Melaka, 78000 Alor Gajah, Malaysia)

* Corresponding author: Email: ztshennju@gmail.com; zs281@cam.ac.uk. Phone number: 0044+7541935253. Fax: 0044+7541935253

Abstract: A field remediation treatment was carried out to examine the long-term effect of biochar on the immobilisation of metals and the revegetation of a contaminated site in Castleford, UK. The extracted concentrations of nickel (Ni) (II) and zinc (Zn) (II) in the carbonic acid leaching tests were reduced by 83 - 98% over three years. The extracted Ni (II) and Zn (II) concentrations three years after the treatment were comparable to a cement-based treatment study carried out parallelly on the same site. The sequential extraction results indicated that biochar addition (0.5 - 2%) increased the residue fractions of Ni (II) (from 51% to 61 - 66%) and Zn (II) (from 7% to 27 - 35%) in the soils through competitive sorption, which may have resulted in the reduction of leachabilities of Ni (II) (from 0.35% to 0.12 - 0.15%) and Zn (II) (from 0.12% to 0.01%) in the plots with biochar compared with that without biochar three years after the treatment. The germination of grass in the plots on site was failed. Further laboratory pot study suggested that larger amounts of biochar (5% or more) and compost (5% or more) were needed for the success of revegetation on this site. This study suggests the effectiveness and potential of biochar application in immobilising heavy metals in contaminated site in the long term.

Keywords: Biochar, Heavy metal, Leaching, Sequential extraction, Revegetation, Soil remediation

1 Introduction

Biochar is the solid and carbon-rich product of heating biomass in a low oxygen environment (pyrolysis) and is used to store carbon in a more recalcitrant form (Lehmann et al., 2008; Sohi, 2012). Its feedstock usually comes from agriculture green wastes (manure, crop residues, trees, grasses etc.), industrial green wastes and urban sludge (Beesley et al., 2011). Its co-products (bio-oil and syn-gas) during pyrolysis can be used as green energy (Lehmann et al., 2008). Moreover, due to its highly porous micro-structure, active functional groups, high pH, surface area and cation exchange capacity (CEC), biochar can effectively immobilise contaminants by adsorption, ion exchange, surface complexation and precipitation (Beesley et al., 2011; Bian et al., 2014; Zhang et al., 2013). Compared with conventional remediation materials (e.g. cement, lime and clay) (Du et al., 2012; Jiang et al., 2014), biochar also assists in revegetation and restoration of the treated contaminated land (Beesley et al., 2011). These are critical processes for the stabilization and sustainable development of the land and reducing further risk to humans and the surrounding ecosystem (Arienzo et al., 2004; Ruttens et al., 2006). Therefore, biochar is a promising material with the potential to be applied in soil remediation for its multiple environmental benefits.

A number of studies have highlighted biochar's role in removing contaminants in aqueous solution (Inyang et al., 2012; Kołodyńska et al., 2012; Meng et al., 2014). Recent studies have also reported the successful applications of biochar in soil remediation in the short term. For instance, Rees et al. (2014) observed a reduction of extractable cadmium (Cd) (II), lead (Pb) (II), copper (Cu) (II), nickel (Ni) (II) and zinc (Zn) (II) in soils after the addition of a 80% coniferous and 20% hardwood biochar in one week. Likewise, Uchimiya et al. (2012) observed a reduction of Pb (II), Cu (II) and Zn (II) after undertaking the Toxicity Characteristic Leaching Procedure (TCLP) extraction after adding cottonseed hull biochar to the contaminated soil within one week. Beesley and Marmiroli (2011) also observed a reduction of metals in column leachate 8 weeks after hardwood biochar treatment. Houben et al. (2013) found a reduction of Cd (II), Pb (II) and Zn (II) in $CaCl_2$ extraction from soil 56 days after Miscanthus straw biochar amendment. These short-term findings demonstrate that the application of biochar in soil remediation is feasible, however limited long-term studties have been carried out to date. Bian et al. (2014) used wheat straw biochar to treat an agriculture land which was lightly contaminated by Cd (II) (0.2 mg/kg) and Pb (II) (12.9 mg/kg) and observed reductions of Cd (II) and Pb (II) concentrations in $CaCl_2$ and Diethylenetriaminepentaacetic acid (DTPA) extractions as well as crop biomass. While Lucchini et al. (2014a) did not observe any significant changes of total metal concentrations in soil or plant three years after wood biochar treatment on a lightly contaminated agriculture land (8-9 mg/kg of Ni (II), and 33-38 mg/kg of Zn (II)). Therefore, the long-term stability of the immobilisation of heavy metals in contaminated land treated by biochar, which is crucial for verifying the feasibility of biochar application in practical remediation projects, remains unclear and needs further investigation.

