INTEGRATED REMEDIATION OF METAL-CONTAMINATED SOILS: BIODEGRADABLE CHELANT-ENHANCED EXTRACTION AND IN-SITU STABILIZATION

BEIYUAN JINGZI

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Department of Civil and Environmental Engineering

Integrated Remediation of Metal-contaminated Soils: Biodegradable Chelant-enhanced Extraction and In-situ Stabilization

BEIYUAN Jingzi

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ABSTRACT

Soil contamination by metal(loid)s has drawn increasing attention worldwide. A national soil contamination survey by the government of China in 2014 showed that around 1/5 of the surveyed lands were considered contaminated according to the national standards. As reported, 82.4% of the surveyed lands were contaminated by metal(loid)s (particularly by Cd, Ni, As, Hg, Cu, Pb, Cr, and Zn). Remediation techniques like soil washing by a readily biodegradable chelant, EDDS (*S,S*-ethylene-diaminedisuccinic acid), has a low extraction efficacy of Pb in comparison with EDTA (ethylenediamine tetraacetic acid) which is hard to biodegrade naturally. Besides, it is found that residual metals become more mobilized after chelant-assisted extraction. At the same time, the lability of metal(loid)s after soil stabilization under varying environmental conditions is still an uncertainty.

Individual studies were conducted using an e-waste contaminated soil to investigate the feasibility of EDDS washing using various washing schemes with mixed use of chelants and an integration with selective dissolution. Stabilization effects of As and Pb in a field soil sample was also studied. Low-cost amendments were used in the stabilization under dynamic redox potential (E_H) conditions which is one of the most crucial environmental factors. Based on the above results, an integrated study of EDDS extraction and stabilization was proposed and conducted to evaluate the mobility, leachability, bioaccessibility, and phytoavailaiblity of residual metals in the soil.

In this research work, the combined use of chelants successfully reduced the use of EDTA by half while keeping high extraction efficiency of all target metals (Cu, Zn, and Pb), which further studied by the modeling results of Visual MINTEQ. Besides, the multi-step washing demonstrated the high extraction efficacy, reduced the undesired mineral washing and readsorbed metal-chelant complexes which might increase metal leachability, in comparison with the 24-h continuous washing. The pretreatment using reductants and organic acids to remove the metals strongly bound on Fe/Mn oxides and organic matter facilitated the subsequent EDDS extraction. Higher metal extraction efficiencies and low leachability and bioaccessibility of the residual metals were observed, yet the reductants and organic acids increased the cytotoxicity and decreased the microbial activities and the amount of available nutrients in the soil.

Frequently changing environmental conditions like E_H altered the stabilization effects of As and Pb by pine sawdust biomass and pine sawdust-induced biochar. An increasing mobility of As was observed with the decrease of E_H, which is associated with the increased mobility of arsenite and dissolved Fe oxides. The increment of pH related to the alkalinity of biochar also contributed to the enhanced mobility of As, especially for the biochar produced at a higher temperature. Meanwhile, the increasing pH suppresses the mobility of Pb through forming Pb-containing precipitations.

An integration of 2-h EDDS extraction and 2-month stabilization by low-cost amendments actually removed the labile metals, which in turn reduced the metal bioaccessibility and phytoavailability. Meanwhile, the immobilization by biochar and coal fly ash facilitated alleviation the potentially mobilized metals by EDDS extraction.

PUBLICATIONS ARISING FROM THE THESIS

<u>Journal Papers:</u>

1. **Beiyuan, J.**, Tsang, D. C. W., Ok, Y. S., Zhang, W., Yang, X., Baek, K., & Li, X. D. (2016). Integrating EDDS-enhanced washing with low-cost stabilization of metal-contaminated soil from an e-waste recycling site. Chemosphere, 159, 426-432. doi:10.1016/j.chemosphere.2016.06.030
2. **Beiyuan, J.**, Tsang, D. C. W., Yip, A. C. K., Zhang, W., Ok, Y. S., & Li, X. D. (2016). Risk mitigation by waste-based permeable reactive barriers for groundwater pollution control at e-waste recycling sites. *Environ. Geochem. Health*, 1-14. doi:10.1007/s10653-016-9808-2
3. **Beiyuan, J.**, Tsang, D. C. W., Valix, M., Zhang, W., Yang, X., Ok, Y. S., & Li, X. D. (2017). Selective Dissolution Followed by EDDS Washing of an E-waste Contaminated Soil: Extraction Efficiency, Fate of Residual Metals, and Impact on Soil Environment. Chemosphere, 166, 489-496. doi:10.1016/j.chemosphere.2016.09.110
4. **Beiyuan, J.**, Awad, Y. M., Beckers, F., Tsang, D. C. W., Ok, Y. S., & Rinklebe, J., (2017). Phytoavailability and Mobility of Lead and Arsenic in a Contaminated Soil after Stabilization by Pine Sawdust Biochar under Dynamic Redox Conditions. (In Preparation)
5. **Beiyuan, J.**, Tsang, D. C. W., Valix, M., Zhang, W., Yang, X., & Li, X. D. (2017). Multiple Washing Schemes and Combined Application of EDDS and EDTA for Soil Washing of an E-Waste Contaminated Soil. (In Preparation)

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ABBREVIATIONS

AMDS	Acid Mine Drainage Sludge
BAF %	Orally Ingested Bioaccessible Fraction
BC300	Pine Sawdust Biochar Produced at 300 °C
BC550	Pine Sawdust Biochar Produced at 550 °C
BET	Brunauer-Emmett-Teller
BM	Pine Sawdust Biomass
CEC	Cation Exchangeable Capacity
CFA	Coal Fly Ash
CS	Control Soil
DCB	Dithionite-Citrate-Bicarbonate
DI Water	Deionized Water
DIC	Dissolved Inorganic Carbon
DTPA	Diethylenetriamine Pentaacetic Acid
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
EDDS	S,S-Ethylene-Diaminedisuccinic Acid
EDTA	Ethylenediamine Tetraacetic Acid
E_H	Redox Potential
E-waste	Electronic Waste
FWC	Food Waste Compost
HI	Hazard Indices
HQ	Hazard Quotients
IDSA	Iminodisuccinic Acid
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
IRIS	Integrated Risk Information System
LMWOAs	Low-molecular-weight organic acids
MC	Microcosm System
MCL	Maximum Contaminant Levels
MGDA	Methylglycinediacetic Acid
MR	Chelant-To-Metal Molar Ratios

NTA	Nitrilotriacetic Acid
OC	Organic Carbon
OM	Organic Matter
OXONE	Potassium Peroxymonosulphate
PAHs	Polycyclic Aromatic Hydrocarbons
PRBs	Permeable Reactive Barriers
PV	Pore Volume
SBC300	Soybean Biochar Produced at 300 ^{o}C
SBC700	Soybean Biochar Produced at 700 ^{o}C
SBET	In Vitro Simplified Bioaccessibility Extraction Test
SOM	Soil Organic Matter
SPLP	Synthetic Precipitation Leaching Procedure
TCLP	Toxicity Characteristic Leaching Procedure
TPF	2,3,5-Triphenyl Formazan
TTC	2,3,5-Triphenoltetrazolium
USEPA	United States Environmental Protection Agency

CHAPTER 1. Introduction

1.1 Background

With an increasing need of land use, the recovery and reuse of metal(loid)-contaminated lands has become a serious problem worldwide, especially in developing countries. For instance, according to a report on land contamination by Environmental Protection Ministry of China in 2014, 16.1% of soil and 19.4% of its arable lands fell short of safety standards (CMEP and CMLR, 2014; Zhao et al., 2015). Moreover, 82.4% of the contamination resulted from inorganic pollutants, such as Cd, Ni, As, Hg, Cu, Pb, Cr, and Zn. Unlike organic contaminants, metal(loid)s do not undergo degradation chemically or biologically on natural environment. They tend to stay in soil persistently and can even be leached to the groundwater. The contaminations lead to adverse effects on the health of human, microorganisms, plants, and animals. Thus, it is necessary to remediate and reuse the metal(loid)-contaminated land.

Remediation technologies can be divided into two groups based on their mechanisms: to mobilize and remove the toxic trace elements from soils and to immobilize them in soils. Chelating agents have been vastly applied in the soil remediation to remove the metal(loid)s from soil (Lestan et al., 2008; Tsang et al., 2013a; Bolan et al., 2014; Tsang and Yip, 2014). In particular, EDDS (*S,S*-ethylene-diaminedisuccinic acid), as a biodegradable chelant, has been extensively studied because of its comparable capacity of removing metals, biodegradability (also for most of its metal-EDDS complexes), low toxicity to the microorganisms and plants (Nowack, 2002; Tandy et al., 2006; Arwidsson et al., 2010). However, the EDDS extraction of metalloids and

Pb in soils was found ineffective; the potential residue of metal-EDDS complexes in the soil are dangerous for human health before their degradation.

Currently, low-cost amendments such as agricultural and industrial waste/by-products for metal(loid)s stabilization have also captured pervasive research interests, due to their remarkable capacity of reducing the mobility and availability of toxic metal(loid)s (Kumpiene et al., 2008; Komárek et al., 2013; Ahmad et al., 2014b; Mohan et al., 2014; Rajapaksha et al., 2016). As one of the amendments, biochar can enhance physiochemical and biological properties of soils and serve as stable carbon sinks (Glaser et al., 2002; Lehmann et al., 2011). However, the long-term lability of stabilization is still not certain, especially under various environmental conditions (Shaheen and Rinklebe, 2015; Rinklebe et al., 2016). Also, one stabilizer might not be able to immobilize all the toxic metal(loid)s due to their different characteristics (Beesley et al., 2010).

In view of the above, there is a need to study the possibility of combining EDDS-extraction with subsequent stabilization. Individual studies on enhanced EDDS extraction using multi-step extraction, mixed chelants, and selective dissolution as pretreatments were evaluated. Immobilization using low-cost amendments under dynamic E_H conditions was also studied. In addition, low-cost adsorbents were evaluated as the media of permeable reactive barriers (PRBs) to remediate potentially contaminated groundwater. The simple inter-relationship within this thesis can be illustrated by Fig. 1-1.

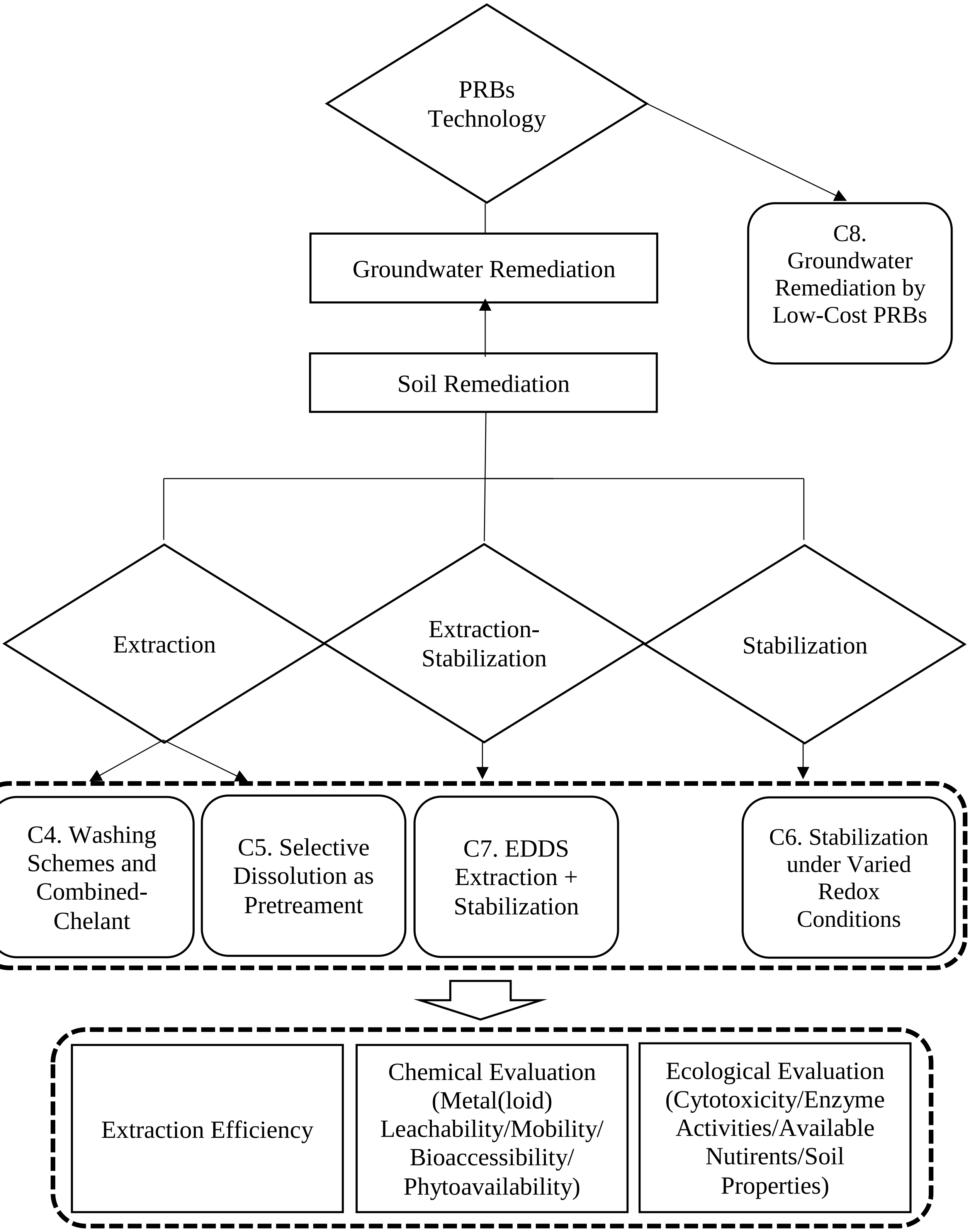


FIGURE 1-1 Flowchart of this study (the capital “C” represents the word “Chapter”).

1.2 Objectives of This Study

The chief objectives are to investigate the effectiveness and mechanisms of the integrated EDDS extraction and low-cost amendment stabilization to remove the metal(loid)s. The EDDS extraction was studied using multi-step washing, a mixture of EDDS and EDTA, and a pretreatment by selective dissolution to extract strongly bound metals. Besides, metal(loid) immobilization by pine sawdust biomass and biochar was evaluated under varied redox potential (E_H) conditions which is considered as one of the significant factors affecting metal(loid) immobilization. The specific objectives of this study are listed as follows:

- To investigate the feasibility of various multi-step washing schemes and the mixture of EDDS and EDTA to remove metal from a field-contaminated soil.
- To study the speciation of metal-chelant complexes and chelant when the mixture of EDDS and EDTA was used as the extractant.
- To determine the practicability and mechanisms of using organic acids/reductants/oxidants/alkaline solvents as a pretreatment for EDDS extraction.
- To investigate the pine sawdust biomass/biochar immobilization of As and Pb under varied E_H conditions.
- To evaluate the feasibility of a single EDDS extraction combined with stabilization by coal fly ash and two types of soybean biochar which produced at different temperatures.
- To provide various chemical (leachability, mobility, bioaccessibility, and phytoavailability of residual metal(loid)s in the treated soil) and ecological evaluation points (cytotoxicity, microbial activities, and available nutrients) to

assess the remediation rather than simply using the total extraction efficiency of metal(loid)s.

- To evaluate the mitigation of human risk of after various remediation.

1.3 Thesis Organization

This thesis contains nine chapters. Chapter 1 introduces the background and the structure of this thesis. Chapter 2 provides a comprehensive literature review of metal(loid) contamination (mainly Cu, Zn, Pb, and As) in soils. In addition, the basic information and recent findings on chemically-enhanced soil washing (especially for a readily biodegradable chelant – EDDS) and stabilization by biochar and coal fly ash were also presented.

Detailed experimental designs of each chapter, as well as materials and methods used in the following chapters was described in Chapter 3. It includes characteristics of soil and amendments used in this study, comprehensive methodologies of various chemical and ecological evaluations, metal and chelant speciation modeling, and human risk assessment.

Chapter 4 studied the various washing schemes (multi-pulse, step-gradient, and continuous washing) and the combination of EDDS and EDTA. The metal extraction efficiency and difference on metal leachability and bioaccessibility and the mitigation of human health risk assessment before and after the treatments were reported here.

In Chapter 5, selective dissolution as a pretreatment was used to dissolve the mineral fractions (Fe/Mn oxide and/or organic matter) in the soil, to enhance the subsequent metal extraction efficacy by EDDS washing. Additionally, metal leachability, bioaccessibility, and human risk assessment were evaluated to study the potential impact generated from residual metal in soil. Meanwhile, the ecological impacts on soil were assessed through studying enzyme activities and available nutrients.

Chapter 6 investigated the As and Pb immobilizations of pine sawdust biomass/biochar-incubated soil samples (105 days) under dynamic E_H conditions (-300 to +250 mV). The varied of mobility and phytoavailability As and Pb were studied to evaluate the stabilization.

