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Assessing the capacity of biochar to stabilize copper and lead in contaminated sediments using chemical and extraction methods

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ABSTRACT

Because of its high adsorption capacity, biochar has been used to stabilize metals when remediating contaminated soils; to date, however, it has seldom been used to remediate contaminated sediment. A biochar was used as a stabilization agent to remediate Cu- and Pb-contaminated sediments, collected from three locations in or close to Beijing. The sediments were mixed with a palm sawdust gasified biochar at a range of weight ratios (2.5%, 5%, and 10%) and incubated for 10, 30, or 60 days. The performance of the different treatments and the heavy metal fractions in the sediments were assessed using four extraction methods, including diffusive gradients in thin films, the porewater concentration, a sequential extraction, and the toxicity characteristic leaching procedure. The results showed that biochar could enhance the stability of heavy metals in contaminated sediments. The degree of stability increased as both the dose of biochar and the incubation time increased. The sediment pH and the morphology of the metal crystals adsorbed onto the biochar changed as the contact time increased. Our results showed that adsorption, metal crystallization, and the pH were the main controls on the stabilization of metals in contaminated sediment by biochar.

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Introduction

Sediment is a major component of river ecosystems and has a fundamental influence on ecosystem health. As such, there is great concern about heavy metal contamination of river sediment (Akcil et al., 2015). The heavy metals commonly found in sediments usually originate from industrial waste discharges through direct emissions, such as dumping, or indirect emissions, such as rain runoff and atmospheric deposition. Approximately 90% of the heavy metals that enter rivers may be deposited onto the sediment surface and incorporated into the lattice structure of minerals *via* adsorption, precipitation, and flocculation (Du et al., 2009; Lin et al., 2013). The stability of metals in sediment depends, to some degree, on the environmental conditions. With changes in the environmental conditions, such as the pH, oxidation reduction potential (ORP), temperature and salinity, the bound metals may be released into water, from where they may be taken up and bioaccumulate in food webs, thereby presenting risks to river ecosystems. In addition, the mobility and

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bioavailability of sediment-bound metals in river ecosystems may increase during resuspension by natural processes, waste disposal, and dredging activities (Akcil et al., 2015). Therefore, sediments act as both a sink and a source of heavy metals in aquatic ecosystems and can switch between these roles under different conditions (Peng et al., 2009). Because, when released, metals are toxic to aquatic ecosystems, the stability of metals in sediment matrices should be enhanced to reduce their potential impacts on the aquatic environment.

Currently physical, chemical, and biological technologies are used to treat contaminated sediments, both *in-situ* and *ex-situ* (Wang et al., 2017). During *ex-situ* remediation, sediment is dredged from the riverbed and disposed of, disturbing aquatic benthic life; *in-situ* remediation, however, does not impact on natural hydrological conditions and methods are designed to prevent the desorption of pollutants from the sediment to the water column (Peng et al., 2009; Wang et al., 2017). In most case, *ex-situ* remediation is the first choice in many restoration projects because of the severity of the pollution and doubts that *in-situ* remediation methods can provide stable results over the long-term (Peng et al., 2009). The concentrations of toxic metals can increase dramatically during dredging operations because of the re-suspension of sediment and release of dissolved metal pollutants (Akcil et al., 2015). Sediment remediation methods are designed to either dislodge or extract contaminants from sediment or to enhance their stability in the sediment. Sorbent amendments and stabilization strategies that mimic biogeochemical processes are used to enhance the stability of heavy metals, and potentially reduce the ecological risks (Bolan et al., 2014). A wide range of materials such as zero-valent iron, hematite, ferrihydrite, apatite, clays, calcium-rich sepiolite, attapulgite, and activated carbon have already been used to remediate metal-contaminated sediments (Ghosh et al., 2011; Qian et al., 2009; Yin and Zhu, 2016). However, while biochar is well-known for its stability and high adsorption, it has been used infrequently in sediment management applications (Wang et al., 2017).

Biochar is a carbon-rich material obtained from the thermochemical conversion of biomass under oxygen-limited conditions (Keiluweit et al., 2010; Tong et al., 2011; Wang et al., 2017; Yuan et al., 2011). Because of its unique properties, it is increasingly used in soil remediation applications (Zhang et al., 2013). Studies to date have shown that biochar can enhance the matrix pH under most acid and neutral conditions, and hold moisture, thereby increasing the soil water content and retaining necessary nutrients for plant growth (Atkinson et al., 2010; Gunes et al., 2014; Jeffery et al., 2015; Major et al., 2010). In a recent study, biochar was used to improve and remediate several metal-contaminated rice fields in China. The results from a series of field trials showed that the bioavailability of metals in soil and the metal concentrations in rice grains decreased by between 20%–70%, and 20%–60%, respectively, in soils treated with biochar (Wang et al., 2017). Studies have addressed the effects of biochar on (1) mercury-related processes such as methylation and demethylation (Liu et al., 2016), (2) the fractions of Fe and As (Chen et al., 2016), and (3) the basic physicochemical properties of sediment such as water retention, CO_2 emissions, total organic carbon, pH, and electrical conductivity (Ojeda et al., 2016). Despite the fact that few studies have addressed how biochar can be used to treat metal-contaminated sediments, we speculate that the benefits already seen in soil management might also apply to sediment remediation.