In the present stduy, Salisbury biochar produced from British broadleaf hardwood was applied to a contaminated site in the UK in 2011. In order to aid revegetation, a small amount of compost was also added to supply nutrients for grass growth. The effects of the treatment on the leaching performances and geochemical phases of Ni (II) and Zn (II) in the site soils were investigated three years after the treatment. Finally, as the extent of revegetation on-site over this period was negligible, the influences of the treatment levels of biochar and compost on the revegetation of the site soils were investigated in laboratory.

2 Materials and methods

2.1 Site information

A site of approximately 2 hectares and located in Castleford, West Yorkshire, UK was adopted for this study. According to the national weather service, the annual average rainfall amount in this area is 600-700 mm. The information of the soil layers and the contamination of the site have been presented elsewhere (Wang et al., 2015). In general, the site exhibited a high degree of heterogeneity in both soil textures and contamination levels due to various chemical industries that took place on the site during World War 1 and before World War 2. In the biochar application area, one borehole and one trial pit investigation revealed the presence of mainly Ni (II) (200 - 740 mg/kg) and Zn (II) (150 - 810 mg/kg) (the main focuses of this study) and several other contaminants (Cu (II), Pb (II), chromium (Cr) (III or XI) and petroleum hydrocarbons).

2.2 Biochar, compost and treatment

Salisbury biochar derived from British broadleaf hardwood was used in this study due to the reliable availability and sustainability of hardwood in the UK (Shen et al., 2015). Salisbury biochar was obtained from Southern Woodland products (Salisbury, UK). It was produced at a pyrolysis temperature of 600 ºC in a retort with a residence time of 13.5 hours. The lid of the retort was on but no additional protective gas was added during the production. 600 kg of raw hardwood was taken for one burn. The physicochemical properties and adsorption characterisation of this biochar have been presented elsewhere (Shen et al., 2015). In summary, the biochar sample revealed a pH of 6.96, BET surface area of 5.30 m^2/g, cation exchange capacity of 7.20 cmol/kg, carbon content of 79.91%, nitrogen content of 0.73% and Ni (II) and Zn (II) contents each less than 0.01%. Compost was purchased from Biogran Natural in Bath, UK. The typical composition provided by the supplier indicates that the compost comprises approximately 50% organic matter with a pH of 7.2. Its typical elements include 3.4% nitrogen, 4.4% phosphorus and 0.3% potassium.

The treatment was employed at the site in May 2011. The field trial design consists of four trial plots with a plan area of 1 m^2 each, 2 m in depth and spaced approximately 0.5 m from each other. After considering the contamination level of the site, the adsorption capacity of the biochar and the engineering costs (Shen et al., 2015), the biochar dosages were selected as 0%, 0.5%, 1% and 2% (w/w) in trial plots labelled TP0, TP1, TP2 and TP3 respectively (Table A1). Additionally 0.5% compost (w/w) was added to each plot to supply nutrients for revegetation as suggested by Beesley et al. (2011). The trial plots were firstly excavated and the soil, biochar and compost were thoroughly mixed in them by a mixer. Grass seeds were then sown at a dosage of 100 g per trial plot and the trial plots were watered twice a day for 15 days before being left open to the environment. The grass was named fast acting lawn seed purchased from Westland Garden Health, UK and comprised a mixture of 50% *creeping red fescue* and 50% *perennial ryegrass*.