Chapter 7 presented an integrated application of EDDS extraction and 2-month stabilization by coal fly ash and soybean-derived biochar produced at 300 and 700 ^{o}C. The leachability, mobility, bioaccessibility, and phytoavailability of metals were investigated before and after the treatments.

In Chapter 8, a potential groundwater contamination by e-waste was simulated and using low-cost adsorbents (compost, biochar, acid mine drainage sludge, coal fly ash, apatite, and limestone) as the reactive media of the permeable reaction barrier to remove the potential leaching metals by acid rain water.

Chapter 9 summarized and concluded all the chief findings and drawbacks in this work. Besides, recommendations were proposed accordingly for future works.

CHAPTER 2. Literature Review

2.1 Metal(loid)s in Soils

2.1.1 Overview

Metal(loid)s like Cu and Zn are required as cofactors and activators of enzyme activities or catalysts by the human, microorganisms, and plants to maintain their functions (Nagajyoti et al., 2010). However, the elements can cause serious problems to organisms when their concentrations are too high. In particular, elements like Ag, Hg, and As were found poisonous for the living organisms even at a low concentration. Nowadays, metal(loid)s can reach the soil via pedogenic and anthropogenic processes including industrial activities (mining, smelting, and manufacturing), agricultural activities (application of fertilizers and pesticides), and improper disposal of domestic or industrial waste (Peters, 1999; Ok et al., 2011c; Wuana and Okieimen, 2011). Those metal(loid)s introduced by anthropogenic methods are found more bioaccessible/ bioavailable, in comparison with the pedogenic input (Lamb et al., 2009; Bolan et al., 2014). Constantly pursuing of industrial development in developing countries leads to a large amount of discharge of waste to the environment, which deteriorate the situation of metal(loid)s contamination. For instance, in China, it was reported that 72 billion tons and 3.3 billion tons of wastewater and industrial solid waste, respectively, were discharged to the environment in 2015 (China Environment Yearbook Editorial Committee, 2015).

Unlike organic contaminants, trace metal(loid)s cannot be degraded naturally by photo-degradation or bio-degradation but exist in the environment persistently after pollution. Moreover, metal(loid)s in soil can be transported to a deeper soil level or even reach groundwater. It is easy to threaten human health by entering their food chain or bodies via direct inhalation and ingestion. Thus, inorganic pollutants lead to serious environmental concerns as some of them are potential or known carcinogens.

2.1.2 Pb, As, Cu and Zn in Soil Contaminations

Cu

Copper is the third most commonly used metals worldwide. The main source of Cu includes agriculture, horticulture (application of fungicides and growth promoter), and mining. It is an essential micronutrient which is required for both plants and animals, though suffering a high concentration of Cu can lead to anemia, damage to liver and kidney, and irritation of human stomach. It is considered as class D (no enough evidence from human and animal to prove its carcinogenicity so far) according to Integrated Risk Information System (IRIS). In soils, Cu forms stable complexes with organic matter (OM) mainly, while few Cu were existed as inorganic Cu. For example, Cu^{II} are mostly found in the solution due to the redox chemistry in the aerated water. The available Cu is associated with the pH, OM, and clay content in soils. Reducing soil pH leads to increasing Cu mobility, thus materials which increase the soil pH can be applied in Cu stabilization (Kumpiene et al., 2008). Organic matter like humic substances can enhance the Cu extraction by forming Cu-humate complexes with oxygen-containing functional groups (Hartley et al., 2014).

Zn

Zinc exists in the soil abundantly with an average concentration of around 70 mg kg^{-1}. The burning of coal and fuel, mining, and smelting activities are the primary source of Zn in soils. Besides, the application of sludge and compost in agriculture can also lead to Zn contaminations. Zinc mobility is considered influenced by factors like phosphorous, Ca, Al, Fe/Mn oxides, and OM in soil. It can form precipitations with hydroxides, carbonates, phosphates, and sulfides, as well as complexes with OM (Kabata-Pendias, 2010). Phosphorus amendments can reduce the mobility of Zn by forming precipitates and be resistant to the soil acidification (Kumpiene et al., 2008). It is considered as class D according to the IRIS, which is the same as Cu. However, adverse effects by Zn on human bodies like nausea, vomiting, diarrhea, and damage to the stomach damage are found.

Pb

As one of the most concerned metals in the world, the average concentration of Pb in uncontaminated soils is between 10 and 200 mg kg^{-1}, while a high concentration of Pb of 30,000 mg kg^{-1} was reported by Austin et al. (1993) in a contaminated soil near a smelter site. Its primary sources contain mining activities, disposal of electronic waste, military activities, and use of Pb-containing gasoline (Kim et al., 2003). General forms of Pb in the environment (soil, groundwater, and surface water) contain lead (hydr)oxides and lead metal oxyanion complexes. Also, lead-containing minerals were found combined with sulfur or oxygen naturally in the soil. Chemical speciation of Pb influences significantly its solubility, mobility, and phytoavailability in soil. Previous research found that the concentration of Pb cation has strong correlations with toxicity and plant uptake than the total concentration of Pb in soils (Shahid et al., 2012). Lead can cause many adverse human health effects, such as injuries to the brain, kidney, and nervous system (Moon et al., 2013a). Additionally, it is considered as class B2 according to the IRIS of USEPA, a probable human carcinogen subject to animal cases.

Inhalation and ingestion are the major pathways for Pb to humans. Lead can be accumulated in organs of human body, which might lead to toxic effects or death chronically.

As

Arsenic exists abundantly in the environment as ranking the 20th high content in the earth (Gorny et al., 2015). It is mainly from geogenic reasons. In most of the rock, the average concentration of As is 2-3 mg kg^{-1}, though a high concentration of arsenic reached 15,000 mg kg^{-1} was found in some manganese minerals (Mandal and Suzuki, 2002; Mohan and Pittman, 2007). Arsenic can be mobilized by many natural activities, such as weathering and biological and geochemical reactions. In the past centuries, human activities, such as mining, combustion of coal and fuels, and consumption of pesticides, release additional As into the environment (Mandal and Suzuki, 2002; Mohan and Pittman, 2007; Wuana and Okieimen, 2011; Gorny et al., 2015). Arsenic is a multi-valence element, including -3, 0, +3, and +5, and it mainly exists in nature as As_2O_3.

Due to its strong toxicity, the World Health Organization recommends a 10 μg L^{-1} limit for As in the groundwater, as well as most of the national guidelines (US EPA and China) worldwide. The toxicity order of the arsenicals is inorganic As^{III} > monomethylarsine oxide ($MMAO^{III}$) > dimethylarsinous acid ($DMA^{III}GS$) > DMA^{V} > monomethylarsonous acid (MMA^{V}) > inorganic As^{V} (Vega et al., 2001; Mandal and Suzuki, 2002). The DMA and MMA are the common products of methylation. The toxicity of arsenic is associated with its ability to react with proteins and enzymes contained sulfhydryl groups and to replace phosphorous in the biochemical reactions

(Manahan, 2002; Tchounwou et al., 2003). These behaviors inactivate the enzymes and/or hinder the biochemical reactions directly. Besides the toxicity, arsenic is also a carcinogen which is dangerous for human beings.

Arsenic behaviors oppositely in comparison with metals, which includes its mobility increases with the rising soil pH and its strong capacity of adsorption on the surface of Fe/Mn (oxyhydr)oxides. Therefore, it can be affected strongly by varying E_H conditions (Smith et al., 1998; Gorny et al., 2015). Major involved redox couples affecting the As behaviors under changing E_H conditions include oxygen (O_2/H_2O), manganese (Mn^{IV}/Mn^{II}), nitrogen containing pairs (NO_3^-/N_2 andNO_3^-/NO_2^-), iron (Fe^{III}/Fe^{II}), sulfur (SO_4^{2-}/HS^-), and carbon (CO_2/CH_4) , which are shown in Fig. 2-1. Both arsenate and arsenite can be undergone chemical and microbial oxidation-reduction and methylation in soils (Smith et al., 1998). Besides, arsenic has strong affinity with amorphous Fe/Al oxides. Under acidic conditions, negatively charged arsenate ($H_2AO_4^-$) can be adsorbed by oxides than arsenite (H_3AO_3), due to the positively charged surface of oxides.

An XANES spectroscopy and sequential extraction were used to study the phytoavailability of As in *Brassica juncea* in a field soil contaminated by pesticide. The results indicated that As in both exchangeable and amorphous Fe oxides fractions are phytoavailable (Niazi et al., 2011). Thus, to reduce the amount of phytoavailable As in soil, dissolving the Fe iron part is one of the potential methods.

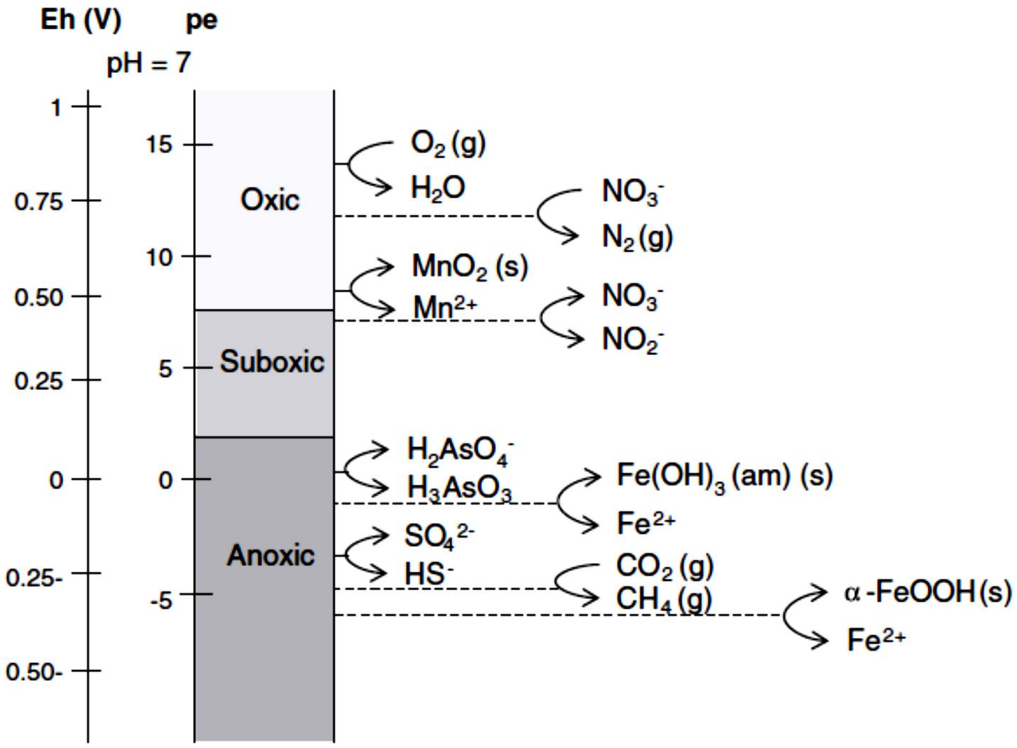


FIGURE 2-1 Examples of relevant redox couples in the flooding environment. The E_H and pe values were calculated at pH 7, while all the concentrations of dissolved components equal to 1 M, excepting Fe^{2+} (10^{-5} M) and CO_3^{2-}(3×10^{-3} M) (Borch et al., 2010; Gorny et al., 2015).

2.1.3 Factors Affect Behaviors of Metal(loid)s in Soils

Metal(loid)s retention in soils significantly depends on their chemical speciation which involves cation exchange, nonspecific or specific adsorption, complexation, and surface precipitation (McBride, 1994; Bolan et al., 2014). These trace elements can be removed from soils via plant uptake, leaching to the deeper layer or groundwater, and volatilization to the atmosphere, while the latter one is only for those elements which can form gaseous compounds (such as As, Hg, and Se) (Fig. 2-2). Factors affect the above mechanisms including pH, type and horizon of soil, cation exchange capacity, natural organic matter, the age of contamination, and the co-presence of other inorganic contaminants. The relationships between the metal(loid) mobility and some common ions as influenced by soil pH at a low redox potential are shown in Fig. 2-3. In general, the mobility of metals decreases when pH over 6, which is mainly due to the increasing surface charge on oxides of Fe, Mn and Al (especially for the cations), complexation with natural ligands, and precipitation of metal(loid) hydroxides. The organic matter in the soil also plays a important role in the retention of metal(loid)s in soil because of the chelation with the presence of ligands (containing functional groups of carboxyl, phenolic, alcoholic, and carbonyl) in soil. The ability of those functional groups to form complexes with metal(loid)s increases with an increasing pH (Harter and Naidu, 1995).

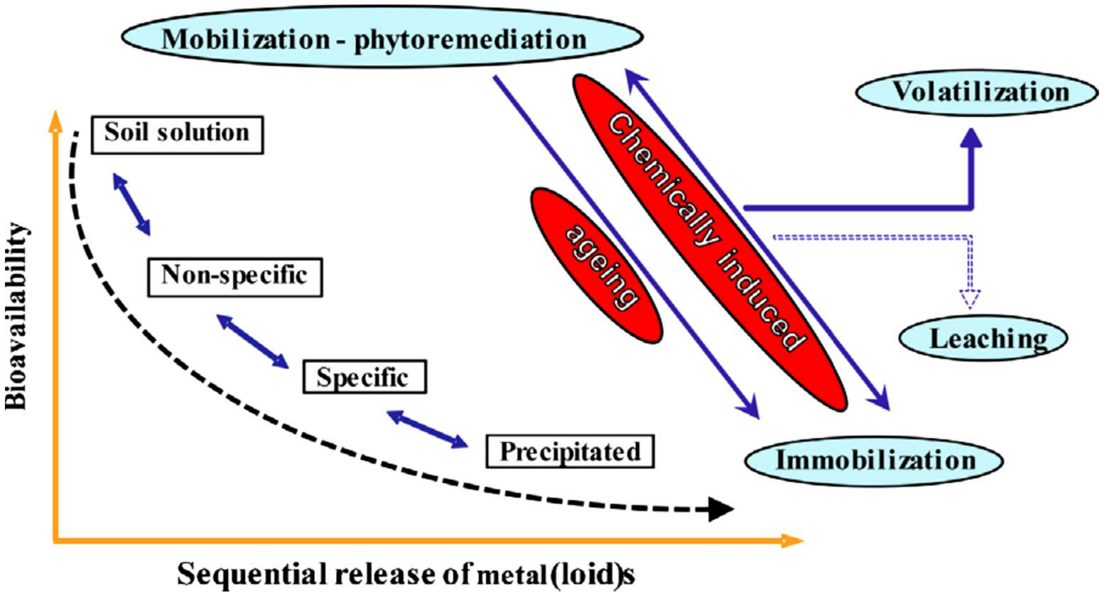


FIGURE 2-2 The interaction between adsorption reactions of metal(loid)s in soil and their bioavailability (Bolan et al., 2014).

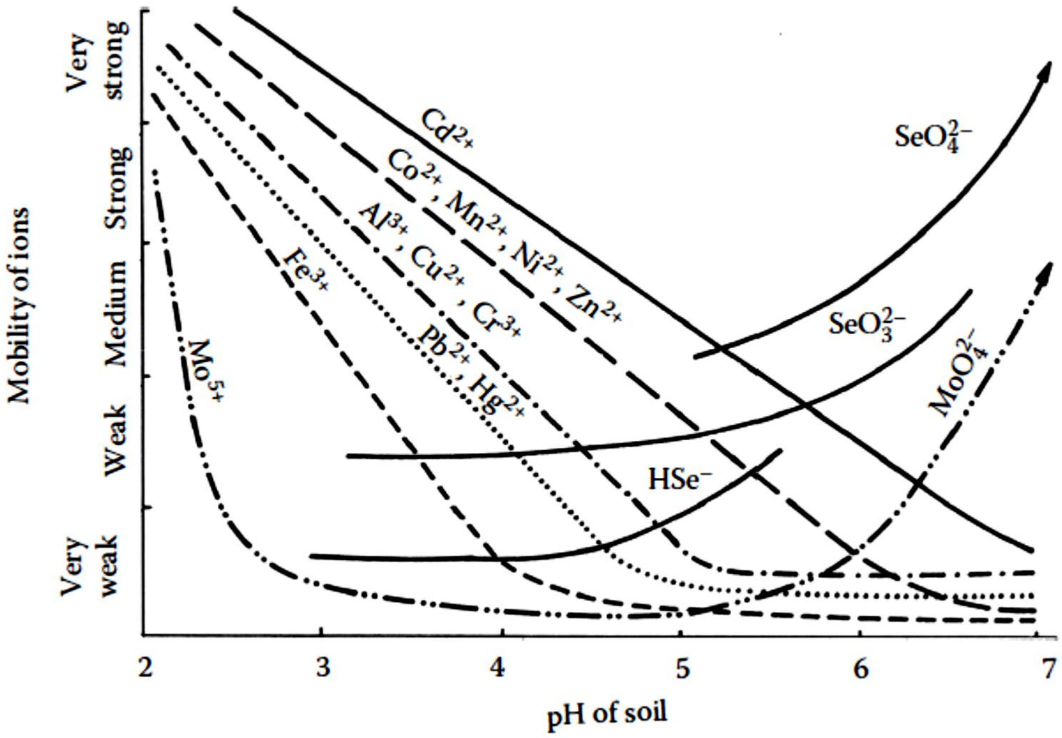


FIGURE 2-3 Schematic trends of the mobility of some metals as influenced by soil pH. Adopted from (Kabata-Pendias, 2010).