In sediment management strategies, sediment quality guidelines have traditionally been based on the total contaminant concentrations rather than the leachability or bioavailability (Qian et al., 2009). However, the total contaminant concentrations cannot adequately represent contaminant mobility, because the mobility, bioavailability and ecotoxicity of metals in sediments are generally controlled by different geochemical fractions and the binding relationships between contaminants and solid phases (Kazi et al., 2005), which can be more accurately explained by the metal fractions. It is well-known that, when incorporated into the lattice structures of minerals, heavy metals are stable and less bioavailable than weakly bound labile metals. To date, a series of chemical methods, including porewater extraction, membrane extraction, and chemical reagent extraction, have been developed to facilitate rapid evaluation of the bioavailability of metals in soils or sediments (Chen et al., 2016; Yin et al., 2014; Yin and Zhu, 2016; Zhang et al., 2001). In these methods, speciation analysis and leaching tests are based on the different abilities of chemical reagents to extract and classify metal geochemical fractions and evaluate their mobility and bioavailability, and membrane extraction is based on the equilibrium between the solid and liquid to assess the dissolved pollutants concentration and their resupply ability from solid phase. These methods provide detailed information about metal species in sediment phases and helps to predict the potential future behavior of these pollutants (Hasan et al., 2018; Kazi et al., 2005; Song et al., 2017).

The objective of this study was to investigate if biochar could be used effectively to remediate sediments that were contaminated with heavy metals. Four extraction methods were employed to evaluate specific components of the performance of the biochar treatments, as follows: (1) diffusive gradients in thin films (DGT) were used to investigate the concentrations of labile metals (*in-situ* sample) (Zhang et al., 2001); (2) a centrifuge method was used to determine the concentrations of dissolved metals in porewater; (3) a multi-step sequential extraction method (the Community Bureau of Reference (BCR) method, Yin and Zhu (2016)) was used to evaluate the distribution of metal fractions, and (4) the toxicity characteristic leaching procedure (TCLP, USEPA (1984)), a one-step extraction method, was used to investigate the potential leachability of metals in sediments under strong or moderately acidic conditions. While this was a laboratory-based study, the information and data from these experiments could form the basis of further engineering applications.

1. Materials and methods

1.1. Sediment collection and biochar preparation

Three different sediments were collected from an inner-city river (CR), a standby reservoir (SR), and an artificial lake (AC) either close to or in Beijing, China. The sediments were collected by a grab sampler, packed into plastic bags and

sealed, then transported to the laboratory, and stored at 4°C. The sediments were then amended with solutions of $Cu(NO)_2$ and $Pb(NO)_2$ to give medium-to-high concentrations of Cu(II) and Pb(II) (Gu and Hua, 2006; Zhu and Wang, 2012). The sediment slurries were hand-stirred several times to homogenize and then incubated in the dark for 40 days. The total concentrations of Cu and Pb in the sediments before and after the $Cu(NO)_2$ and $Pb(NO)_2$ solutions were added are presented in Table 1. A palm sawdust-based gasification biochar (SBIO), details of which are reported in an earlier study, was selected as the metal stabilization agent (Supplementary Data). Briefly, to prepare the biochar, the palm sawdust was air-dried and then pyrolyzed at approximately 550°C in a kiln in O_2-limited conditions for 2 hr.

1.2. Sediment and biochar properties

The physicochemical properties of the biochar and air-dried sediments were characterized as follows. The pH was measured in a 1:1 suspension of solid and deionized water and shaken for 3 hr at 160 r/min. This test showed that the samples were alkaline (Table 1). The concentrations of total organic carbon (TOC) were determined with a TOC analyzer (Multi N/C 3100, Analytik Jena AG). The surface area was determined with the Brunauer–Emmett–Teller (BET) equation with multipoint adsorption isotherms of N_2 at 77K. Solid samples of biochar and sediment were digested with HNO_3, HF, and $HClO_4$ (3/2/3 mL) in a Teflon bomb, the metal concentrations in the extract solution were measured by flame atomic absorption spectrometry (FAAS) or inductively coupled plasma mass spectrometry (ICP-MS). The chemical compositions were characterized by X-ray fluorescence (XRF) spectrometry (Yin and Zhu, 2016).

Table 1 – Characterization of sediments and SBIO samples.

Materials	SR	CR	AC	SBIO
pH	7.2	7.28	7.14	11.7
Total organic carbon (g/kg)	39.1	43.08	18.34	275.75
Water content (%)	52.2	42.5	45.1	–
BET (m^2/g)	–	–	–	90.4
[a]K (mg/kg)	20,445	19,943	21,134	41,700
[a]Ca (mg/kg)	58,279	104,274	22,974	132,576
[a]Mg (mg/kg)	13,793	19,322	11,684	11,906
[a]Na (mg/kg)	13,175	6650	17,772	3563
*Cu (mg/kg)	35.3	43.9	30.6	55.3
*Pb (mg/kg)	30.8	40.9	25.3	40.2
Zn (mg/kg)	77.5	105.3	56.2	170.3
Cu spiked (mg/kg)	635.3	643.9	630.6	–
Pb spiked (mg/kg)	730.8	740.9	725.3	–
[b]SiO_2 (%)	51.22	54.85	63.27	53.35
[b]CaO (%)	12.69	14.05	5.01	21.48
[b]Al_2O_3 (%)	18.194	15.16	16.06	4.12
[b]K_2O (%)	2.63	2.35	2.68	6.19
[b]Fe_2O_3 (%)	7.89	5.31	5.07	2.34
[b]MgO (%)	4.11	4.92	3.28	2.64
[b]MnO (%)	0.1	0.1	0.1	0.93

BET: Brunauer–Emmett–Teller surface; –: not measured.
[a] The result from ICP-MS; [b] the result from XRF.
* The original concentration without Cu(II) or Pb(II) spiking.