2.3 Chemical analysis of the site soils

Soil samples were collected three years after the treatment to verify the long-term effect of the treatment. Three samples (taken from between 0 and 10 cm in depth) were collected at different locations of each plot. The soils were dried at 40 °C in an oven for 48 h and homogenised to form one representative sample for each plot.

Then the soils were sieved to less than 2 mm and sealed in sample bags for further analysis. According to the particle size analysis (< 2 mm) using an AccuSizer 780 Optical Particle Sizer (Particle Sizing Systems, California, USA), 97% of the particles of the plot soils fall within 0.05 - 2 mm.

2.3.1 Carbonic acid leaching of the site soils

Standard leaching tests are widely used as indicators to estimate the release potential of hazardous and toxic elements from solid waste (Wang et al., 2014). The carbonic acid leaching (based on BS EN 12457-2 and Lewin et al. (1994)) was used in this study. Firstly 10 g dry soil was mixed with 100 mL carbonic acid (pH = 5.6) and rolled at 20 rpm for 24 h. Then the mixture was filtered with 0.45 µm filter and the metal concentrations in the leachates were tested by inductively coupled plasma/optical emission spectrometry (ICP-OES) (Perkin-Elmer, 7000DV).

2.3.2 Sequential extraction of the site soils

The soil samples were further investigated using a 5-step sequential extraction (based on Li et al. (1995, 2001), Tessier et al (1979) and Wang et al., (2014)) to determine the different geochemical phases of heavy metals present in the soils three years after the treatment. The metals were partitioned into five operationally defined fractions through the following steps:

Step 1 - exchangeable fraction (non-specific adsorption): Soil sample (1 g) was extracted with 8 ml of 0.5 M $MgCl_2$ at pH of 7 with continuous agitation for 20 min at room temperature;

Step 2 - fraction bound to CO_3^{2-}/PO_4^{2-} (specific adsorption): The residue from Step 1 was extracted with 8 mL of 1 M NaOAc (adjusted to pH 5.0 with HOAc). Continuous agitation was maintained for 5 h at room temperature;

Step 3 - fraction bound to Fe/Mn oxides: The residue from Step 2 was extracted with 20 mL of 0.04 M $NH_2 \cdot OH \cdot HCl$ in 25% (v/v) HOAc followed with occasional agitation for 6 h at 96 °C;

Step 4 - fraction bound to organic matter: The residue from Step 3 was extracted with 3 mL of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 (adjusted to pH 2.0 with 70% HNO_3). The mixture was then heated at 85 °C with occasional agitation for 2 h. After cooling, 3 mL of 30% H_2O_2 (adjusted to pH 2.0 with 70% HNO_3) was added and the extraction was heated at 85 °C with occasional agitation for 3 h. After cooling, 5 mL of 3.2 M NH_4OAc in 20% HNO_3 was added and the mixture was continuously agitated for 30 min;

Step 5 - residue fraction: The residue from step 4 was digested with 9 mL of 36% HCl and 3 mL of 70% HNO_3 for 16 h at room temperature and then heated at 95 °C for 2h.

Continuous agitation was performed using a shaker at 200 rpm. Following each step, the samples were centrifuged at 3000 rpm for 10 min at room temperature. The supernatant was then collected and filtered through a 0.45 µm filter and acidified or diluted when necessary before analysed by ICP-OES. The remained solid samples were washed with 8 ml deionized water prior to the next extraction step, and the washing solution was discarded after centrifugation at 3000 rpm for 10 min.

Combining the amount of the heavy metals extracted from each step of the sequential extraction gives the total amount of the heavy metals in the soil. All laboratory analysis in this study was conducted in a temperature controlled lab at 20 ± 1 °C and 50 ± 2% humidity based on the department lab standard.