Sorption and desorption

Adsorption/desorption is an important process which affects metal(loid) behaviors in soils, as it happens all the time and controls soil properties. Adsorption can be divided into specific (chemical) adsorption and non-specific (physical) adsorption as shown in Fig. 2-4. The specific adsorption forms stable inner-sphere complexes which is more steady and selective than the outer-sphere complexes which are formed by the non-specific adsorption (McBride, 1994; Bradl, 2004). The stability of the complexes is because the coordinate-covalent bonding generated by inner-sphere complexation is more reliable than the electrostatic bonding or hydrogen bonding formed by outer-sphere complexation. However, it was found that the outer-sphere complexation is formed before the formation of inner-sphere complexation. Clay minerals, Fe/Mn (hydr)oxides, and OM are believed as the most important soil components for adsorption/desorption.

Trace elements can be electronically attached to negatively charged surfaces (organic matter, clay, and Fe/Al oxides), which can be illustrated by the cation exchange capacity (CEC).

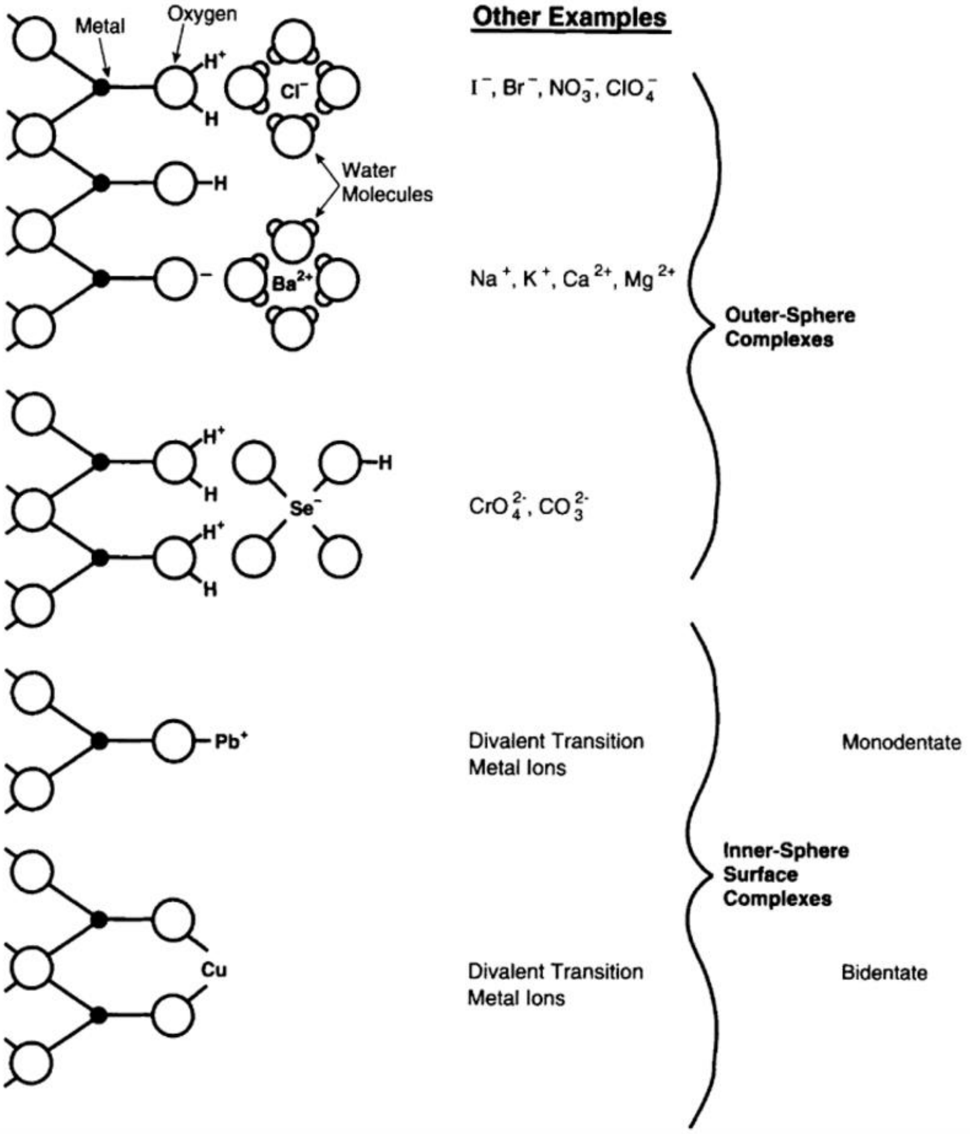


FIGURE 2-4 Schematic diagram showing the difference between inner-sphere and outer-sphere difference (Sparks, 2003).

Precipitation and dissolution

Forming precipitates with anions such as phosphates/carbonates/hydroxides is one of the significant mechanisms for the immobilization of metal(loid)s, especially under alkaline conditions and with large amount of metal(loid)s. For instance, forming phosphate-containing precipitates is the major mechanism for stabilizing Pb, Cd, and Zn (McGowen et al., 2001). Besides, co-precipitation of metal and metalloids has also been reported.

Oxidation and reduction

The speciation and mobility of metal(loid)s are greatly influenced by the oxidation/reduction processing, especially for As, Cr, Hg, and Se. It is mainly because the mobility and solubility of those elements are affected strongly by their oxidation state and ionic form. For example, arsenite has higher mobility and toxicity than arsenate. The oxidation-reduction reactions in soils are believed chiefly controlled by soil pH, redox conditions, and microbial activities.

Methylation and demethylation

Methylation is considered as a mechanism to alleviate the toxicity of metal(loid)s by transforming them to methyl derivatives which can be volatilized and released from the contaminated lands. The methylation of As undergoes chemical and biological reactions and frequently changes its mobility, solubility, toxicity, and volatility.

2.1.4 Effect of Redox Condition on Metal(loid) Retention in Soils

Various redox conditions affect the retention of metal(loid)s in soils. Because of the frequent change of water level, flood plains and paddy soils undergo varied aerobic and anaerobic conditions (Yu et al., 2007). The change of redox condition influences the dynamics of metal(loid)s indirectly via impact on pH, dissolved organic carbon (DOC), and the redox chemistry of iron, manganese, and sulfur, to which trace metal(loid)s might be fixed (Du Laing et al., 2009b; Rinklebe and Du Laing, 2011; Schulz-Zunkel et al., 2015). For instance, Fe/Mn (hydro)oxides were reduced to Fe^{2+} and Mn^{2+} as redox potential decreased, so the metal(loid)s bound with these parts become more mobile in soils (Reddy and DeLaune, 2008). In addition, previous studies have shown that metal(loid)s those have multiple valences are affected directly by the variation in redox condition, such as arsenic and chromium. Under reduction condition, an increment of arsenic mobility can be observed as the arsenate is reduced to arsenite which is more mobile and toxic, while Cr(VI) changes into the less mobile and toxic Cr(III) (Frohne et al., 2011; Frohne et al., 2015)

2.1.5 Trace Element Removal Technologies

According to the mechanism, soil remediation techniques to remove inorganic contaminants can be divided into two groups: *in situ* or *ex situ* technologies that remove the metal(loid)s to the other phase (soil washing, soil flushing, heap leaching, phytoextraction, electrokinetic remediation, and vitrification) and technologies that leave the comtaminants in soils (solidification/stabilization and phyto-stabilization) (Peters, 1999; Kumpiene et al., 2008; Lestan et al., 2008; Komárek et al., 2013; Bolan et al., 2014). The first type removes the toxic/hazardous content from the soils, which means it directly reduces the total amount. The latter type reduces the mobility, leachability, and bioavailability/bioaccessibility of the contaminants with cost-effective outcomes without excavation and further treatments of the wastewater. Currently, having a cost-effective and environmental-friendly remediation technique has become one of the utmost goals in the environmental research area.

Mobilization of metal(loid)s in soils contains solubilization, desorption, chelation, and complexations. Remarkably, mobilization increases the metal(loid) solubility as well as their bioavailability/mobility. On the other hand, immobilization decreases the bioavailability/mobility of metal(loid)s in soils by adsorption, precipitation, and complexation, without removing them.

2.2 Soil Washing

2.2.1 Principles of Soil Washing

As one of the important methods to mobilize the metal(loid)s, soil washing is a technique to wash the fine part of soils (clay and silt) mainly by chemical reagents. This is because that the contaminants (both organic and inorganic) in soil tend to bind to fine soil particles (Peters, 1999). Thus, a physical separation is needed to remove the coarse part from the fine component of soils before the chemical washing, which also minimize the volume of contaminated soils and the cost of remediation. Water-based washing only is able to remove limited contaminants because of the poor dissolution and mobilization. Many chemical solvents can be applied in soil washing, such as chelants, acids, alkaline solvents, electrolytes, oxidizing agents, and surfactants (Polettini et al., 2009; Zou et al., 2009; Tsang et al., 2012; Hartley et al., 2014).

The chemical-enhanced soil washing process includes four steps: (i) excavation, (ii) removing the coarse part of soil, (iii) washing with chemicals, and (iv) recovering the clean part back to the field. Figure 2-5 demonstrates the flow chart of soil washing.

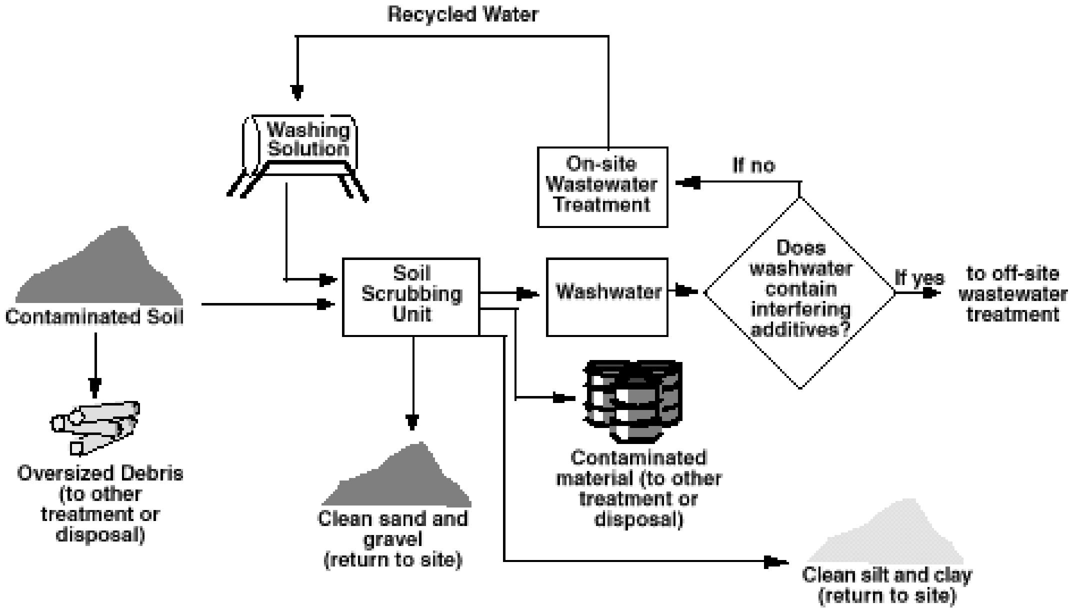


FIGURE 2-5 Soil washing process (USEPA, 1996)

2.2.2 Chelant-Assisted Soil Washing

Chelant, which is also called as chelating agent, is ligand that contains multiple coordination sites that can form bindings between the metal ion and the ligand (Peters, 1999). It forms stable, strong, and water soluble metal-chelant complexes with metals at a 1:1 molar ratio, which facilitates the removal processes of trace elements from soils. The formation of metal-chelant complexes can be divided into two steps: metal-water complexation (an outer-sphere complex: $[M(H_2O)]^{a+}$) and metal-chelant complex formation that replaces the water molecules. The replacement is shown as Equation 2-1 (Chauhan et al., 2015):

$$[ML_n\mathrm{X}]^{z+} + Y^- \rightleftharpoons [ML_n\mathrm{Y}]^{z+} + X^- \qquad (2\text{-}1)$$

(In the above formula, X represents H_2O and Y represents metal.)

Thus, chelant can directly mobilize target metal(loid)s from the solid phase, or via ligand-promoted dissolution which dissolves the metal-containing minerals (Al/Fe/Mn (hydr)oxides and organic matter). EDTA and its metal-chelant complexes dissolve the Fe/Mn oxides by adsorption on the mineral surface, slow detachment of mineral metals, and then fast protonation restoring the surface functional groups (Nowack and Sigg, 1997; Nowack et al., 2001; Tsang et al., 2007a). Soil washing assisted by chelating agents extracts the metal(loid)s from soils, which has high extraction efficiency and maintains biological properties of soils without dramatically changes the soil pedological properties (Udovic and Lestan, 2012; Jelusic and Lestan, 2014).

Chelant like EDTA, EDDS, nitrilotriacetic acid (NTA), and diethylenetriamine pentaacetic acid (DTPA) was commonly used for their high efficiencies on removing the metal(loid)s. Nitrilotriacetic acid and DTPA were considered as Class II carcinogen and toxin and potential carcinogen respectively (Peters, 1999; Neilson et al., 2003; Zou et al., 2009). EDTA is the most popular chelating agent for remediation of metal-contaminated soils because of its effectiveness to form strong metal-chelant complexes. It can extract metal(loid)s from most of the non-silicate-bound phases that are considered more bioavailable and easily-mobilized in the soil (Peters, 1999; Tandy et al., 2004). It was reported that EDTA successfully reduced metal(loid)s (mostly for the metals) in soil and plants after EDTA extraction (Qiu et al., 2009; Begum et al., 2012; Zupanc et al., 2014). However, the removal of anions (e.g. As and Se) is less efficient because it is hard for anions to form stable chelant complexes (Polettini et al., 2006). In the meanwhile, during the past ten years, research works found that EDTA and its metal complexes are difficult to be naturally degraded by biochemical processes and exist persistently in the environment (Nörtemann, 1999; Bucheli-Witschel and Egli, 2001). Only Fe(III)-EDTA shows photodegradable under sunny days. A higher concentration of EDTA than other organic pollutants was found in the river water, which indicates that the persistent EDTA might remobilize metals from sediment or soil into groundwater and drinking water (Sun et al., 2001; Nowack, 2002; Yip et al., 2009). Therefore, post risks to human health in a long term should be considered. Also, a guideline value of 0.6 mg L^{-1} for EDTA concentration was set by World Health Organization (Chauhan et al., 2015).

Due to its stability in the environment, recycling use of EDTA during the application has attracted research interest. According to Zeng et al. (2005) Na_2S and $Ca(OH)_2$ were successfully used to recycle EDTA by forming precipitates with Cd, Cu, Pb and Zn; and the reclaimed metal-EDTA complexes ($CaEDTA^{2+}$ and $FeEDTA^{2-}$) were used for seven times and reached a final loss of 19.5% to 23.5%. A single large dose was proved to be less effective than several successive small doses in EDTA extraction of Pb and Zn (Finzgar and Lestan, 2007). Meanwhile, increased metal mobility and bioaccessibility after washing by EDTA, can lead to further groundwater contamination (Lei et al., 2008; Zhang et al., 2010).

TABLE 2-1 Log K values for metal complexation of EDTA and EDDS.