The surface physical morphology of the SBIO was analyzed using scanning electron microscopy (SEM). The functional groups were recorded using Fourier transform infrared spectra (Chen et al., 2016). There was a peak at 3438 cm^{-1} that corresponded to the hydroxyl group stretching vibration. Bonds at 1615 and 1440 cm^{-1} were caused by C=O deviational vibration and symmetrical stretching, and the stronger peak at 1038 cm^{-1} was assigned to the C–O stretching vibration (Keiluweit et al., 2010; Yuan et al., 2011) (Appendix A Fig. S5). Analysis of the mineralogical composition of the related solid samples using powder X-ray diffraction (XRD) (Yin and Zhu, 2016) indicated that the solid samples were dominated by calcite and quartz (Appendix A Fig. S7a).

1.3. Batch experiments to stabilize Cu and Pb with biochar

The biochar was mixed with approximately (200 ± 10) g of each of the contaminated sediment slurries, which corresponded to 95.6, 115.0, and 109.8 g of dry sediment from SR, CR, and AC, respectively, at ratios of 0%, 2.5%, 5%, and 10%. The mixtures were placed into PVC cylinders that were covered with caps that measured 8 × 10 cm, and homogenized using a glass stirring rod. The containers were then incubated in the dark at room temperature for 15, 30, or 60 days. The sediment-biochar microcosms for each incubation time were grouped together and each cluster was kept separate from the others. The water content of each microcosm was maintained at the same level (60%) by adding deionized water. Each treatment was performed in triplicate.

1.4. Metal stabilization evaluation

The remediation ability of the biochar was assessed by various methods, namely the DGT technique, the porewater concentration, the BCR 4-step sequential extraction procedure and the TCLP. Analytical grade reagents, including HNO_3, HF, $HClO_4$, CH_3COOH, H_2O_2, $NH_2OH{\bullet}HCl$, CH_3COONH_4, copper nitrate trihydrate, and lead nitrate, were used throughout.

1.4.1. DGT and porewater analysis

The DGT device used in this study was purchased directly from the manufacturer (Nanjing Weisheng Huangbao Keji Co. Ltd., China). The structure of this device is shown in Appendix A Fig. S3. After incubation, about one-third of the sediment slurry of each treatment was placed into a PVC box (Dimensions 2 × 3 cm) with a lid, and the DGT devices were carefully pressed onto the surface of the sediment slurry, and placed in an incubator at 25°C for 24 hr. The resin layer of DGT was then detached from the device and soaked in 1 mL of 1 mol/L HNO_3 to elute extracted metal by DGT for 10 hr in a shaker (160 r/min). The elution solution was diluted for a suitable time and stored at 4°C until analysis. The DGT extracted concentration (C_{DGT}) can be calculated from the analysis results, as in earlier study (Supplementary Data). Porewater samples were collected by centrifuging the sediment slurry at 5000 r/min for 20 min. The supernatant was filtered through a 0.45-μm membrane and stored at 4°C until analysis.

Table 2 – Extraction conditions used for the fractionation process of BCR.

Step	Fraction	Reagents/conditions*
1	F1, acid-soluble fractions	20 mL of 0.11 mol/L HAc, shaken for 16 hr
2	F2, reducible fractions	20 mL of 0.5 mol/L (pH 2) $NH_2OH•HCl$, shaken for 16 hr
3	F3, oxidizable fractions	5 mL of 8.8 mol/L H_2O_2, placed in a water bath at 85 °C for 1 hr; An additional 5 mL of 8.8 mol/L H_2O_2, placed in a water bath at 85 °C until the solution was evaporated to a few milliliters; 25 mL of 1 mol/L (pH 2) NH_4Ac, shaken for 16 h
4	F4, reducible fractions	the rest of residuals were digested as solid sample for metal content analysis

* All shaking was conducted at a temperature of 25 °C and centrifuged at 160 r/min.

1.4.2. Sequential extraction (BCR)

The BCR method (Yin and Zhu, 2016), which involves four steps and four fractions, was used to evaluate the distribution of the metal fractions in sediments with or without biochar (Table 2). The sediment slurries were air-dried in an airing chamber and ground to pass through a 100-mesh sieve. Then 0.50 g of the dry weight solid sample was sequentially extracted by four reagents in 50-mL polyethylene centrifuge tubes. After each step, the supernatants of all the solutions were filtered with a 0.45-μm polytetrafluoroethylene syringe filter, and the filtrates were stored at 4°C until analysis. The average recoveries of the fractions extracted (F1 + F2 + F3 + F4) ranged from 85% to 100% of the total concentrations.