2.4 Grass growth test

The visual assessment indicated no grass growth in any of the four trial plots. Further lab tests using a range of biochar and compost additions to soil samples collected from the site were conducted. The mixtures (50 g) containing 0 - 20% biochar and 0 - 40% compost were placed into germination pots. The pots were covered to prevent the soil drying out and left to incubate overnight. Each pot was then sown with 1 g of grass seeds (the same as that applied on site) and watered daily with 10 mL water. The pots were kept on bench tops under fluorescent light, and the temperature and relative humidity were maintained at 20 ± 1 °C and 50 ± 2% respectively. The grass was harvested after 4 weeks and placed in a fan-assisted oven at 80 °C for 3 days before being weighed.

2.5 Quality assurance and quality control

An advanced quality assurance (QA) and quality control (QC) system was developed and conducted according to Perera et al., (2005). The details of QA/QC in this project were presented in the SMiRT project final report (Al-Tabbaa and Liska, 2012). In general, prior to the application, the commercially available and quality controlled additives (biochar and compost) were purchased from Southern Woodland products (Salisbury, UK) and Biogran Natural (Bath, UK) as described in section 2.2, and stored and transported by professional industrial partners. During the application, the in-situ mixing was conducted and controlled by professional industrial partners. After the application, the sampling was also conducted and controlled by professional industrial partners. The procedures and methods of the chemical tests in lab were controlled according to existing standards or published papers. The QA/QC checks of the testing instruments (ICP-OES and pH meter etc.) in lab were conducted during and after installation by the suppliers. The testing instruments were also calibrated in lab before the chemical analysis.

2.6 Statistical analysis

All the experiments in this study were carried out in triplicates. The means and standard deviations were calculated and presented for each experiment. The significance of differences between two groups were evaluated by a one-way analysis of variance (ANOVA) at the significance level of 0.05 using SPSS 16.0 when necessary.

3 Results and discussion

3.1 Carbonic acid leaching performance of the site soil

The dissolved Ni (II) and Zn (II) concentrations in the leachates significantly ($P < 0.001$) reduced three years after the treatment for all the four plots (Fig. 1). Specifically, the Ni (II) concentrations in leachates from TP0, TP1, TP2 and TP3 soils reduced with respect to the pre-treatment measurements by 98%, 93%, 90% and 92% respectively. Likewise, the Zn (II) concentrations in the leachate from TP0, TP1, TP2 and TP3 soils reduced 83%, 97%, 97% and 95% from the original concentrations. The soil pH values of the four plots were consistently between 7.9 and 8.1 and show no significant trends ($P > 0.05$) indicating a change over time (Fig. 1), which was probably due to the low contents of biochar and compost addition.

Leaching performance indicates the release potential of hazardous elements from the contaminated soils (Wang et al., 2014). The reduction of Ni (II) and Zn (II) concentrations in the leachates (Fig. 1) suggested the hazards associated with soils had been successfully decreased by the treatment compared with that before treatment. Bian et al. (2014) also conducted a three-year study applying wheat straw biochar in a contaminated paddy field and observed a similar reduction of extracted metal concentrations. The Ni (II) and Zn (II) concentrations in the leachates three years after the treatment in this study were comparable to conventional cement-based stabilisation/solidification trials carried out in parallel on the same site (Wang et al., 2015), suggesting that the field performance of biochar may be similar to technologies currently being used. Wang et al., (2014) conducted another cement-based remediation on a similar site in the UK. The 17-year data confirms the long-term effectiveness of the immobilisation of metals after the treatment. However, as biochar's potential in soil remediation was only addressed recently (Beesley et al., 2011), it is difficult to find existing studies over such a long term and make a relevant comparison. The dark earth in Amazon revealed the high stability of biochar in soils over 800 years (Lehmann, 2007), therefore its effectiveness in immobilising metals in soils over decades or even centuries can be expected.

3.2 Fractions of Ni (II) and Zn (II) in the site soils three years after the treatment

The fractions of Ni (II) and Zn (II) in the site soils three years after the treatment were investigated by sequential extraction tests and the results are shown in Fig. 2 and Table A2. The results indicated that Ni (II) exists primarily in residue form although to a lesser extent in TP0 (51%) compared with TP1, TP2 and TP3 (61 - 66%). Conversely, the fractions bound to Fe/Mn oxides and to organics were greater in TP0 than the other trial plots. Exchangeable and CO_3^{2-}/PO_4^{3-} bound fractions were negligible in all trial plots.