Abbreviation	**log K Cu(II)**	**log K Zn(II)**	**log K Pb(II)**	**log K Fe(III)**	**log K Ca(II)**	**log K Al(III)**
EDTA	18.8[a]	16.5[a]	17.9[a]	25.1[a]	10.6[a]	19.1[b]
EDDS	18.4[a]	13.4[a]	12.7[a]	22.0[a]	4.6[a]	12.9[c]

[a] Adopted from (Tandy et al., 2004)
[b] Adopted from (Martell et al., 2004)
[c] Adopted from (Koopmans et al., 2008)

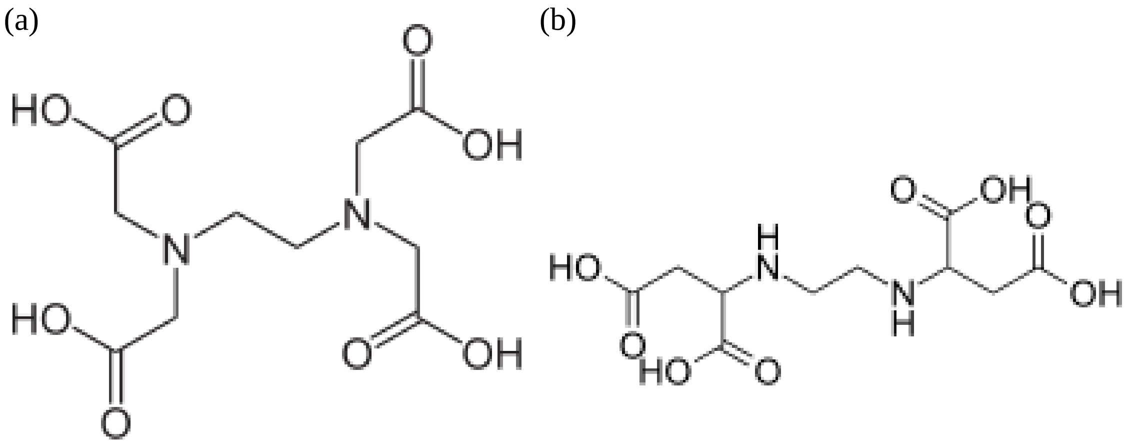


FIGURE 2-6 Skeletal formula of (a) EDTA and (b) EDDS (adopted from Wikipedia).

Biodegradable chelating agents, such as EDDS, methylglycinediacetic acid (MGDA), and iminodisuccinic acid (IDSA) have been proposed to replace non-degradable chelant during the past ten years. As a structural isomer of EDTA, EDDS is suggested to be a promising substitute for EDTA because of its relatively strong ability of forming stable complexes with metals, lower toxicity to plants, fungi, and microorganisms, and higher capacity of biodegradation in the natural environment (Nowack, 2002; Grčman et al., 2003). The EDDS and its metal-EDDS complexes (Ca, Cr, Fe, Pb, Al, and Zn) normally have a lag phase and half-life of 7-32 days in the biodegradation (Vandevivere et al., 2001; Tandy et al., 2006). A complete degradation of EDDS was found after 36 days in a field experiment by Wang et al. (2012). This lag phase is suitable for industrial application since it is not too short for practical extraction, chemical storage, and transportation and not too long for the biodegradation or photodegradation (Yan et al., 2010). Furthermore, a research work by Jaworska et al. (1999) showed EDDS has low toxicity to the aquatic organisms, such as fish and daphnia.

The affinities with various metals (Cu, Zn, and Ni) of EDDS are comparable with EDTA, except for Pb (Table 2-1). After 24-hour washing by EDDS, 53-67 % of Cu, 19-60 % of Zn, and 16-67 % of Pb in soils were removed at a chelant-to-metal ratio of 1 or 10 (Tandy et al., 2004). Increased amounts of mineral dissolution (Al, Fe, and Mn) was found after 180-h extraction by EDDS (Yip et al., 2009), especially for Al. Under slight acidic condition (pH at 5), only limited amount of dissolution of Fe and Mn was found. Thus, under EDDS deficiency, dissolved Al was the major competitor against the target metal(loid)s in soils. The fates of metal-EDDS complexes in soils before biodegradation were studied in the uncontaminated and contaminated soils (Tsang et al., 2009b). Strong adsorption of the metal-EDDS complexes and mineral dissolution happened on the surface of the uncontaminated soils, while intensive metal exchange underwent with the sorbed metals (Cu, Pb, and Zn) on the contaminated soil. Metal-EDDS complexes and especially the uncomplexed EDDS can dissolve the amorphous and poorly crystalline oxides (e.g. ferrihydrite) and release Fe and Al, which affects the extraction of target metals in soils (Komárek et al., 2009).

2.2.3 Factors Affecting Metal(loid) Removal by EDDS Extraction

Many factors affect the EDDS washing efficiencies of metal(loid)s (Lim et al., 2004; Tandy et al., 2004; Polettini et al., 2007; Lestan et al., 2008). They can be divided into three groups: soil properties (soil pH, particle size distribution, mineral composition, CEC, organic matter, age of the contamination, and the co-existence of other contaminants), contaminants in the soil (type of the contaminant, distribution, lability and speciation/physiochemical forms in soil), and the chelant properties (chelant-to-metal ratio (concentration), pH of the chelant, washing time, soil-to-solution ratio, and electrolyte).

In most situations, washing by chelant under acidic conditions induces a higher extraction efficiency by influencing the metal(loid)s adsorption therefore enhancing the mobility. However, an acidic condition favors the release of Fe from Fe oxides by ligand-promoted dissolution in soils. Therefore, the mobility of target metals can be depressed by the competition between the target metals with Fe ions (Nowack and Sigg, 1997). On the other hand, Yip et al. (2009) reported that a lower pH condition facilitated EDDS adsorption on the surface of Fe oxides. In application, the pH of chelant solution is selected typically within the range of 5-9 which is close to the original soil pH to avoid the unwanted effects on soil properties.

Organic matter in soil could reduce the extraction capacity of chelating agents. Suppressed interaction between EDDS and metals was found by Yip et al. (2010b), which could due to the competition between humic acid and metals and the adsorption of metal-humate complexes on the soil surface. A high concentration of OM can hinder the EDDS extraction of Cu, because of the strong binding affinity of Cu to SOM which ascribes to bidentate inner-sphere coordination of functional groups (Strawn and Baker, 2008). On the other hand, Yan and Lo (2011) reported that an enhanced metal extraction was observed under EDDS excess, which is probably because of the improved Al and Fe dissolution by humic acid.

Metal extraction is affected directly by metal lability which is ascribed to the total metal concentration, steric distribution, bonding characteristics and chemical speciation more than the metal-chelant stability, according to the study by Yip et al. (2009). Though Zn and Pb have relatively low stability constants of metal-EDDS complexes (log K($ZnEDDS^{2-}$))=13.4 and log K($PbEDDS^{2-}$=12.7), Table 2-1), removal of 60% and 40%, respectively, was found after 1-h extraction. It was reported that EDDS mainly extracts the metals from exchangeable, carbonate and marginally from organic matter and residue fraction of soils after short-time washing (Tandy et al., 2004; Yip et al., 2009), while EDTA can extract metals from amorphous and poorly crystalline Fe/Mn oxide fraction (Nowack and Sigg, 1997).

Previous studies revealed that the common chelant-to-metal ratio in should be used over 1 for higher extraction efficiency in application. Low chelant-to-metal ratios lead to a deficiency of chelating agents, which result in significant conflicts between mineral metals (Al, Fe, and Mn) and target metals (Yan et al., 2010; Yip et al., 2010b). High concentrations of mineral metals exist in the soil, thus the target metals might not be fully extracted by the chelants. However, an increasing dosage of the chelants was found not increase with the removal efficacy of the metal(loid)s in proportion. Thus, multiple steps of washing with a low stoichiometric dosage of chelant is recommended rather than a high single dosage (Finzgar and Lestan, 2007; Polettini et al., 2007; Polettini et al., 2009). Longer washing time mostly enhances the extraction of metals, but for economic and practical consideration two-hour washing is normally used in research and application (Zou et al., 2009).

The interaction between chelant and the Fe/Mn oxides is one of the crucial factors affecting soil washing. Chelant can adsorb on the mineral surface such as Fe/Mn oxides, which reduces the availability of the chelant for metal extraction and hence hinders the extraction efficiency (Nowack, 2002; Yan et al., 2010). Besides, chelant-assisted dissolution consumes a vast amount of chelant on extracting mineral metals (Ca, Fe, Mn, and Al) and dissolves the minerals which play important roles in soil structure, which leads to an undesired increase of cost and damage to the soil properties (Tsang et al., 2007b; Yip et al., 2009). The dissolution of soil minerals is mostly due to the ligand exchange reactions following the adsorption of chelant and the broken of metal-oxygen bonds (Nowack, 2002). Komárek et al. (2009) demonstrated that the dissolution of amorphous minerals is likely the most significant factor to control the interaction of dissolved Fe and Al with metal-EDDS complexes and uncomplexed EDDS. Also, metal-chelant complexes can be adsorbed on minerals and undergo metal exchanges with the sorbed metallic contaminants (Tsang et al., 2009b; Yip et al., 2009; Fabbricino et al., 2013), yet low dissolution capacity of Cu-EDDS complexes was found on ferrihydrite and goethite in comparison with free EDDS and Al-EDDS complexes (Komárek et al., 2009).

2.2.4 Limitations of Chelant-Assisted Soil Washing

Co-Existence of Metalloids in the Soils

Metalloids (such as As and Se) can hardly form stable metal-chelant complexes, which result in low extraction efficiencies of them by chelant (Tokunaga and Hakuta, 2002). It was also found that the solubility of As is strongly related to the dissolution of Fe and Mn oxides, indicating that the dissolution of Fe/Mn oxides is the key factor of enhancing As extraction. At the same time, arsenate, as the dissolved oxidized form of As, has a lower solubility, affecting the extraction of As in the liquid phase (Polettini et al., 2007). Multiple trace elements co-exist in soils due to the mineral source or industrial contamination, therefore, it is hard only to use one-step soil washing to remove all contaminants, especially when metals and oxyanions (e.g. As) co-exist. Integrated treatments with different mechanisms were recommended to deal with the complicated situation with co-existence of metals and oxyanions.

Affecting the Soil properties

After EDTA washing, significant impact on soil properties (water retention, aggregate soil fractionation, and stability) and decrease of yield of plant was observed (Zupanc et al., 2014). Besides, soil structure is damaged after washing by strong reagents, by dissolving the Fe/Mn/Al oxides which are considered the important contributors for soil structure (Tsang et al., 2007b). Moreover, the dissolved Al and Mn residue in soils might be phytotoxic after washing by chelants. Therefore, a high dosage and long-term washing by chelant should be avoided, which reduce the extraction efficacy of total trace elements.

Potential Leachability in Soils

Chelant extracts metals from soils by forming strong and reliable metal-chelant complexes which are soluble in the water and have low affinity to the soil particles. According to Nowack (2002), the formation of metal-chelant complexes is controlled by the kinetics of all complexation reactions, adsorption on soil particles, mineral dissolution and the potential loss of chelating agents or their metal complexes by degradation. At low concentrations, chelant tends to adsorb on the mineral surface by ligand-exchange reactions. Thus, they can cause the immobilization of chelate complex particularly in acidic conditions (Davis and Leckie, 1978; Nowack, 2002). Also, it has been noted that after extraction by chelant, the metals become more mobilized in soils (Barona et al., 2001; Lei et al., 2008).

2.2.5 Organic Ligands- and Reducing Agent-Assisted Washing

Low-molecular-weight organic acids (LMWOAs), including oxalic, citric, fumaric, and acetic acids, are root exudation of the plants, decomposed products from OM, and metabolites of microorganisms. They have a strong ability to mobilize the metals, especially for those organic ligands with functional groups like amino and carboxyl (Wasay et al., 1998; Wasay et al., 2001; Qin et al., 2004; Shahid et al., 2012). Ligands like oxalate and citrate can form stable complexes with metals without toxicity, whose skeletal formula are shown in Fig. 2-7. Also, they are biodegradable, naturally existing in soil, non-toxic, and inexpensive.

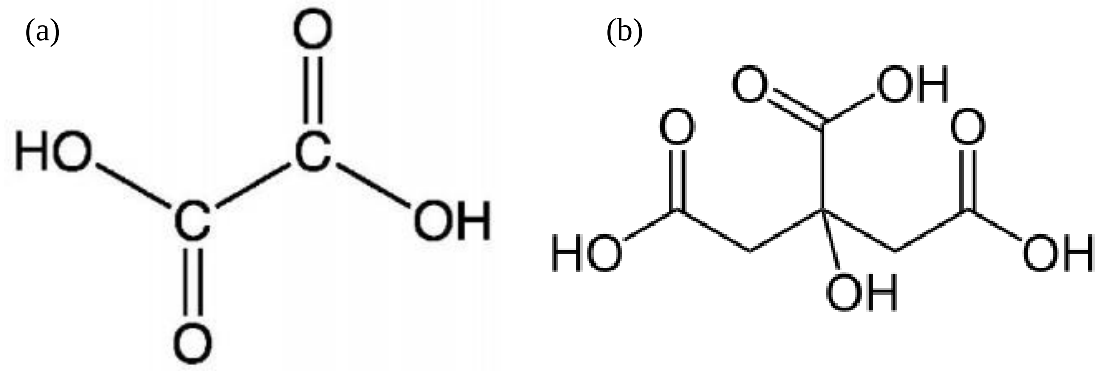


FIGURE 2-7 Skeletal formula of (a) oxalate and (b) citrate (adopted from Wikipedia).

It was found that oxalate can attack and dissolve hydrous oxides, which helps to dissolve the metals which are strongly bonded with Fe/Mn oxide part. Though the stability constants of metal-oxalate complexes are obviously lower than the metal-EDTA complexes, oxalates can reach satisfied extraction efficiency (Stumm, 1992; Elliott and Shastri, 1998, 1999). The number of carboxylate groups of ligands plays an important role in the dissolution of Fe oxides according to Blesa et al., (1994). Maximum Fe oxide dissolution was found by ligands with two to three carboxylate groups since monocarboxylic acids are weakly adsorbed on the surface of oxides and incompetent to disconnect the bonds which connects Fe with the lattice. In contrast, polycarboxylate ligands like EDTA and EDDS tend to passivate the oxide surface. Oxalate revealed high Fe oxide dissolution (30 %) than EDTA (10 %) at pH 6 in same molecular concentration (Elliott and Shastri, 1999). However, low extraction efficiency of Pb by oxalate was found because of the low solubility ($K_{sp} = 2.74 \times 10^{-11}$) of PbC_2O_4 (Qiu et al., 2009). In addition, oxalate, as a strong reducant, dissolves the Fe/Mn oxyhydroxides by reductive dissolution therefore releases the metal(loid)s entrapped in the oxides (Qiu et al., 2009).

The removal of As is believed strongly associated with the dissolution of Fe/Al/Mn-containing minerals (mainly oxides) since the minerals are the most important natural sinks of As in soils. A combination of dithionite and oxalate was successfully applied to enhancing the dissolution Fe/Mn oxide and preventing the re-adsorption and re-precipitation of As on the potentially regenerated Fe oxides or the positively charged soil surface (Kim and Baek, 2015; Lee et al., 2015).

2.3 Soil Stabilization

2.3.1 Overview of Soil Stabilization

Stabilization is referred as using organic or inorganic amendments to immobilize and reduce the metal(loid) mobility, bioavailability, bioaccessibility and transportation without changing the original concentration in the soil, which can be included by solidification/stabilization (S/S) method (Garrido et al., 2005; Tica et al., 2011; Komárek et al., 2013). Amendments can be industrial byproducts, natural minerals, alkaline compounds, agricultural waste, and bio-products that are able to adsorb contaminants to mineral surface, complex with contaminants, (co)precipitate trace elements or conduct ion exchange to reduce the bioavailability of contaminants (Kumpiene et al., 2008; Lestan et al., 2008). Organic amendments, such as biochar and compost, contain large amounts of oxygen-containing functional groups (primarily carboxyl and hydroxyl groups) which have a strong binding affinity for various metals (Cu, Zn, Cd, and Pb) and offer large surface areas to promote the adsorption process (Beesley et al., 2010; Uchimiya et al., 2010a; Uchimiya et al., 2012). Inorganic amendments (sludge, zero-valent iron, limestone, fly ash, and zeolites) which contain high concentration of Fe, Al, or Ca that can immobilize metals or organic pollutants via adsorption on surface hydroxyl groups, and co-precipitation (Tyrovola and Nikolaidis, 2009; Tsang et al., 2013b; Tsang et al., 2014; Shaheen and Rinklebe, 2015). These sorption/precipitation mechanisms are affected by many factors, such as pH, $E_{H,}$ contaminants, and CEC.

In addition, the amendments such as wastes, natural minerals or by-products can lower the cost, therefore the immobilization can be applied in a large scale especially for regions with comparatively low contamination. The application of these amendments results in improvement of soil qualities (water holding capacity, nutrients, and plant yield) (Tsang et al., 2013b). Besides, the immobilization benefits for the soil ecosystem, for recovering soil enzyme activities, increasing the microbial biomass, and decreasing plant and microtoxicity (Kumpiene et al., 2006; Ascher et al., 2009). Also, to reuse/reduce these industrial and agricultural waste is also an environmental-friendly strategy to use these waste sustainably.