1.4.3. TCLP test

The leachability of Cu and Pb was estimated by the TCLP (USEPA, 1984). The TCLP reagents were prepared by diluting acetic acid until a pH of 2.88 was achieved. Then, 1.00 g of sediment (dry weight) and 20 mL of reagents were added into 50-mL polyethylene centrifuge tubes and shaken at 160 r/min for 18 hr. Finally, the supernatant was filtered through a 0.45-μm polytetrafluoroethylene syringe filter, and the filtered extracts were stored at 4 °C until analysis.

2. Results

2.1. Bioavailability of Cu and Pb reduced by biochar

The results from the tests with different amounts of biochar and for different incubation times with the C_{DGT} and porewater concentration (C_p) tests are shown in Fig. 1. The bioavailabilities of Cu and Pb were much lower in AC than in the other sediments. For higher doses of SBIO, the C_{DGT} was considerably lower in the sediment microcosms than in the blank sample. The rates at which the bioavailabilities of Cu and Pb decreased were highest in CR with an amendment

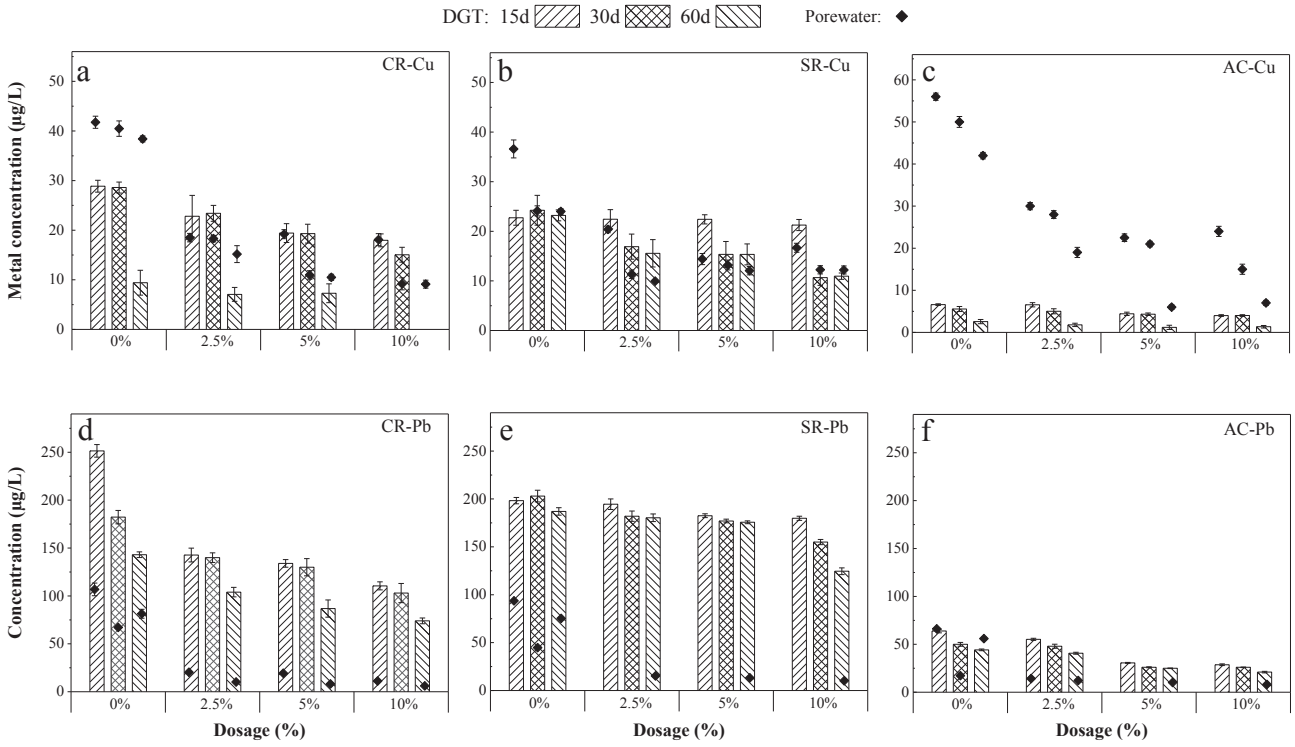

Fig. 1 – Diffusive gradients in thin films (DGT) and porewater concentration in different treatment sediments. The figure of a, b and c were inner-city river (CR), standby reservoir (SR) and artificial lake (AC) sediment contaminated by Cu, respectively; and d, e and f were inner-city river (CR), standby reservoir (SR) and artificial lake (AC) sediment contaminated by Pb, respectively. No marked porewater sign is indicated below the detection limit of ICP-MC.

ratio of 10%; at the end of the incubation, the C_{DGT} (Cu) was below the detection limit (1 μg/L) and C_{DGT} (Pb) was almost 40% lower than in the blank.