The sequential extraction also indicated that Zn (II) exists primarily bound to Fe/Mn oxides (59 - 66%). The proportion bound to organics was higher in TP0 than in TP1, TP2 and TP3 while the residue in TP0 (7%) was much lower than the other plots (27 - 35%). As with Ni (II), the amounts bound to CO_3^{2-}/PO_4^{3-} were low (< 8%) in all trial plots and exchangeable fraction was negligible.

The fraction of Ni (II) (29 - 40%) and Zn (II) (59 - 66%) bound to Fe/Mn oxides formed a significant proportion of the total amounts in all four trial plots. The biochar and compost each contained very small amounts of Fe and Mn (Shen, 2015) and therefore metals were most likely bound to Fe/Mn oxides in the site soils. This finding is in line with Wang et al. (2014) who observed that the fraction bound to Fe/Mn oxides was the most significant constituent when sequentially extracting the contaminated soil in a similar site after the treatment with cement-based binders.

The fraction bound to organics in TP0, which may probably transferred from weaker Fe/Mn oxides fraction after compost addition, was larger than in the trial plots both containing biochar and compost (TP1, TP2 and TP3) and is most likely due to the surface complexation of metals with carboxyl and acidic groups in the compost. For the trial plots with biochar addition as well as compost, this fraction decreased and transferred to the more stable residue fraction. This suggests that competitive sorption took place and that the biochar addition resulted in the preferential formation of more stable bonds between metals and biochar than those resulting from complexation with organics. Likewise, this competitive effect may have also caused the reduction of Ni (II) bound to Fe/Mn oxides and Zn (II) bound to CO_3^{2-}/PO_4^{2-} in TP1, TP2 and TP3 compared with TP0. The absence of an exchangeable fraction may also be due to the competition after the addition of compost and biochar with the soil. Similar competitive effects were observed by Ahmad et al. (2014) and Beesley and Marmiroli (2011). No significant relationship between the fractions and biochar dosage was found, suggesting that more addition of biochar did not necessarily result in significant change in metal fractions when biochar was adequate.

3.3 Leachabilities of Ni (II) and Zn (II) in the sites soils three years after the treatment

The leachabilities of Ni (II) and Zn (II) in soils were obtained by dividing its extracted amount by its total amount in the soil. The extracted amounts from the carbonic acid leaching test are shown in Fig. 1 and the total amounts were obtained by calculating the sum of the five fractions in the sequential extraction tests (Table A2). Table 1 presents the leachabilities of Ni (II) and Zn (II) in the site soils three years after the treatment. The soils in TP0 exhibited higher leachabilities for Ni (II) (0.35%) and Zn (II) (0.12%) compared with TP1, TP2 and TP3 (0.12 - 0.15% for Ni (II) and 0.01% for Zn (II)).

This project was initially focused on reducing the concentrations of metals leached by rainfall and groundwater, therefore only leaching tests on the four plot soils were investigated before treatment to form a comparison with those after treatment. As the industrial site investigation, which contains 13 boreholes and 9 trial pits, only provide an overview of the contamination level of the site and did not exactly involve the four trial plots in this research, the initial total metal amounts in the four plot soils were unclear. Therefore, although the concentrations of Ni (II) and Zn (II) in the four plot soils significantly reduced three years after the treatment. It is hard to make a similar comparison on their leachabilities over time.

After three years, the plots with both biochar and compost additions exhibited much lower leachabilities of Ni (II) and Zn (II) than the plot with compost only (Table 1), which suggests that although all the treatments for the four plots reduced the concentrations of Ni (II) and Zn (II) in the carbonic acid leachate, the leachabilities of them were different and the addition of biochar reduced the leachabilities of Ni (II) and Zn (II) in the plot soils. This finding agrees with Liang et al. (2014) who also observed a significant reduction of leachability of Cd (II) for a contaminated soil 56 days after the treatment by dairy manure biochar. As suggested by the sequential extraction results in this study, the reduction of the leachabilities of Ni (II) (from 0.35% to 0.12 - 0.15%) and Zn (II) (from 0.12% to 0.01%) in TP1, TP2 and TP3 compared with TP0 was likely caused by the competitive effect resulting in stronger bonds (residue fraction, increase from 51% to 61 - 66% for Ni (II) and from 7% to 27 - 35% for Zn (II)) being formed due to the addition of biochar.