2.3.2 Biochar

Nowadays, biochar has received considerable interests because it could be a win-win strategy for the waste management. It reduces a decent volume of agricultural and industrial waste in the meantime produces energy during pyrolysis process, as well as relieve the climate change by sequestration of carbons. As a solid residue formed during fast or slow pyrolysis of biomass in a closed condition with limited oxygen applied, biochar is widely regarded as an effective soil amendment. According to the International Biochar Initiative, it can be defined as “a solid material obtained from the thermochemical conversion of biomass in an oxygen-limited environment’’ (IBI Biochar Standards, 2015). Biochar improves physicochemical and biological soil properties by increasing soil water retention capacity, plant growth, crop yield, and microbial population and activities, contributes to waste reduction, and sequesters carbon to mitigate climate change (Lehmann et al., 2006; Lehmann, 2007; Ahmad et al., 2014b; Hussain et al., 2016; Inyang et al., 2016). Also it is able to reduce the mobility of metal(loid)s in soils, which may due to its strong ability of adsorption and complexation for the high surface area, porosity, abundant functional groups which are generated from the pyrolysis, as well as the increased soil pH and CEC which result from the high contents of silicates and mineral oxide (Uchimiya et al., 2010a; Park et al., 2011a; Houben et al., 2013; Tan et al., 2015; Ahmad et al., 2016a). The significant chemical difference between biochar and the other natural organic components in soils is the larger proportion of aromatic carbon (amorphous and turbostratic carbon) and its fused structure, which makes it stable and hard to be utilized by microorganisms (Lehmann et al., 2011).

The properties of biochar greatly depend on its feedstock and production parameters including the temperature of pyrolysis, heating rates, and atmospheric conditions. Two key factors affecting the biochar property are the selections of the feedstock and pyrolysis temperature (Tang et al., 2013). Basically, two major types of materials can be used as biochar feedstocks: (i) unprocessed feedstocks: crop residues (rice hull, straw, stover), forestry waste (hardwoods and softwoods); and (ii) processed feedstocks: animal litter, sewage sludge, municipal solid waste, and food industrial waste. (Cantrell et al., 2012; Mukome et al., 2013) (IBI Biochar Standards, 2015). One thing should be carefully handled with is the persistent existence of the toxic trace elements inside the biochar especially when sewage sludge or municipal solid waste is used as the feedstock. Pyrolysis temperature is strongly related to the carbon (C) content of the biochar since the hydrogen (H) and oxygen (O) concent decreased dramatically. As reported by previous studies, despite the different feedstock of the biochar, > 90% of C content were found when the temperature of pyrolysis over 700 °C (Uchimiya et al., 2011a; Ahmad et al., 2014b). The decreased H and O contents also result in a lower H/C and O/C molar ratio, which indicates a higher aromaticity of the product under the process of dehydration and deoxygenation (Chen and Chen, 2009; Uchimiya et al., 2010b). In contrast, N content in the biochar is less related to the pyrolysis temperature but the type of feedstock. For example, manure- and sewage sludge-derived biochar has higher N content.

Morphology of biochar is also controlled by pyrolysis temperature and the feedstock (Liu et al., 2009; Uchimiya et al., 2011a). In general, a higher pyrolysis temperature increases the surface area of the biochar. However, retention of the trend was reported when the temperature is higher than 700 °C, which might be due to the damage the structure (Uchimiya et al., 2011a). The possible reasons lie on the decomposition of the aliphatic alkyl and ester groups and the exposure of the aromatic lignin core under a higher temperature (Chen and Chen, 2009). Besides, animal manure- and sludge-based biochar revealed lower surface area than the biochar produced from lignin and cellulose based materials, despite the pyrolysis temperature (Dai et al., 2014). In addition, porosity is another important property of biochar that can affect the retention ability of metal(loid)s. According to the size (< 2, 2 – 50, and > 50 nm), the pores can be divided into micro-, meso- and macropores, respectively. Micropores have better capacity to remain the contaminants. Similar to the morphology, pyrolysis temperature affects the size of pore significantly. Research works show that high temperatures (≥ 700 °C) in pyrolysis can crack the wall of micropores, generate meso- or macropores.

The metal-retarding functional groups are also related to the pyrolysis temperature and the feedstock of biochar. It is reported a loss of oxygen-containing functional groups with increasing pyrolysis temperatures, which attributes to dehydration, decarbonylation, and decarboxylation (Bourke et al., 2007; Uchimiya et al., 2011c). FT-IR results of the biochar showed decreases of O−H stretching (200 – 500 ºC) and C−O stretching (200 – 350 ºC), and an increase at (200 – 350 ºC) and then a reduction of (350 – 500 ºC) C=O bonding (Figure 2-8), which is related to the oxygen-containing functional groups (carboxyl, carbonyl and hydroxyl groups) on the biochar surface. Dai et al. (2014) observed abundant functional groups in both staw- and manure-derived biochar produced at 300 ºC.

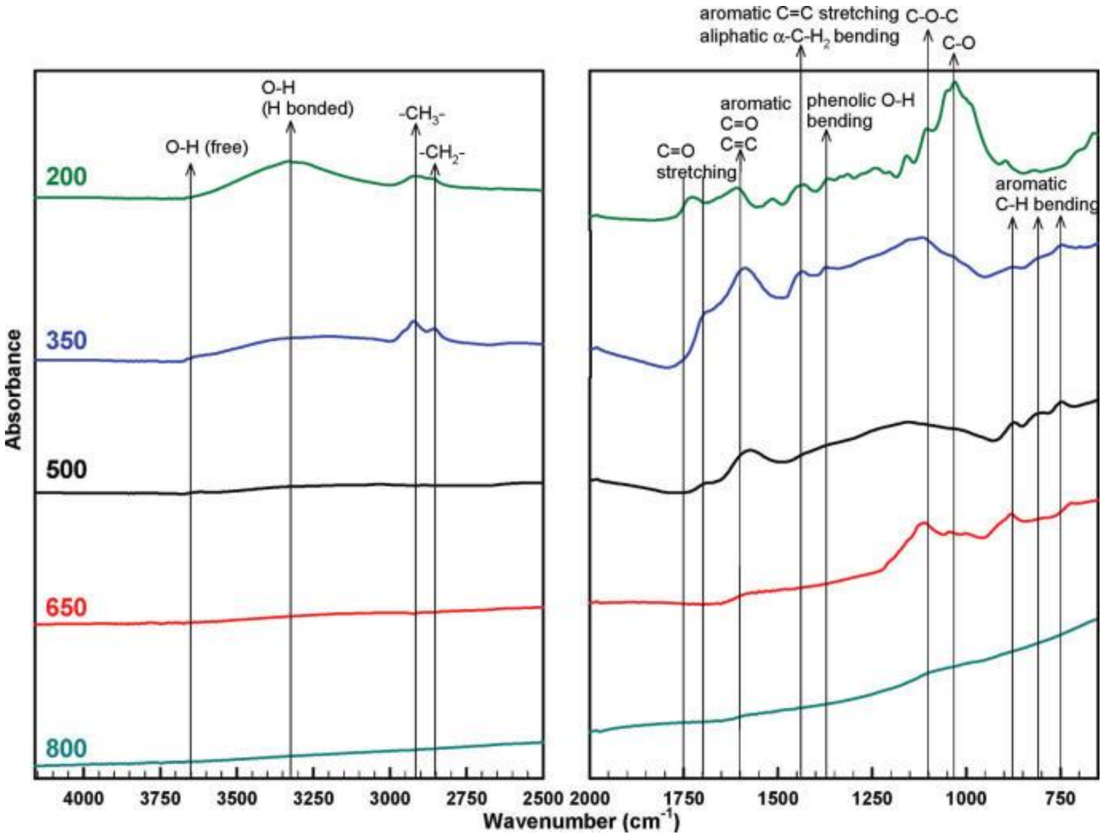


FIGURE 2-8 FTIR spectra of cottonseed hull biochar produced at various pyrolysis temperatures (Uchimiya et al., 2011c).

2.3.3 Factors Affect Biochar Retention on Metal(loid)s

The mechanisms for biochar retention of metal(loid)s can be summarized as (i) electrostatic outer-sphere complexation due to surface ion change (chiefly for K^+ and Na^+), (ii) electrostatic outer-sphere complexation of anionic elements (As and Se), (iii) electrostatic outer-sphere complexation of cations (Cu, Pb, and Zn), (iv) co-precipitation and inner-sphere complexations between metal(loid)s and organic matter, mineral oxides and phosphorus (especially for Pb), and (v) surface complexation with oxygen-containing functional groups on the surface of biochar, according to Lu et al. (2012) and Ahmad et al. (2014b). Figure 2-9 shows the mechanisms (i)-(iv).

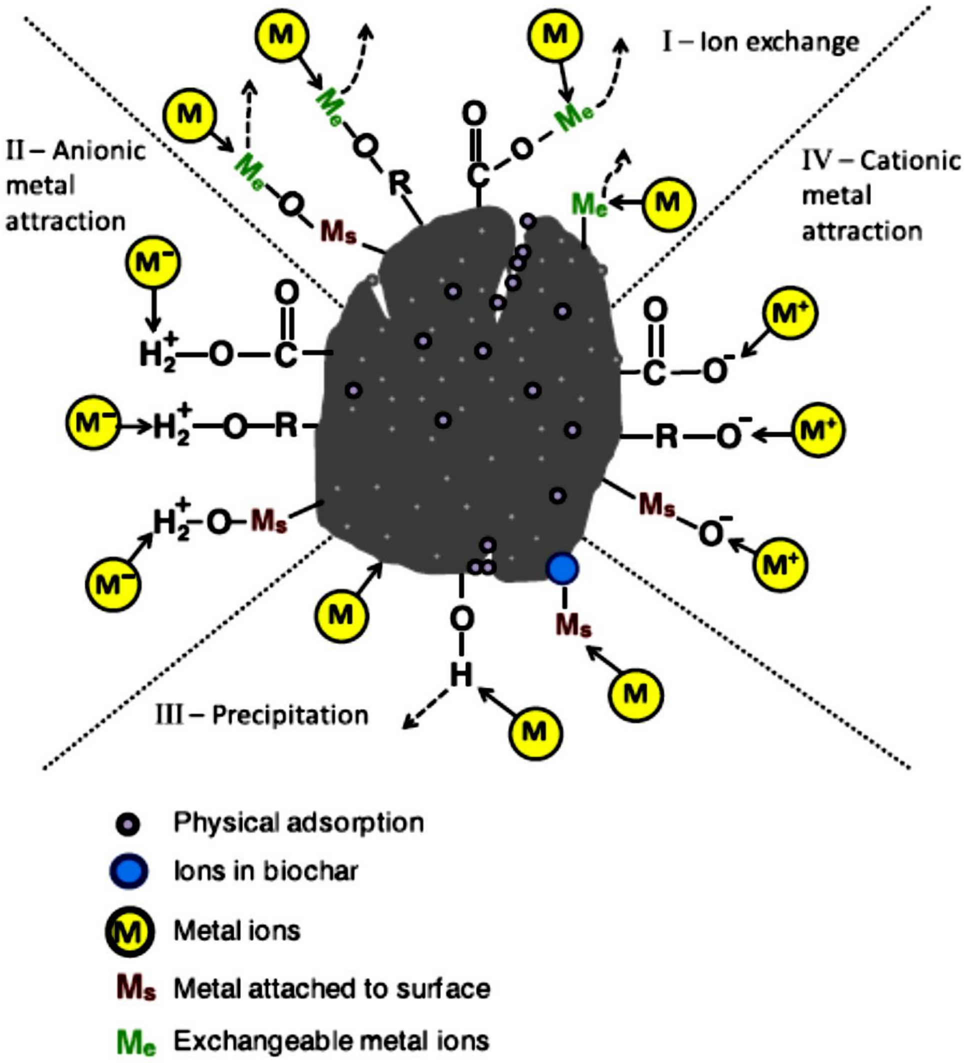


FIGURE 2-9 Postulated mechanisms of biochar interactions with inorganic contaminants. Circles on biochar particle show physical adsorption. I – ion exchange between target metal and exchangeable metal in biochar, II – electrostatic attraction of anionic metal, III – precipitation of target metal, and IV – electrostatic attraction of cationic metal (Ahmad et al., 2014b).

The behaviors of metal(loid)s vary after biochar application. Beesley et al. (2010) reported that mobilized Cu and As were found after an application of hardwood-based biochar to the contaminated soil. This study suggested that high DOC released by biochar in the soil increase the mobility of Cu after biochar application, while the increment of soil pH leads to the growing mobility of As. The relationships between Cu and DOC as well as As and soil pH were also reported by other researchers (Hartley et al., 2009; Park et al., 2011a; Almaroai et al., 2013a). Copper can form soluble complexes with DOC; while biochar produced at a low temperature (e.g., < 500 ºC) can release a large amount of DOC. Also, DOC could hinder the Cu adsorption on the surface of biochar (Bolan et al., 2011; Cao et al., 2011). By contract, biochar produced at higher temperatures (e.g., < 700 ºC) have a lower discharge of DOC. Therefore it is possible to use the biochar to stabilize Cu (Uchimiya et al., 2011c). Besides the rising pH, the enhanced mobility of As can be due to the reductive property of biochar, since arsenite (As^{III}) has higher mobility and toxicity than arsenate (As^{V}) (Park et al., 2011b; Zhang et al., 2015). The liberating phosphorus (P) from biochar may also contribute to the increasing As mobility, because of the similarity of chemical structure between P and As.

In contrast, Cd and Zn were immobilized with biochar in the study of Beesley et al. (2010), which could result from the higher soil pH that forming precipitations as metal hydroxides consequently and affecting adsorption behaviors. Similarly, a rising soil pH facilitates the sorption of Pb on kaolinite which is a common mineral in soils, since Pb can form stable inner-sphere bidentate surface complexes with this mineral (Grafe et al., 2007; Almaroai et al., 2013a). A 3-year field experiment conducted by Bian et al. (2014) observed a consistently rising soil pH with significantly decreased plant uptake of Cd and Pb after wheat straw biochar application. Beside the soil pH, high contents of available P, K, and Ca in the ash component of biochar ascribe to the Pb immobilization via ion exchange and forming precipitations. Based on an XRD study, Cao et al. (2011) reported that insoluble hydroxypyromorphite ($Pb_5(PO4)_3(OH)$) was found after stabilization with the dairy manure-derived biochar that contains high concentration of P that origins from the feedstock. Also, the oxygen-containing functional groups (carbonyl, lactonic, carboxylic, hydroxyl, and phenol) of a husk-based biochar produced at a low temperature (350 ^{o}C) resulted in high retention of the mobility of cations (such as Cu, Ni, Cd, and Pb) (Uchimiya et al., 2011a). In addition, as mentioned in the above sections, the functional groups on the biochar surface can be cracked by higher pyrolysis temperatures. Thus, the situation is complicated when multiple elements were considered in the soil system.

Recently, more and more researchers are paying attention to the effects of varied environmental conditions on the biochar-assisted immobilization to provide more information before application. Floodplain soils undergo dynamic E_H whose variations influence the pH, DOC, dissolve inorganic carbon (DIC), Fe, Mn, and sulfur. This affects the mobility and availability of metal(loid)s in soils consequently. Varied E_H affects the biochar immobilization on the metal(loid)s significantly, however, only a few studies explored the problem. A study by Rinklebe et al. (2016) indicated that the use of biochar successfully decreased the concentrations of dissolved Al, As, Cd, Cu, Ni, and Zn under various E_H. Also, the concentration of As, Cd, Cu, Ni, and Zn increased with a growing E_H conditions as well as the pH, no matter if the contaminated soil amended with biochar. It was also considered that the solubility of the metal(loid)s were controlled by the E_H and the consequent variation of pH, DOC, DIC, Fe, Mn and sulfate. However, in the above study, the content of As was low in the soil, only around 91 mg kg^{-1}. Thus, further studies should be carried out the lability of metal(loid)s after biochar immobilization in soils. Meanwhile, a current study revealed that a decreasing temperature (from 45 to 5 ^{o}C) helped to release the immobilized Cr^{VI} and As^{III} except Pb^{II} by a sludge-derived biochar, but a long time incubation hindered this remobilization (Fang et al., 2016).

It was reported that biochar reduces the toxicity of trace elements in plants via alleviating metal(loid) uptake by plants and enhancing both growth and yield of plants under high stress with metal(loid)s, except the improvements on soil properties (Beesley et al., 2014; Shaheen and Rinklebe, 2015; Zeng et al., 2015; Rizwan et al., 2016). Several mechanisms were suggested as followed: (i) stabilization capacity of biochar, (ii) change of redox state of the trace elements, (iii) alteration of the soil properties, and (iv) change on the antioxidant enzymes in plants. The mechanisms highly depend on the plant species, genotypes, metal(loid)s, growth conditions, and biochar properties. Still, research works showed that some biochar applications retarded the nutrients in soils and hence decreased plant growth (Rizwan et al., 2016). Therefore, the selection of biochar should be investigated clearly before its application.