The biochar had positive effects on the porewater concentration (C_p), and reductions were more closely related to the incubation times than to the biochar doses. In the Cu stabilization test, the C_p always decreased as the stabilization time increased. However, in the Pb stabilization test, the C_p decreased when incubated for 30 days but increased when incubated for 60 days. This may reflect the high affinity of the biochar for Pb as almost all dissolved Pb was adsorbed by SBIO without enough sustainable resupply from the sediment phase, which cannot be detected by centrifugation (C_p) but DGT extraction due to labile metals measured by DGT not only existed as a dissolved fraction but also as a solid fraction (Yin et al., 2014). Also, the pH and ORP both decreased during the incubation period (Appendix A Fig. S4). Because the ability of the biochar to adsorb Pb was sensitive to changes in the pH (Appendix A Fig. S2), the dissolved Pb detected at 60 days may reflect the decreases in the pH, and this phenomenon can be alleviated largely by adding biochar.

2.2. Metal fractions in the treated and untreated sediments

The distribution of the Cu and Pb fractions in the treated and untreated sediments incubated for different periods are shown in Fig. 2. When treated with the biochar, the contaminated sediment was more stable than the blank treatment. The potentially available fractions of Cu (F1 + F2 + F3) gradually decreased as the biochar amount and incubation time increased, and the residual fraction (F4) was 61.4%, 54.7%, and 87.7% higher in the CR, SR, and AC contaminated sediments, respectively, than in the blank samples for a biochar dose of 10% and an incubation of 60 days. The acid-soluble fraction (F1) of Pb decreased, and the F1 fraction in the SR sediments treated with biochar were 64.4% lower than that in the blank at the end of the experiment for a 10% dose. As well as Cu, the residual fraction (F4) of Pb increased as the biochar dose and the length of the incubation period increased. In fact, the chemical reagents used in the sequential extraction to classify the metal fractions, especially the reagents for F3 (H_2O_2–NH_4Ac) and F4 (HNO_3–HF–$HClO_4$), were very harsh. In the real environment, such harsh conditions would not occur; both F3 and F4 would be stable in the environment and they were more sensitive to the biochar in this experiment.

2.3. Effect of SBIO on the leachability of Cu and Pb

As shown in Fig. 3, the results from the leachability tests were similar to those from the DGT and BCR tests. As the proportion of biochar in the sediment sludge increased, the stability of the metal pollutant also increased and the metal concentrations in the leachate decreased. Over a period of 60 days, the stabilization of both Cu (58.6% and 27.5%) and Pb (37.1% and 17.7%) were highest and lowest in CR and AC.

3. Discussion

3.1. Relationship between DGT and other extraction methods

The DGT method has been used for several years to predict the supply of heavy metals and the bioavailability of other pollutants in soil and sediment (Zhang et al., 2001). Various studies have shown that there is a good correlation between the amount of metal taken up by plants and the metal

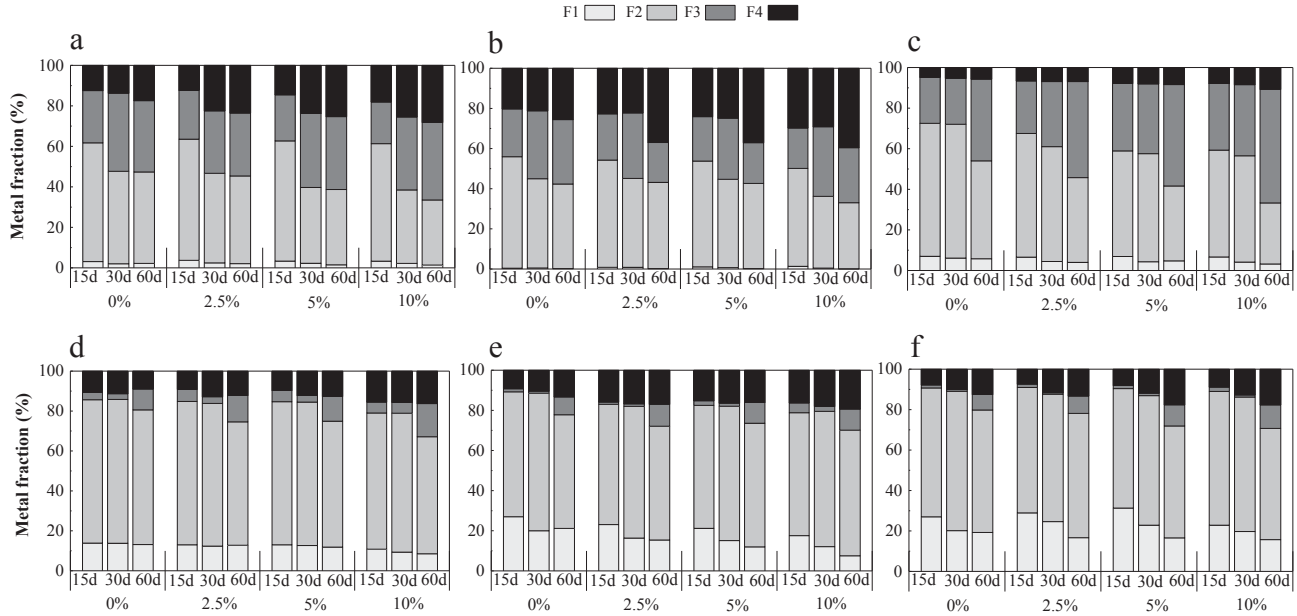

Fig. 2 – Metal fraction in treated sediment with the addition of 0%, 2.5%, 5%, 10% of sawdust-based gasification biochar (SBIO) and different incubation time (day). The figure of a, b and c were inner-city river (CR), standby reservoir (SR) and artificial lake (AC) sediment contaminated by Cu, respectively; and d, e and f were inner-city river (CR), standby reservoir (SR) and artificial lake (AC) sediment contaminated by Pb, respectively.