The low leachabilities of metals in the four plot soils probably resulted from the relatively high equilibrium pH (7.64 - 7.71) of the leachates (Table A3), which is due to the buffering capacities of the alkaline soil and biochar (Fig. 1). Ni (II) and Zn (II) were unlikely to largely dissociate from the binding sites (complexes and precipitates formed between metals and biochar and compost) at such high pH (Christensen and Christensen, 2000; Kongdee and Bechtold, 2009).

No significant relation between the leachabilities of Ni (II) and Zn (II) and biochar dosage was found in the present study. The suitable dosage of biochar addition is dependent on various factors such as the contamination level of the site, the soil characteristics and the adsorption capacity of biochar (Bian et al., 2014; Lucchini et al., 2014b). As the addition of 0.5% biochar was sufficient to immobilise the metals in the soils for this site and more biochar addition did not result in better performances, considering the costs of the materials and the transportation, 0.5% addition of biochar is believed to be a suitable dosage for immobilising the metals on this site.

3.4 Effect of the treatment on plant growth

The visual assessment revealed that the grass germination on site was failed during the three years, suggesting that the site soil is in a poor condition for grass growth, which could result from various factors. First, the sandy soil can lead to a low retention of organic matter and nutrients that are necessary for plant germination and growth. Further, the presence of organic pollutants (total petroleum hydrocarbons: 0 - 8400 mg/kg) in this site (Wang et al., 2015) can also inhibit plant growth (Beesley et al., 2011). Moreover, the high concentrations of metals in the soil can bind to the soil organic matter (SOM) and limit its biodegradation, reducing the uptake of nutrients from SOM by grass roots (Bolan et al., 2014). However, the added compost could supply the nutrients (nitrogen and phosphorus) and meanwhile the high adsorption capacity of biochar could help retain the nutrients in the soils. The biochar can also adsorb the organic pollutants and therefore cut the access of grass roots to them. Likewise, the biochar can adsorb and immobilise the metals and help provide a suitable habitat for soil microbes to decompose SOM. Therefore, the addition of biochar and compost was expected to successfully aid the revegetation on site.

The failure of revegetation was very likely due to the insufficient dosage of biochar addition. Further laboratory tests focusing on exploring the reason why the revegetation was failed were carried out. The amounts of grass growth as a result of biochar and compost treatments are given in Fig. 3. Only 7 of 19 treatment ratios resulted in successful germination of grasses. The pots with 10% biochar + 10% compost, 10% biochar + 20% compost and 20% biochar + 40% compost exhibited relatively more grass growth (7.06 - 12.32 mg). While small amounts of grass (1.50 - 2.13 mg) were observed from the pots with 10% biochar + 0% compost and 20% biochar + 20% compost and less amount (0.20 mg) was observed from the pots with 5% biochar + 5% compost and 5% biochar + 10 % compost.

It can be found that in order to aid the germination and growth of grass, higher additions of both biochar and compost (Fig. 3) were needed to adsorb the contaminants, keep the plant roots away from pollutants and supply sufficient nutrients. However, high dosages of biochar can also lead to the immobilisation of available nutrients in the soils due to the adsorption and subsequently lead to failure of germination when the compost was not sufficient (Bolan et al., 2014). Therefore, only when the biochar addition level was adequate to adsorb the organic pollutants and heavy metals and the compost addition was equal to or higher than the biochar addition to supply sufficient nutrients was germination and plant growth successful in the lab trials carried out in this study (Fig.3). The results from this study suggest that 5% biochar + 5% compost addition is the minimum requirement for a successful revegetation on this site, however this will be dependent on site characteristics, contamination levels and the type of biochar being applied for other sites. The pot with 10% biochar + 0% compost germinated despite not fitting the above criteria; this is most likely a reflection of the high degree of heterogeneity of the site soil.