2.3.4 Coal Fly Ash

Coal fly ash (CFA), as a by-product from heat/energy generation systems in industry, is commonly used in the production of glass, ceramics, and concrete (Wang and Wu, 2006). The main components of CFA are quartz (SiO_2), Fe/Al oxides like hematite (Fe_2O_3), magnesioferrite ($MgFeO_4$), and mullite ($Al_6Si_2O_{13}$), and high Ca containing minerals like anhydrite ($CaSO_4$) and lime (CaO) which have a strong alkalinity (Gomes et al., 2016). The annual production of CFA is around 600 million tons worldwide according to Montes-Hernandez et al. (2009), thus making a good use of CFA could be profitable.

Coal fly ash is successfully applied in mine tailings and wastewater treatments because of its strong ability of stabilization of metal(loid)s (Pb, Cr, Cu, Hg, and As) (Wang and Wu, 2006; Wang et al., 2013; Tsang et al., 2014). The adsorption capacity of CFA is believed as good as activated charcoal. Currently, research found that CFA increases soil pH, which is able to reduce exchangeable and plant-available metals in soils and improve soil quality especially for acidic soils (Kumpiene et al., 2007; Gu et al., 2011; Moon et al., 2013b). In addition, it has a high surface area which can adsorb hazardous metal(loid)s.

Coal fly ash contains large amounts of $CaCO_3$ that have strong neutralizing capacity which can reduce soil pH, therefore, the mobility of metals can be influenced strongly. It is believed that Fe/Mn oxides can also reduce the available metal(loid)s in soil by sorption and co-precipitations (Komárek et al., 2013). Interactions between metal(loid)s and surface functional groups such as –OH. The functional groups can be negative or positive charged depending on the pH. Dissolved organic matter in soil can either enhance or hamper the sorption behaviors by forming stable surface metal(loid)-ligand complexes or soluble organic complexes (Violante et al., 2003). Besides the sorption, metal(loid) co-precipitation with oxides is another crucial mechanism for immobilization. These newly formed secondary minerals containing the toxic metal(loid)s can hardly be dissolved in water, therefore stabilize them (Kumpiene et al., 2008; Komárek et al., 2013).

2.3.5 Limitations of Stabilization

Long-term stability of the stabilization is one of the concerns of its application. It is difficult to make the long-term predictions only based on the short-term laboratory tests which cannot cover all the possibility in the real field. Redox reactions and microbial processes are normally omitted, although they are important. Long-term lability tests should be conducted to examine the biochar interactions inside soils in the future.

Abundant studies are focusing the ability of biochar stabilization and its potential effects on soil properties, yet only a few studies noticed that under incomplete combustion and pyrolysis may lead to the formation of polycyclic aromatic hydrocarbon (PAHs) inside the biochar. It can result in serious contaminations after the application of biochar in the soils. Qiu et al. (2015) revealed that the concentration of PAHs is influenced strongly by the heating treatment temperature during the pyrolysis and the type of feedstocks of biochar. High concentration of minerals inside the plant-derived biochar may enhance the depolymerization of organic matter, thus facilitate the production of PAHs.

The amendments of stabilization might not be suitable for all the contaminants in the soils. For instance, it is found that Mn oxides can remove Pb efficiently in soils, while they oxidize Cr, therefore, increase the mobility and toxicity of Cr (Kumpiene et al., 2008). Besides, strong alkaline materials like fly ash can increase soil pH was found favorite the immobilization of Pb but increase the risk for As and Cr due to the higher mobility and toxicity of their oxidizing forms (As^{III} and Cr^{VI}) (Kumpiene et al., 2008; Cao et al., 2011). Thus, to reach balanced effects on stabilization, the metal(loid) behaviors with amendments have to be investigated thoroughly before the long-term application.

2.4 Groundwater Contamination

2.4.1 Overview

Metal(loid)s in soils might be dissolved and leached into groundwater because of natural or anthropic reasons, such as the soil pH change or directly contaminations by leakage (Hashim et al., 2011). Groundwater is widely used for urban water supply (directly as drinking water) and use for agriculture and industry. Thus, metal(loid)s inside the groundwater can directly enter the human food chain. Generally, contaminants in groundwater can be divided into two types based on their source: point sources and non-point (diffuse) source (Richardson and Nicklow, 2002; Thiruvenkatachari et al., 2008). Table 2-2 presents examples for point and non-point sources of groundwater contaminations respectively. Common inorganic contaminants are listed in Table 2-3 with their maximum contaminant levels (MCL) according to USEPA.

TABLE 2-2 Point source and non-point source for groundwater contamination adopted from (Thiruvenkatachari et al., 2008).

Point source	Municipal landfills, industrial waste disposal sites, leaking gasoline storage tanks, leaking septic tanks, and accidental spills and leaks of petroleum products and of dense industrial organics
Non-point source	Atmospheric deposition, contaminated sediments, and many land activities that generate polluted runoff, such as agriculture (pesticides and fertilizers), logging, and onsite sewage disposal

TABLE 2-3 Metal(loid) chemical speciation and maximum contaminant level in drinking water (USEPA). Adapted from (Hashim et al., 2011).

Metal(loid)	**Speciation**	**MCL in drinking water (mg L^{-1})**
Pb	0 and +2	0.015
Cr	0, +6, and +3	0.1
Zn	0 and +2	-
Cd	0 and +2	0.005
As	-3, 0, +3, and +5	0.01
Cu	0, +1, and +2	1.3
Hg	0, +1, and +2	0.002

2.4.2 Permeable Reactive Barriers for Controlling Groundwater Contaminations

Permeable reactive barriers (PRBs) are reactive media placed in the path of a plume of contaminated groundwater as shown in Fig. 2-10. Contaminants are transformed to less mobilized and/or toxic forms when passing though the PRBs by natural hydraulic gradient (Di Natale et al., 2008; Thiruvenkatachari et al., 2008; Tsang et al., 2009a).

The PRBs have several advantages in comparison with traditional pump-and-treat methods: (i) it is an *in situ* treatment, which is less costed and no extra treatment is needed; (ii) there is no additional energy needed for pumping the contaminants; (iii) for removing the organic contaminants, PRBs degrade them directly rather than transporting them to other phases. To have a better control of the contaminants, the reactive media in PRBs is required to have these listed properties according to Richardson and Nicklow (2002): (i) satisfactory reactivity to degrade the organic pollutants, (ii) long-lasting stability for years under specific geochemical conditions, (iii) suitable particle size, (iv) environmentally friendly reaction products, and (v) a reasonable price.

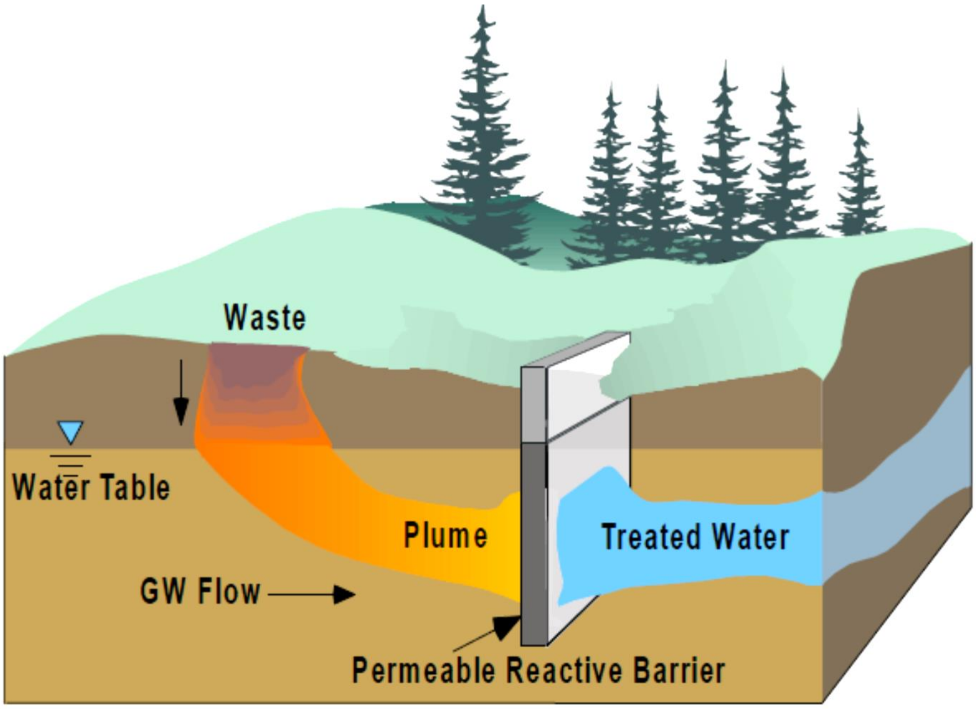


FIGURE 2-10 Using a permeable reactive barrier to treat a contaminated plume (USEPA 1998).

Zero-valent iron, activated carbon, natural minerals like zeolites, and alkaline materials like lime are commonly served as the main media of the media of PRBs. A commercial mineral, Apatite II^{TM}, was successfully applied to the media of PRBs to immobilize Zn, Pb, Cd and Cu under field condition (Conca and Wright, 2006). The mechanisms for stabilization are believed related to the formation of precipitates like sulfur-containing and pyromorphite ($Pb_{10}(PO_4)_6(OH, Cl)_2$).

Stable and low-cost waste and by-products from industry and agriculture with strong ability of adsorption are being proposed as the media of PRBs nowadays. Mondal et al. (2016) investigated two low-cost organic materials, peat and sawdust, acted as the media materials of PRBs for degradation of trichloroethene, while it is suggested that peat has a better capacity.

2.5 Significance of Proposed Studies

2.5.1 Multiple Washing Schemes and Combined Application of EDDS and EDTA for Soil Washing of an E-Waste Contaminated Soil

A recent national soil quality survey in China, covering 70% of the total area, revealed that over 82.4% of the invested soils were contaminated by metals and metalloids (mainly Cd, As, Hg, Cu, Pb, Cr, Zn, and Ni) (CMEP and CMLR, 2014; Zhao et al., 2015). This has resulted from various anthropogenic activities. A particular cause appears to be attributed to the rise in improper processing and storage of waste electrical and electronic equipment (WEEE or e-waste). Improper processing includes leaching by strong acid and direct burning of e-waste resulting in release of high levels of metal(loid) and thus contaminations of soils. The contamination has led to adverse effects on the environment, plants, crops, and human health (Huo et al., 2007; Liu et al., 2013). Chelants have been studied extensively as metal extractants for soil remediation by soil washing, soil leaching, soil flushing, and phytoextraction (Lestan et al., 2008; Arwidsson et al., 2010; Bolan et al., 2014; Hartley et al., 2014; Beiyuan et al., 2016). The ex situ chelant-assisted washing is considered to pose fewer risks than in situ technologies because it extracts metal(loid)s from the soil, while the ex situ techniques need extra soil excavation and transportation. EDTA (ethylenediaminetetraacetic acid) is a chelating agent that has been recently used widely in increasing the solubility of metals in soils. EDTA and its metal-EDTA complexes, however, are harmful to humans, plants and animals. Because of its low biodegradability it is also persistent in the environment. The long lifetimes of EDTA could increase the mobility of metals in surface run-off or in ground water and this may also promote the uptake of metals in plants (Bucheli-Witschel and Egli, 2001; Nowack, 2002; Voglar and Lestan, 2013). A structural isomer of EDTA, EDDS ([S,S]-ethylene-diamine-disuccinic-acid) has been proposed as a substitute for EDTA because of its relatively strong ability to complex with metals, as well as its biodegradability and low toxicity (Vandevivere et al., 2001; Tandy et al., 2006; Epelde et al., 2008; Lo et al., 2011a; Wang et al., 2012). A reduced dosage of EDTA has been recommended because of its potential risk including unwanted non-biodegradation, mineral dissolution, effects on soil physical and chemical properties and the metal residue that remains in the soil after its use (Zhang et al., 2010; Tsang et al., 2007).

It has been found that EDDS is effective in the removal of copper (Cu), while EDTA achieved higher lead (Pb) extractions than EDDS (Tandy et al., 2004; Polettini et al., 2007; Begum et al., 2012). This suggests that EDDS washing alone may not be able to remove multi-metals from contaminated soils. A mixture of EDDS and EDTA however appear more potent in dissolving a number of metals, in particular Pb the metal of concern in this study. The use of such mixture has been successfully applied in the phytoextraction to enhanced translocation of Pb from the plant roots to shoots (Tsang et al., 2007; Zhang et al., 2010). Yan et al. (2011) has successfully used a mixture of EDDS and EDTA to remove higher quantities of Pb than either EDDS or EDTA alone under deficient usage of chelant. However, the speciation of metals and chelant of a mixed chelant usage is still unclear. While a better understanding of the speciation of metals and chelants can help to understand the mechanism lay in the use of mixed chelant and improve the selection of chelant and their ratios.

The use of multi-pulse chelant-assisted washings in small dosage enhanced the extraction efficiencies of metals, in comparison with high dosage single-step extraction by previous studies (Polettini et al., 2006; Zou et al., 2009; Lo et al., 2011b). Research on chelant-assisted leaching found multiple step leaching with small dosages have higher extraction efficacies than those used a single step but higher concentration (Finzgar and Lestan, 2007). A lower dissolution, however of specific minerals such as Fe was reported by Finzgar et al. in a multi-step washing, which suggest this method may have reduced ability to remove target metals (A lower Fe-containing mineral dissolution was reported by Finzgar et al. in a multi-step washing, which suggest a favored condition of reducing competitions between mineral metals and targeted metals) (Finzgar and Lestan, 2007). Also, a step of background solution rinsing after chelant-assisted leaching was found helpful in removing adsorbed or entrapped EDDS and metal-EDDS complexes from the soil (Lo et al., 2011b).

In view of the above considerations this study considered (evaluated?) the use of EDDS, EDTA, and their equimolar mixture under various washing schemes (multi-pulse, step-gradient, and continuous washing) for soil washing of metals. The metal and chelant speciations were evaluated by Visual MINTEQ to establish (study?) the interactions of metal and chelant during the washing. In addition the extraction effectiveness, the metal leachability, bioaccessibility, and human health mitigation in the residual soils were also assessed.

2.5.2 Selective Dissolution Followed by EDDS Washing of an E-Waste Contaminated Soil: Extraction Efficiency, Fate of Residual Metals, and Impact on Soil Environment

Waste electrical and electronic equipment (WEEE or e-waste) is one of the pervasive problems worldwide. Despite the Basel convention, e-waste is continuously exported to developing countries where primitive processing and improper storage have led to severe soil contamination at e-waste recycling sites (Leung et al., 2008; Zhang et al., 2012; Zhao et al., 2015). For contamination hotspots that cause immense ecological and human health issues, *ex-situ* remediation methods such as chemical-enhanced soil washing can be considered for the sake of short treatment duration and minimal contaminant dispersion (Lestan et al., 2008; Tsang et al., 2012; Voglar and Lestan, 2013; Tsang and Yip, 2014). Chelating agents are widely recognized as effective metal extractants by forming metal-chelant complexes that subsequently destabilize and desorb from the soil phase (Nowack, 2002; Tsang et al., 2009b; Almaroai et al., 2012), of which biodegradable EDDS ([S,S]-ethylene-diamine-disuccinic-acid) has been considered as an environmentally benign substitute of EDTA (ethylene-diamine-tetraacetic-acid) (Arwidsson et al., 2010; Begum et al., 2012).

However, field application of chelating agents is challenged by facile biodegradation (Komárek et al., 2010; Wang et al., 2012) and lack of complexation selectivity in soils where mineral cations (Fe, Al, Ca, etc.) compete and exchange with target metals (Komárek et al., 2009; Lo et al., 2011a; Zhang and Tsang, 2013). The effectiveness of metal extraction is also dependent on the age and characteristics of contamination. For instance, chelating agent readily extract metals with weak affinities to the soil that are present as exchangeable and carbonate fractions (Udovic and Lestan, 2010; Tsang and Hartley, 2014). Insufficient extraction efficiency by chelating agents is often reported (e.g., Tsang et al., 2013a and Beiyuan et al., 2016), when metals are strongly bound to minerals of Fe, Al, and Mn as well as organic matter or when metal (co-)precipitates are present due to high concentration and aged contamination.

In order to enhance the removal of metals strongly bound on Fe/Mn oxides and organic matter, recent studies on soil and groundwater remediation have attempted to use: (i) reducing agents such as sodium oxalate, ascorbic acid, hydroxylamine hydrochloride, and sodium dithionite (Im et al., 2015; Kim et al., 2015); and (ii) oxidizing agents such as hydrogen peroxide and persulphate (Pham et al., 2012; Yan and Lo, 2012; He et al., 2013; Liu et al., 2014). In view of their promising enhancement for contaminant extraction/degradation, these reducing/oxidizing agents may be employed before chelating agents in a two-step soil washing. A recent study also revealed that sequential washing with mineral/organic acids and chelating agent (e.g., phosphoric acid-oxalic acid-EDTA) facilitated dissolution of residual fraction and reduced labile fractions of the remaining metals (Wei et al., 2016). Hence, this study evaluated if the selective dissolution of oxides and organic matter could desorb strongly bound metals directly/indirectly and thereby facilitating subsequent EDDS extraction.