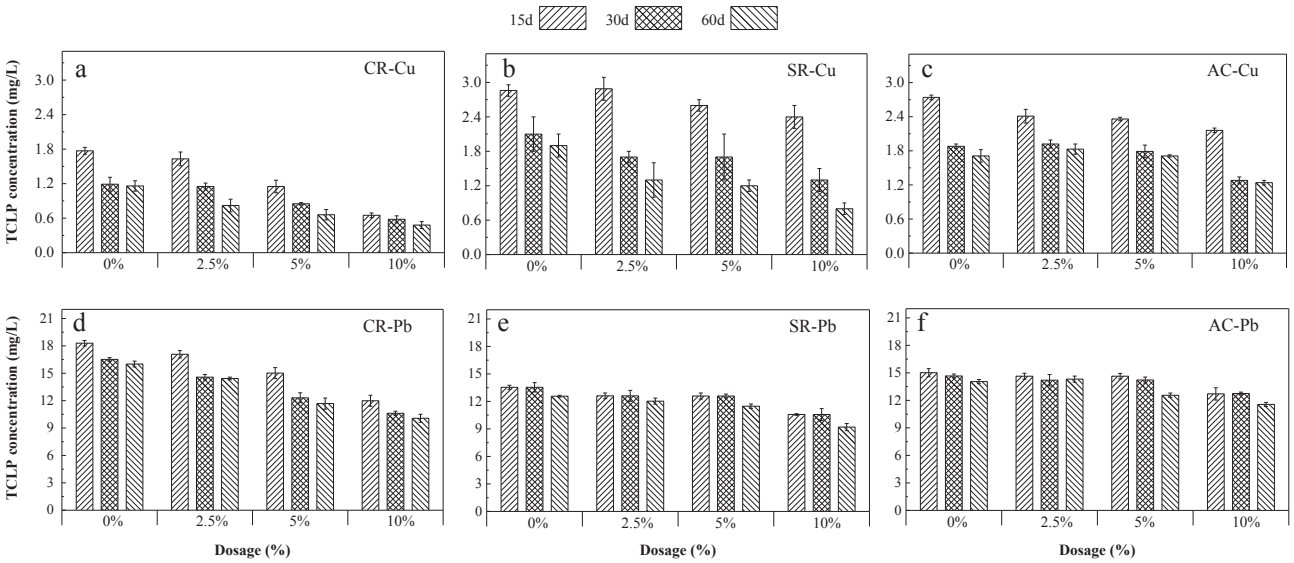

Fig. 3 – Leaching Cu and Pb from (un)treated sediment by toxicity characteristic leaching procedure (TCLP). The figure of a, b and c were inner-city river (CR), standby reservoir (SR) and artificial lake (AC) sediment contaminated by Cu, respectively; and d, e and f were inner-city river (CR), standby reservoir (SR) and artificial lake (AC) sediment contaminated by Pb, respectively.

concentration measured by DGT (Zhang et al., 2001, 2014). To obtain better insights into the relationships between the extraction assessment methods used in this study, the relationships between DGT,C_p, BCR, and TCLP (from Pearson correlation analysis) were compared (Appendix A Tables S3–S8). The DGT results were strongly correlated with those of BCR and TCLP, but weakly correlated with the C_p results. There were significant correlations between DGT and TCLP for all treatments and different sediments at least at the $p < 0.05$ level. The highest R^2 values for Cu and Pb were 0.71 ($p < 0.01$) and 0.79 ($p < 0.01$), respectively, in the SR sediments.

The Cu and Pb that are weakly bound with carbonates through specific adsorption and covalent forces, such as Fe/Mn oxides or hydroxides or weaker stable organic matter, are labile and can be captured by DGT (Roulier et al., 2010). In the sequential extraction, the F1 and F2 fractions that were classified as easily-exchangeable and weakly bound to organic or inorganic sites were well correlated with C_{DGT} as well as F1 + F2 + F3 (Fig. 4). This further indicates that the DGT measurement is not specifically confined to a single metal fraction (Ernstberger et al., 2002; Roulier et al., 2010). The results of metal isotope tracer experiments have also shown that labile Zn was strongly correlated with the extractable fractions (Roulier et al., 2010; Young et al., 2010), and that there was a good correlation between C_{DGT} and the labile isotopic exchange (Ernstberger et al., 2002). Therefore, a DGT device can be used to replace predictions of the bioavailability of metals from the BCR and TCLP methods.