5 Conclusions

In this paper, a field remediation study was carried out on a contaminated site using biochar and compost mixed into four trial plots. The extracted concentrations of Ni (II) and Zn (II) in the carbonic acid leaching tests were successfully reduced three years after the treatment. The leachabilities of Ni (II) and Zn (II) in the plots with biochar addition exhibited much lower than that without biochar addition. Biochar is believed to play a key role in reducing the leachability of soils. This was confirmed by sequential extraction tests which indicated that biochar addition enhances the residue fractions of Ni (II) and Zn (II) in the soils through competitive sorption and consequently reduces their mobility. The laboratory pot study on plant growth suggested that larger amounts of biochar and compost were needed for successful revegetation on this site. The specific mechanisms between the soil and amendments of biochar and compost that govern plant germination have not been investigated in this study and are essential for further understanding the suitability of biochar for revegetating a contaminated site. This study suggests the effectiveness of biochar in immobilising metals in contaminated site in the long term.

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Content of tables

Table 1 The leachabilities of Ni (II) and Zn (II) in the site soils three years after the treatment

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	TP0	TP1	TP2	TP3
Ni (II)	0.35%	0.15%	0.12%	0.13%
Zn (II)	0.12%	0.01%	0.01%	0.01%

Content of figures

Fig. 1. The dissolved concentrations of Ni (II) (a) and Zn (II) (b) in carbonic acid leachates as well as the pH values of the plot soils before and three years after the treatment.

Fig.2. Fractions of metals in each step of sequential extraction (a - Ni (II), b - Zn (II)).

Fig. 3. Plant growth (dry mass) in laboratory pot trials with different biochar and compost dosages (w/w).

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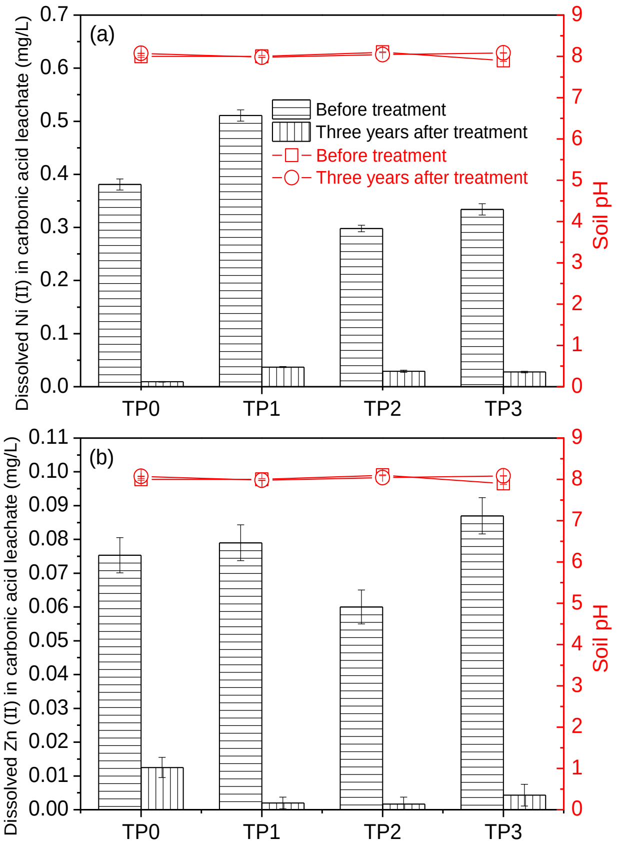
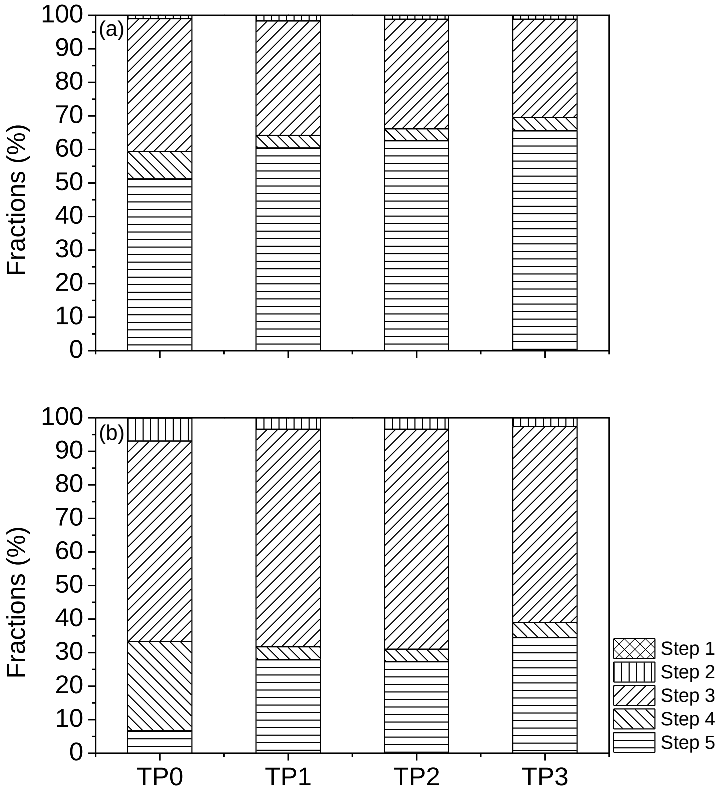