The effectiveness of metal extraction is of importance with regard to remedial goals, prudent attention should be paid to the fate of residual metals and the associated environmental impact for ensuring safe reuse of the treated soil (Udovic and Lestan, 2009; Tsang et al., 2013a). For example, the metal re-distribution to weakly bound fractions and increase of metal mobility were observed in the treated soils (Zhang et al., 2010; Tsang and Hartley, 2014; Yang et al., 2015). In addition to physicochemical properties, soil enzyme activity could serve as a representative evaluation index of the remediation performance (Tica et al., 2011; Im et al., 2015), because residual metals would alter the substrate, protein-active groups, or enzyme-substrate complex in soils. In particular, dehydrogenases (intracellular enzymes) play a significant role in the oxidation of organic matter and is indicative of the average microbial population, while urease and acid phosphatase activity reflect the biogeochemical cycling of nitrogen and phosphate in soil (Moreno et al., 2001; Caldwell, 2005). Therefore, this study assessed the above enzyme activities together with available nutrients (nitrogen, phosphorous, and organic carbon) before and after sequential washing.

In this study, we examined the potential of sequential washing employing selective chemical agents followed by EDDS for an e-waste recycling site. In addition to the metal removal efficiency, the associated impact of residual metals was examined by means of leachability, bioaccessibility, and sequential extraction tests as well as health risk calculation. The reuse value and ecological quality of the treated soil were also evaluated in terms of cytotoxicity (Microtox), enzyme activities, and available nutrients.

2.5.3 *Phytoavailability and Mobility of Lead and Arsenic in a Contaminated Soil after Stabilization by Pine Sawdust Biochar under Dynamic Redox Conditions*

Metal(loid) contamination of soils due to anthropogenic activities threats agriculture sustainability (Park et al., 2016). For instance, metal(loid)s including arsenic (As) and lead (Pb) are very toxic to plant, animals and humans because of their high bioavailability and listed among the priority hazardous contaminants (Shih et al., 2016). Few studies on anionic and cationic metal(loid) remediation have been investigated (Fang et al., 2016). Nowadays, the goals of soil remediation technologies have changed from reducing the total amount to the easily mobilized and bio-/plant-available amount of metal(loid)s. Low-cost amendments (industry by-products, agricultural wastes, and carbonaceous recycled products (e,g. compost and biochar), and inorganic natural minerals) successfully reduce the mobility and phytoavailability of trace metal(loid)s in soil by adsorption, (co-)precipitation, surface complexation, and cation exchange (Kumpiene et al., 2008; Ahmad et al., 2014b; Tsang et al., 2014; Zhang et al., 2015). Biochar, a by-product of pyrolysis produced under limited oxygen condition, become a popular amendment to immobilize the trace elements in contaminated soils (Beesley et al., 2011). It is because of the cost-effective stabilization of the pollutants, as well as the ability of carbon sequestration and enhancement of soil quality by providing a large amount of nutrients, improving the moisture retention, and reinforcing the enzymatic and microbial activity (Beesley et al., 2011; Lehmann et al., 2011; Awad et al., 2013; Ahmad et al., 2014b; Ahmad et al., 2016a; Ahmad et al., 2016b). The characteristic of biochar was decided chiefly on the various feedstocks that can be agricultural or industrial wastes, industrial by-products, sludge, and manures, as well as the pyrolysis temperature. In general, biochar produced at a lower temperature (< 300 ˚C) have more oxygen-containing functional groups; while those produced at a higher temperature (500-700 ˚C) are considered have higher surface area and more micropores (Uchimiya et al., 2011c; Ahmad et al., 2012b; Rajapaksha et al., 2014). These above factors influence the capacity of immobilization. It is also found that biochar have different effects on the mobility/availability of trace elements in soils. The mobility of Pb was successfully reduced as supported by many cases (Cao et al., 2011; Park et al., 2011a; Uchimiya et al., 2012), whereas the mobility of As was enhanced due to the rising soil pH, release of phosphorus and the increasing amount of arsenite which is more easily mobilized (Beesley and Marmiroli, 2011; Park et al., 2011b).

A large number of studies focused on the mobility/phytoavailability of metal(loid)s after application of amendments; yet the long-term stability of stabilization under variable environmental conditions is still questioned (Beesley et al., 2010; Tsang et al., 2013b; Beiyuan et al., 2016; Rizwan et al., 2016). In application, the alter of redox conditions influences the fate of metal(loid)s indirectly via changes in pH, dissolved organic carbon (DOC), and the redox chemistry of iron (Fe), manganese (Mn), and sulfur (S), to which metal(loid)s might be fixed on (Du Laing et al., 2009b; Frohne et al., 2015; Schulz-Zunkel et al., 2015). For instance, increasing E_H favored the oxidation processes which generate protons and subsequently decrease pH which significantly influence the mobility of elements (Yu et al., 2007). The solubility of arsenate (As^V) increases in soil with increasing pH which in a range of 3-8, whereas arsenite (As^{III}) acts in an opposite way (Fitz and Wenzel, 2002). Moreover, Fe/Mn (hydr)oxides were reduced to Fe^{2+} and Mn^{2+} as redox potential decreased, so the metals bonded to these parts or adsorbed on the surface of the minerals became more mobile in soil. In addition, metal(loid)s with multiple valences are affected directly by the variation in redox conditions, therefore changed their mobility behaviors. Under reduction condition, an increment of arsenic mobility can be observed as As^{V} is reduced to the more mobilized and toxic As^{III}, while the addition of biochar could enhance the reduction (Frohne et al., 2011; Frohne et al., 2015; Choppala et al., 2016).

The E_H condition variation could affect the biochar immobilization for the metals, while only a few studies focus on it (Rinklebe et al., 2016). Thus, we aimed to investigate the liability of stabilization by amendments on a field-contaminated soil (mainly by As and Pb) via evaluation of the mobility and phytoavailability under dynamic E_H conditions. A 105-day pre-incubation was conducted for all amendments included the control soil to provide a stable immobilization. To study the difference of amendments under oxidizing and reducing conditions, an agricultural waste, pine sawdust, and two types of biochar produced by it at two different temperatures were used.

2.5.4 Integrating EDDS-enhanced washing with low-cost stabilization of metal-contaminated soil from an e-waste recycling site

Widespread soil contamination presents a long-term risk to human health and surrounding ecosystems. Improper e-waste recycling and disposal are one of the major sources of soil contamination, which releases large quantities of inorganic (Cu, Pb, Cd, etc.) and organic pollutants (such as polychlorinated biphenyls and polybrominated diphenyl ethers). Particular attention should be paid to Pb release for its highly toxic and potentially carcinogenic nature; moreover, children living near e-waste recycling sites had a higher blood lead level that impaired their intelligence development (Canfield et al., 2003; Zheng et al., 2008).

Chelant-enhanced extraction by means of *in-situ* phyto-remediation or *ex-situ* soil washing has been widely investigated to develop effective remediation technologies for metal (Nowack et al., 2006; Lestan et al., 2008; Zhang and Tsang, 2013). Readily biodegradable EDDS (ethylenediaminedisuccinic acid) was proposed to replace persistent chelants such as EDTA (ethylenediaminetetraacetic acid) that was commonly used in the previous century (Yip et al., 2010a; Almaroai et al., 2012; Begum et al., 2012). However, extraction efficiency was often found insufficient to meet remediation goals due to facile biodegradation and metal exchange in soils (Komárek et al., 2010; Lo et al., 2011a; Wang et al., 2012). As a result, prolonged washing duration and/or multiple washing steps might be required (Arwidsson et al., 2010; Lo et al., 2011b; Voglar and Lestan, 2012), which would increase treatment costs, chemical use and energy consumption.

In-situ soil stabilization has in recent years gained increasing popularity as a low-cost and low-carbon alternative remediation method, employing locally abundant industrial by-products and agricultural waste as soil amendments for in-place metal sequestration. The mobility, phytotoxicity and bioavailability of metals in contaminated soils were suppressed via adsorption, cation exchange, surface complexation, (co-)precipitation, surface precipitation, and/or transformation/incorporation on the surface of soil amendments (Kumpiene et al., 2008; Tica et al., 2011; Komárek et al., 2013). Among the amendment materials, biochar has captured extensive attention for soil stabilization (Mohan et al., 2014;

Zhang and Ok, 2014; Rajapaksha et al., 2016), which could be produced from agricultural waste, sewage sludge, and manure under limited oxygen conditions. Biochar was shown to improve soil properties (soil aggregation, water holding capacity, nutrient availability and microbial activity), crop yield, and act as a carbon sink (Ahmad et al., 2016a; Hussain et al., 2016; Rizwan et al., 2016). The leachability of metal(loid)s, such as Cd, Cu, Pb, Zn, and As, was also proved to be significantly reduced (Cao et al., 2009; Uchimiya et al., 2011b; Lu et al., 2014; Ahmad et al., 2016b). Similarly, CFA produced from power generation was also found useful for stabilization of metal-contaminated soil because of its Fe-, Al-, and Ca-rich components (Komárek et al., 2013; Tsang et al., 2014).

Recent studies have attempted to evaluate and compare the effectiveness of extraction-based and stabilization-based approaches (Bolan et al., 2014; Tsang and Yip, 2014). In chelant-enhanced extraction, residual metal-chelant complexes would shift metal distribution to weakly bound fractions and hinder (co-)precipitation in the treated soils, arousing concerns about long-term metal release and on-site reuse (Tsang and Hartley, 2014; Yang et al., 2015). On the other hand, for stabilization approach, short-term leaching potential and long-term stability/bioaccessibility of the immobilized metals in the amended soils would require further investigation (Komárek et al., 2013; Bolan et al., 2014). As revealed by recent studies, metal release under continuous leaching and acidic conditions might still occur despite soil stabilization with biochar or dewatered sludge (Houben et al., 2013; Tsang et al., 2013b). Therefore, this study proposes to employ biodegradable EDDS to accelerate extraction of labile and weakly bound metals from contaminated soils, and subsequently applies biochar and CFA as soil amendments for effective sequestration of residual metals. This novel integration hypothesizes that the increased mobility of residual metals after chelant application can be resolved by re-distribution towards biochar and CFA, while potential leachability and bioaccessibility of metals immobilized by soil amendments can be further mitigated.

This study evaluated the change of metal leachability and bioaccessibility after 2-h EDDS washing, 2-month stabilization with biochar and CFA, and both treatments in sequence, respectively. Standard leaching tests of toxicity characteristic leaching procedure (TCLP) and synthetic precipitation leaching procedure (SPLP), simplified bioaccessibility extraction test (SBET), diethylenetriamine pentaacetic acid (DTPA) extraction, and human health risk assessment were conducted for a field-contaminated soil from an e-waste recycling site after the various treatments.

2.5.5 Risk Mitigation by Waste-Based Permeable Reactive Barriers for Groundwater Pollution Control at E-Waste Recycling Sites

Pollution levels of metals and the associated health risks were found to be moderate to high in developed coastal regions and former industrial areas (Luo et al., 2012a). In particular, uncontrolled e-waste recycling activities such as strong acid leaching and open burning of dismantled components of electronic and electrical wastes (e-waste) at numerous recycling sites have resulted in high levels of metals (e.g., Cd, Cu, and Pb) in paddy fields, polished rice, edible vegetable tissues, and human blood and placenta in surrounding areas (Fu et al., 2008; Zheng et al., 2008; Guo et al., 2010; Luo et al., 2011). Phytoremediation, soil washing, and soil amendments are potentially useful remediation approaches for the contaminated soils (Ok et al., 2011a; Wang et al., 2012; Zhang et al., 2012; Tsang et al., 2013a; Hartley et al., 2014; Rajapaksha et al., 2015), yet the cleanup of contaminated groundwater at e-waste recycling sites has received much less attention, which presents a major exposure pathway to impose human health risks.

In-situ remediation of contaminated groundwater using permeable reactive barriers (PRBs) has proved to be a promising passive treatment technology, which intercepts the contaminated plume and transforms/immobilizes the pollutants over the reactive media (Di Natale et al., 2008; Liu et al., 2008; Tsang et al., 2009a). Materials with strong adsorption ability are recommended to be used as the reactive media. Once the absorbent get saturated, it would be replaced by new fill materials and disposed as hazardous waste in landfill, which depends on its liability and based on the results of monitoring. Zero-valent iron has been the most popular material for PRBs as it can remove metals by reduction, adsorption, and/or precipitation. However, continuous iron dissolution should be carefully considered when deploying zero-valent iron in field (Tsang et al., 2013b; Tsang and Yip, 2014). Although there is no health-based guideline value for iron in drinking water (WHO, 2011), high iron in the root zone may induce oxidative stress on plants and lower crop yield, especially under anaerobic conditions of paddy field (Ramírez et al., 2002; Jucoski et al., 2013). Therefore, increasing research is focused on exploring alternative materials for PRBs technology, such as zeolites, organic materials, and industrial by-products (Conca and Wright, 2006; Boni and Sbaffoni, 2009; Hashim et al., 2011).

This study investigated six low-cost adsorbents for PRBs treatment of contaminated groundwater at e-waste recycling sites: (i) natural minerals – limestone and apatite; (ii) industrial by-products –AMDS and CFA; and (iii) products of waste recycling –FWC and wood-derived biochar. Previous studies showed that limestone transformed exchangeable Cd and Pb into more stable carbonate faction in the soil (Hussain et al., 2011; Lee et al., 2011), while apatite formed low-solubility phosphate precipitates of Pb, Cd, Zn, and Cu (Conca and Wright, 2006; Oliva et al., 2010). As a by-product of acid mine drainage treatment, AMDS possessed high surface area and reactive Fe-/Al-hydroxyl groups that effectively immobilized phosphate and metals from wastewater (Cui et al., 2011; Qi et al., 2011; Wang et al., 2013). Similarly, CFA from thermal power plants contained abundant calcium hydroxide and silica-alumina compounds for metal adsorption and precipitation (Wang and Wu, 2006; Ruttens et al., 2010; Moon et al., 2013b; Tsang et al., 2014). On the other hand, organic carbon-rich FWC and biochar proved effective for improving soil qualities and immobilizing metals via surface complexation with oxygen-containing functional groups (Tong et al., 2011; Paradelo and Barral, 2012; Uchimiya et al., 2012; Tsang et al., 2013b; Ahmad et al., 2014b). Nevertheless, it should be noted that immobilization by adsorption and precipitation may be reversible upon dynamic changes in environmental conditions (e.g., pH and redox).

Acidic rainfall in industrialized areas (where e-waste recycling is based) would leach through the contaminated soil and facilitate desorption of metals, polluting shallow groundwater and causing human health risks. Recent findings revealed that soil amendments may be unable to immobilize the contaminants indefinitely under continuous leaching at acidic pH (Houben et al., 2013; Tsang et al., 2013b), and the stability of the immobilized metals and metalloids is a concern that needs long-term monitoring (Farrell and Jones, 2010; Bolan et al., 2014; Tsang et al., 2014). Thus, the potential longevity and risk mitigation of waste-based PRBs is worth investigation for pollution control of contaminated groundwater at e-waste recycling sites.

Therefore, the objective of this study was to explore the use of low-cost adsorbents for PRBs treatment of polluted groundwater, which was simulated using an unbuffered acidic solution of synthetic precipitation leaching procedure of an e-waste contaminated soil. Batch adsorption isotherms were conducted to evaluate the characteristics of these adsorbents, then column tests were conducted with continuous leaching and the breakthrough curves were analyzed with respect to potential human health risks.

CHAPTER 3. Materials and Methods

3.1 Characteristic of Soils

3.1.1 The E-Waste-Contaminated Soil (for Chapter 4, 5, 7, and 8)

The field-contaminated soil was collected from an e-waste recycling hotspot of Qingyuan City, Guangdong Province, China. The soil was highly contaminated by Cu, Zn and Pb, due to uncontrolled recycling activities such as strong acid leaching and burning of dismantled components. Soil samples were air-dried and passed through 2-mm sieve. The basic characteristics of the soil were listed in Table 3-1. Soil pH was measured after 30 min shaking at a soil-to-water ratio of 1:2 in an end-over-end rotator.

TABLE 3-1 Characteristics of the e-waste soil

Cu/Zn/Pb (mg kg^{-1})	1280/706/520
Fe/Al/Ca/Mg/Mn (%)	1.33/3.55/5.62/0.150/0.0200
Soil pH	5.30
Soil Organic Matter (SOM, %)	4.81
Available Phosphorous (mg kg^{-1})	61.0
Available Nitrogen (mg kg^{-1})	1990

3.1.2 As and Pb Contaminated Soil (Only for Chapter 6)

The contaminated soil was collected from the upper 30 cm of a previous agricultural field in Gongju Chungcheongnam-do Province, Korea near the Tancheon mine. The field was banned for agricultural usage after detection of a high content of As and Pb in the soil. Soil samples were air-dried and sieved under 2 mm before use. Metal contents in soil were analyzed according to the USEPA Method 3051a. Soil pH was measured at a soil-to-water ratio of 1:5 kg L^{-1}. Table 3-2 shows the soil properties.