3.2. Possible mechanisms of stabilization induced by biochar

Regardless of whether biochar, in this case SBIO, is added to sediments or not, the stability of the Cu and Pb fractions in sediments always increases. Nevertheless, when SBIO is added, the process of natural stabilization may be reinforced or the metal fractions may be redistributed, and metals may also be incorporated into the lattice of the treatment agent as the incubation time increases (Yin and Zhu, 2016). The mechanisms used by biochar to stabilize metals are complicated, and, to date, are not fully understood. In prior studies, metal adsorption by biochar has been regarded as the major driver for metal stabilization (Fang et al., 2016; Roulier et al., 2010; Zhu et al., 2017). The main mechanisms of metal adsorption by biochar include (1) electrostatic complexation resulting from ion exchange, (2) surface complexation with active functional groups on biochar surfaces (such as carboxyl and hydroxyl), (3) metal transport from the outer sphere to the inner sphere, and (4) the formation of inner-sphere complexes with metals (Fang et al., 2016; Yin and Zhu, 2016; Zhu et al., 2017).

The results from this study also support these mechanisms for metal adsorption by biochar. The results from the FT-IR and XPS analysis (Appendix A Figs. S5 and S6) show that the surface oxygen functional groups of SBIO changed after adsorption of Cu and Pb. Also, the SEM measurements (Appendix A Fig. S8) demonstrate that the surface morphology of SBIO changed considerably after reacting with heavy metals, which indicates that surface precipitation contributes to the adsorption process. Further, a recent study reported that the crystal morphology of biochar-Cu could be transformed as the contact time increased. The XRD analysis (Appendix A Fig. S7) showed that the crystal signal of Quartz and Malachite gradually weakened and *Gerhardtite* strengthened with time. Until the 30-day point, Gerhardtite, Malachite, Paramelaconite, and Posnjakite were detected, and were perhaps related to metal stabilization in sediment-metal-biochar systems. This phenomenon has not been observed in Pb adsorption tests in this study. However, in another study,

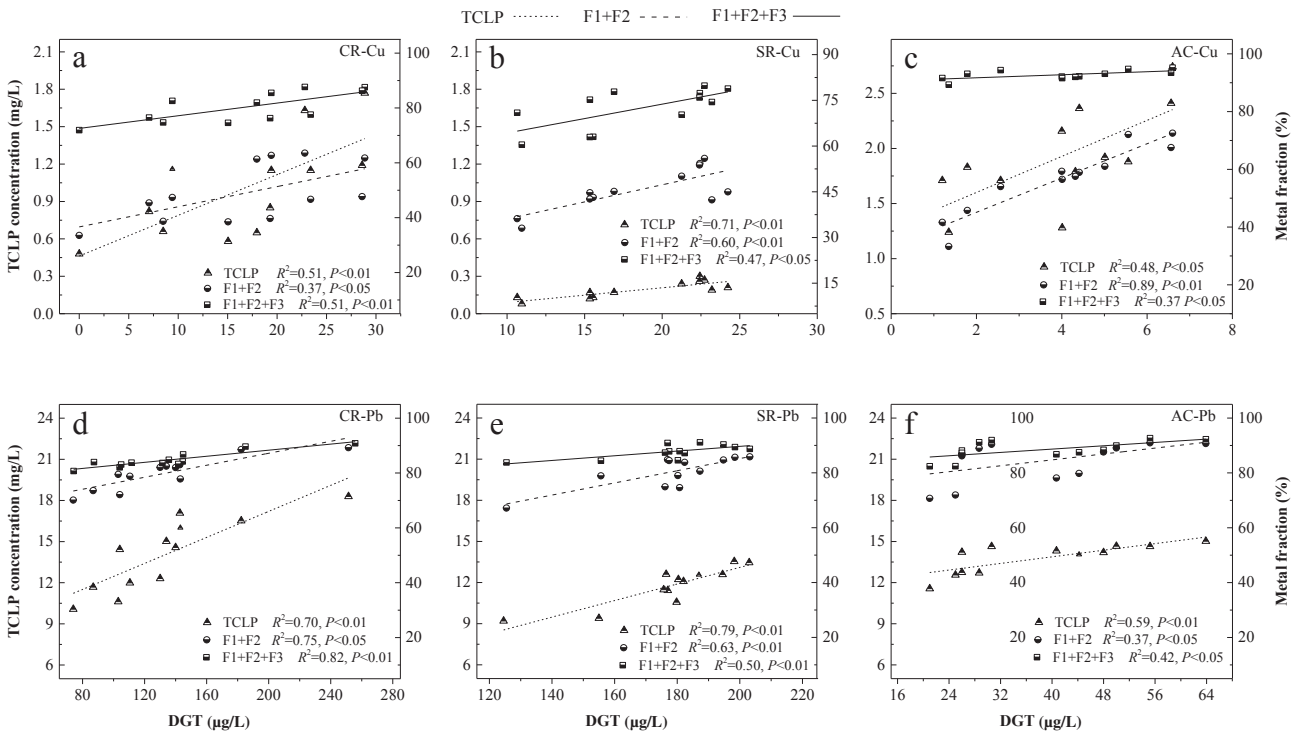

Fig. 4 – Correlation between diffusive gradients in thin films (DGT) and toxicity characteristic leaching procedure (TCLP)/ metal fraction distribution. The figure of a, b and c were inner-city river (CR), standby reservoir (SR) and artificial lake (AC) sediment contaminated by Cu, respectively; and d, e and f were inner-city river (CR), standby reservoir (SR) and artificial lake (AC) sediment contaminated by Pb, respectively.

over a period of 30 days, a new compound formed on the surface of Pb-loaded biochar, but was not observed in the early stages (Fang et al., 2016). This therefore shows that time has a positive influence on the metal stability.