Fig.2. Fractions of metals in each step of sequential extraction (a - Ni (II), b (II) - Zn).



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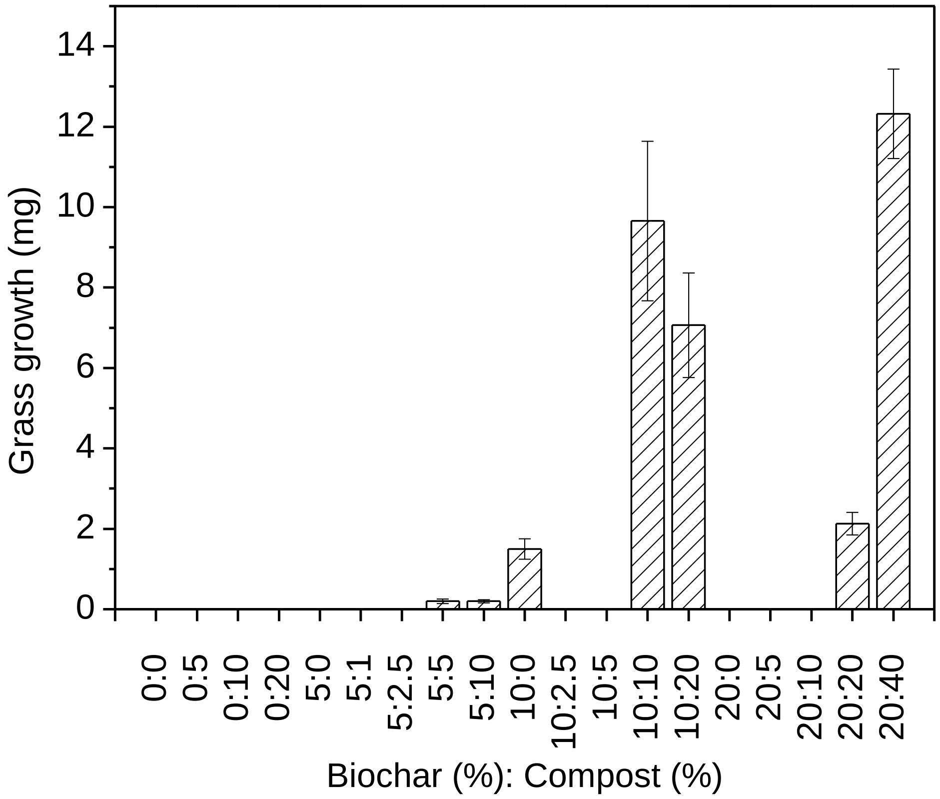

Supplementary Interactive Plot Data (CSV)