Because of the biochar, the pH was higher in all the SBIO tests than in the blank systems, and the ORP was also lower. During incubation, all treatment systems became weakly alkaline and showed stronger reducibility (Appendix A Fig. S4). At the end of the incubation, the pH had increased by almost one unit and the ORP was between 150 and 200 mV lower in the tests with 10% biochar than in the blank. The carbonates and functional groups such as $–COO^-$ (–COOH) and $–O^-$ (–OH) contained in the biochar are mainly responsible for enhancing the pH value (Shen et al., 2016; Yuan et al., 2011). Under a higher pH, there is less competition between the H^+ and heavy metal ions for ligands (CO_3^{2-}, SO_4^{2-}, S^{2-}, Cl^-, OH^-, phosphate, *etc.*), the sorption and/or precipitation is enhanced, and metal ions combine more easily with ligands into a relatively more stable form (Peng et al., 2009; Shaheen et al., 2013).

In this current study, the F3 and F3 + F4 fractions were considerably higher in the control tests than in the blank, which shows that the biochar transformed metals into stable fractions. As a sorbent treatment, biochar has a high solid organic matter (SOM) content and so the content of SOM in sediment increases when mixed with biochar (Shaheen and Rinklebe, 2015). Metals, therefore, may bind to organic matter, like humic substances, and form metal–organic complexes, which can reduce the metals' mobility (Srivastava et al., 2008). Several related studies have also shown that, under enhanced organic matter, more stable metal fractions could form (Ahmad et al., 2014a; Bian et al., 2013; Ok et al., 2011).

However, while the results indicate that biochar may be able to stabilize metals in contaminated sediments under certain conditions, it is clear that biochar is not as effective as phosphate or iron-bearing materials. For example, when phosphate compounds were added to contaminated soils, the concentrations of extractable heavy metals decreased by more than 90% (Ahn et al., 2015; Sima et al., 2015), while the oxidizable and residual phases of Pb and Cu increased by between 70% and 90% when nano-zero-valent iron, an activated carbon composite, and ferrihydrite were added (Chen et al., 2016; Qian et al., 2009). While there were clear decreases in C_p and C_{DGT} and clear increases in F3 and F4 in this study, the removals and transformations reported in these other studies are much higher than those reported in this and other biochar-related studies (Zhang et al., 2017; Igalavithana et al., 2017; Lu et al., 2017). The lower efficiencies in this study may be related to the inherent physicochemical properties of both the sediments and the biochar. First, metals in sediments exist as different fractions bound to, or enveloped by, Fe or Mn oxides, hydroxides, or organic matter that account for a large amount of the total metal, and it is difficult for biochar to increase the stability of these fractions by directly participating in physicochemical reactions; on the other hand, soluble and carbonate metals only account for a

smaller fraction of sediment and can be easily captured and bound by biochar. So, while the C_p and C_{DGT} results showed that the stabilization was effective, these tests could not show obviously changes in the distributions of the metal fraction. Second, when biochar is mixed with sediment slurry, the SOM and finer particulates will either be adsorbed onto the surface of the biochar or may block the pore structure, which further reduces the possibility of contact between the metal and the treatment agent (Wang et al., 2017). Meanwhile, the outer surface of biochar may undergo oxidation or aging first, followed by the interior pores, which may cause the cation exchange capacity to shift and reduce element retention (Ahmad et al., 2014b). Finally, the stabilization period also has an important influence on the metals' stability. In fact, regardless of whether a treatment is applied or not, metals can gradually stabilize because of natural attenuation. This natural process may be accelerated by adding biochar, but short-term incubations do not support the formation of stable compounds (Fang et al., 2016; Rajapaksha et al., 2015).

4. Conclusions

The bioavailability and mobilization of metals, rather than the total metal content, were used to predict the risks of heavy metals to the environment. The degree to which biochar was able to stabilize metals in contaminated sediments in laboratory incubations was evaluated using DGT, the porewater concentration, the BCR sequential extraction, and the TCLP. The DGT and TCLP tests showed that the bioavailability and labile fractions of the metals decreased because of the biochar. The results of the C_p tests improved more when the incubation time increased than when the amount of biochar was increased. The stable F3 and F4 fractions also increased as the dose of biochar increased. Adsorption, transformations in the crystal morphology, and changes in the environmental conditions (*e.g.*, pH and SOM) induced by the biochar were the main mechanisms of metal stabilization. There were good correlations between the DGT, BCR, and TCLP, but these methods were more weakly correlated with the porewater concentrations. These methods are interchangeable in field applications, but the DGT method should be considered the main approach for assessing the bioavailability because of its convenience, analysis capacity, and speed. These results represent an initial application of biochar in sediment management. The approach needs to be refined and field studies should be carried out before any real-life practical applications are attempted. We would hope that this approach using biochar will be useful for curbing the release of metals during sediment dredging and re-suspension; alternatively, biochar-treated sediments could be used in land reclamation initiatives.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2018.11.007.

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