TABLE 3-2 Characterisitics of the contaminated Korean soil

Properties	
pH	4.90
EC (dS m^{-1})	0.100
Texture	Loamy Sand
Exchangeable cations (cmol kg^{-1})	
K	14.9
Mg	5.40
Na	1.30
Ca	28.1
Metal(loid)s (mg kg^{-1})	
Pb	1550
Cd	2.70
As	1650
Cr	64.6
Zn	191
Cu	62.3
Ni	17.1
Hg	0.0521

3.2 Experimental Design for Different Sections

3.2.1 Multiple Washing Schemes and Combined Application of EDDS and EDTA for Soil Washing of an E-Waste Contaminated Soil

3.2.1.1 Individual and Mixed Chelants Preparation

For soil washing experiments, individual solutions of EDDS and EDTA were prepared by dissolving 35% Na_3EDDS solution (Sigma-Aldrich) or Na_2EDTA (Ajax chemicals) into 10 mM sodium nitrate ($NaNO_3$, Riedel-de Haen) and 2 mM MES (2-morpholinoethane-sulfonic acid, Sigma-Aldrich) buffer. Their mixture of EDDS and EDTA was prepared at 1:1 molar ratio. The solution pH was adjusted to 5.5 ± 0.05 (using 0.1 N HNO_3 or NaOH), which was comparable to the indigenous soil pH. The EDDS solutions were prepared with 1 g L^{-1} sodium azide (NaN_3, International Laboratory USA), wrapped in aluminum foil paper and kept in the dark at 4 ^{o}C to prevent the possible biodegradation during the experiment.

3.2.2 Multiple Soil Washing Schemes

Figure 3-1 illustrates the design of different soil washing schemes for the purpose of maximizing the chelant utilization and metal extraction efficiency. The total molar concentrations of individual/mixed chelants corresponded to chelant-to-metal molar ratios (referred to as MR hereafter) ranging from 0.5 to 6 with respect to the sum of target metals (Cu, Zn and Pb) at the soil-to-solution ratio of 1 g : 10 mL. The soil-solution suspensions were shaken in 50-mL polypropylene centrifuge tubes (BD Falcon) using an end-over-end rotator at 30 rpm and room temperature. After specific washing time (Table 3-3), the supernatants were separated by centrifugation at 4000 rpm for 10 min, filtered through 0.45-μm membrane filters, and then digested by concentrated nitric acid for metal analysis by ICP-AES (Perkin Elmer Optima 3300DV).

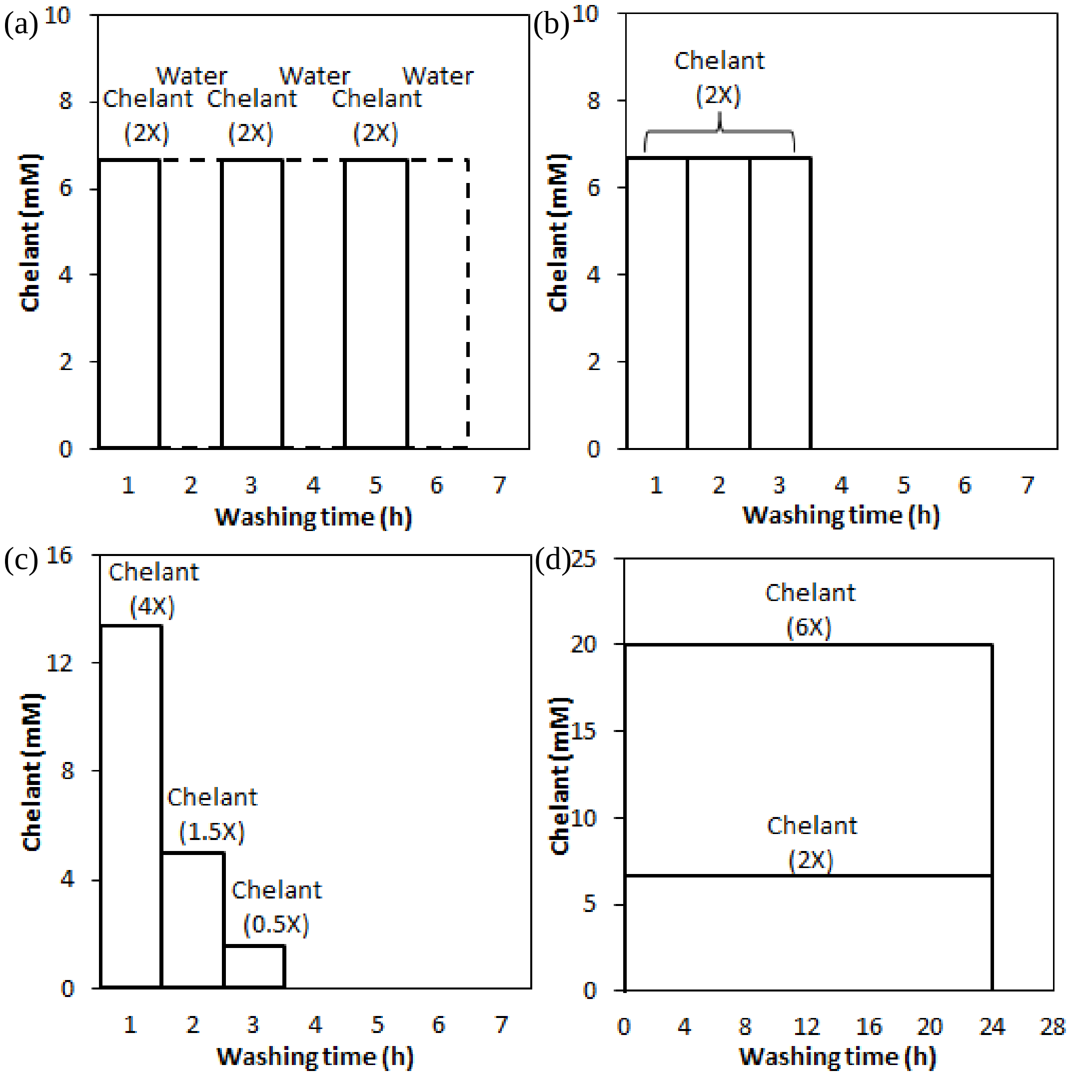


FIGURE 3-1 Multi-pulse washing scheme A (a) with water rinsing, (b) B without washing: C for chelating agent washing, W for water washing, (c) gradient washing scheme: C1, C2 and C3 means MR4, MR1.5 and MR0.5 to target metal molar ratio respectively; (d) continuous washing scheme in one dosage of chelants.

To enable progressive extraction of less labile metals from the soil, the first multi-pulse washing scheme was composed of three 1-h chelant washing steps at MR 2 (6.68 mM) followed by three deionized water (DI water) rinsing steps , i.e., 6-h washing in total (Figure 3-1a). To examine the necessity of removing newly extracted metals from the washing solution, the second multi-pulse washing scheme omitted intermittent water rinsing between the three 1-h chelant washing steps at MR 2, i.e., 3-h washing in total (Figure 3-1b). To facilitate extraction of metals that were more strongly bound to the soil, the gradient washing scheme employed an intensive use of chelant at MR 4 (13.36 mM) in the first 1-h chelant washing step, followed by less concentrated solutions at MR 1.5 (5.01 mM) and MR 0.5 (1.67 mM) in the second and third chelant washing steps, respectively (Figure 3-1c). For comparison, the total washing time and the total chelant consumption were selected to be the same as those of the second multi-pulse washing scheme.

To reduce the volume of washing solution and subsequent wastewater treatment, continuous washing scheme involved a 24-h washing at MR 2 (6.67 mM, representing the most widely studied condition in the literature) and MR 6 (20.03 mM, indicating the maximum possible extent of metal extraction using the same total chelant consumption), respectively (Figure 3-1d). Compared to multi-pulse and gradient washing schemes, a longer washing period of 24 h was selected for continuous washing to reach an apparent equilibrium based on preliminary results, but the throughput rate (i.e., tonnes of soils to be treated per day) would be compromised in field application. Three chelant solutions were evaluated for each of the above washing schemes, including EDDS, EDTA, and EDDS-EDTA mixture (1:1). The chelant concentrations used in this study (1.67-20.03 mM) were comparable to the most commonly used range in the literature. All the experiments were conducted in duplicate (in triplicate if necessary) to ensure reproducibility and reliability, and the average values with deviations were reported. The Duncan's multiple range tests were used to determine the statistical significance ($p < 0.05$) between different soil washing schemes using the same chelant solution using computer program SPSS 17.0 for

Windows (SPSS, USA).

TABLE 3-3 Detailed designed of various washing schemes.

Washing scheme	**Concentration, (mM)**	**Chelating washing time, (h)**	**Others**
Multi-pulse washing scheme (A)	6.67 (MR 2)	3 × 1 hour	With 3 × 1 hour DI water washing
Multi-pulse washing scheme (B)	6.67 (MR 2)	3 × 1 hour	Without DI water washing
Gradient washing scheme	MR 4, MR 1.5 and MR 0.5 respectively	3 × 1 hour	
Continuous washing scheme (A)	6.67 (MR 2)	24 hour	
Continuous washing scheme (B)	20.0 (MR 6)	24 hour	

3.2.2.1 Speciation Modelling, Leachability, Bioaccessibility, and Health Risk Calculation

To calculate the solution speciation of metals and chelants in each step of different soil washing schemes with individual and mixed chelants, the programme Visual MINTEQ version 3.0 (Gustafsson, 2012) was employed with the measured metal concentrations (Cu, Zn, Pb, Al, Fe, and Ca), concentrations of EDDS and/or EDTA, dissolved organic matter (DOM) concentrations, solution pH, and background ions (Na and NO_3^-). Detailed information is provided in Section 3.10. Toxicity characteristic leaching procedure (TCLP, USEPA Method 1311) was employed to evaluate the residual leachability of target metals (section 3.3.1). In addition, to assess the bioaccessibility of residual metals in the treated soils, an in vitro simplified bioaccessibility extraction test (SBET) was conducted to simulate acidic digestion in a human stomach (Section 3.3.3). Also, for comparison purpose, a theoretical and non-site-specific calculation of non-cancer and cancer risks for adults and children were performed using the bioaccessible fraction based on the SBET results (Section 3.9).

3.2.3 Selective Dissolution Followed by EDDS Washing of an E-waste Contaminated Soil: Extraction Efficiency, Fate of Residual Metals, and Impact on Soil Environment

3.2.3.1 Two-Step Soil Washing by Selective Chemical Agents and EDDS

A two-step soil washing was employed to selectively extract the strongly bound metals on Fe/Mn oxide minerals and/or organic matter. The first step applied selective chemical agents for mineral dissolution or organic matter oxidation liberating the target metals, followed by the second step applied EDDS (35% Na_3EDDS, Sigma-Aldrich) to complex with labile or weakly bound metals for effective extraction from the soil surfaces. Four types of chemical agents were selected based on promising results in the literature: (a) reductants (i.e., dithionite-citrate-bicarbonate (DCB, $Na_2S_2O_4$ in buffer) and acidified hydroxylamine hydrochloride (NH_2OH-HCl)); (b) oxidants (i.e., potassium peroxymonosulphate (OXONE, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), sodium hypochlorite (NaOCl), and hydrogen peroxide (H_2O_2)); (c) alkaline solvents (i.e., NaOH and $NaCO_3$); and (d) naturally present organic acids (i.e., oxalate and citrate).

Table 3-4 summarizes the corresponding extraction conditions including the concentrations of reagents, pH values, washing duration, and operating temperature. Citrate, oxalate, and hydroxylamine hydrochloride were selected to study the effect of dosage, i.e., high dosage corresponding to the empirical values for complete dissolution (Shang and Zelazny, 2008), and low dosage corresponding to the amount of oxide fraction of sequential extraction. The EDDS concentration was selected to achieve 1:1 EDDS-to-metal molar ratio (i.e., 3.34 mM), and the solution pH was 5.5 in view of the soil pH (5.3). Background solution was composed of $NaNO_3$ (10 mM), MES buffer (2-morpholinoethane-sulfonic acid, 2 mM), and biocide (0.2 g L^{-1} NaN_3), for the sake of results comparison under constant ionic strength and pH without biodegradation. All the washing tests were conducted at a soil-to-solution ratio of 1:10 g mL^{-1} for 2 h using an end-over-end rotator at 30 rpm and 20±2°C. The experiments were performed in 50 mL polypropylene centrifuge tubes in the dark, and the supernatants were separated by centrifugation at 4000 rpm for 10 min followed by 0.45-μm membrane filtration. The solution samples were digested in concentrated HNO_3 and stored in 5% HNO_3 matrix under 4°C before ICP-OES analysis. The Duncan's multiple range tests ($p < 0.05$) (IBM SPSS Statistics 22) were used to determine the statistical differences in extraction efficiency after sequential washing.

3.2.3.2 Leachability, Bioaccessibility Test, Sequential Extraction, and Health Risk Calculation

The leachability and bioaccessibility of the metals in the soil residue were evaluated before and after chemical-assisted washing by the TCLP and SBET method (section 3.3.1 and 3.3.3) respectively. Health risk assessment was calculated based on the results of orally ingested bioaccessible fraction (BAF %) that described in detailed in section 3.9. The distribution of metals in the untreated/treated soil was assessed using a five-step Tessier sequential chemical extraction (Section 3.6, Table 3-7) for selected washing reagents (hydroxylamine hydrochloride, oxalate, and citrate) that revealed higher extraction efficacy, which were operationally defined yet indicative of binding strength.

3.2.3.3 Cytotoxicity, Enzyme Activities, and Available Nutrients

Treated soils were further evaluated for cytotoxicity (Section 3.4), enzyme activities (dehydrogenase, acid phosphatase, and urease activity, Section 3.5), available nitrogen and phosphorous, and organic carbon (OC) (Section 3.7) after washing by selected promising methods (i.e., hydroxylamine hydrochloride, oxalate, and citrate that showed higher extraction efficiency).

TABLE 3-4 Detailed experimental design of selective dissolution part

	Chemical formula	Concentration and pH	Condition
Mineral Oxides			
DCB (sodium dithionite buffered with citrate and bicarbonate)	$Na_2S_2O_4$	0.4:1:10 g:g:mL at pH 7.30	2-h water bath at 75ºC
Hydroxylamine hydrochloride	NH_2OH-HCl	Low dosage (L): 1 × $[Me]_{Fe/Mn\ Ox}$ (2.20 mM) High dosage (H): 0.250 M	2-h shaking[a]
Ammonium citrate	$HOC(CO_2NH_4)(CH_2CO_2NH_4)_2$	Low dosage (L): 1 × $[Me]_{Fe/Mn\ Ox}$ (2.20 mM) High dosage (H): 0.300 M	2-h shaking[a]
Ammonium oxalate	$(NH_4)_2C_2O_4 \cdot H_2O$	Low dosage (L): 1 × $[Me]_{Fe/Mn\ Ox}$ (2.20 mM) High dosage (H): 0.200 M	2-h shaking[a]
Sodium pyrophosphate	$Na_4P_2O_7 \cdot 10H_2O$	0.100 M at pH 10	2-h shaking[a]
Sodium carbonate	Na_2CO_3	0.500 M	2-h water bath at 95 ºC
Sodium hydroxide	NaOH	0.500 M	2-h water bath at 95 ºC
Organic Matter			
OXONE	$2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$	1 × $[Me]_{OM}$ (0.450 mM)	2-h shaking[a]
Sodium hypochlorite	NaClO	1 × $[Me]_{OM}$ (0.450 mM)	2-h shaking[a]
Hydrogen peroxide	H_2O_2	1 × $[Me]_{OM}$ (0.450 mM)	2-h water bath at 85ºC

[a] End-over-end rotation at 30 rpm.

3.2.4 Phytoavailability and Mobility of Lead and Arsenic in a Contaminated Soil after Stabilization by Pine Sawdust Biochar under Dynamic Redox Conditions

3.2.4.1 Amendment Materials

Biomass of pine sawdust (BM) was collected from a sawmill company in Seoul, South Korea and washed with deionized water, air dried, ground and sieved under 1 mm. Pine sawdust biochar, which was successfully applied, were produced at 300 ˚C (BC300) and 550 ˚C (BC550) with a heating rate of 7 ˚C min^{-1} according to the described method in Lou et al. (Lou et al., 2016a, b). The detailed characterization of BC300 and BC550 were described by Lou et al. (Lou et al., 2016a, b). Table 3-5 provides the physiochemical characteristics of BM, BC300, and BC550.

TABLE 3-5 Selected properties of pine sawdust biomass (BM), biochar produced at 300 ºC (BC300) and biochar produced at 550 ºC (BC550).

	Unit	BM	BC300	BC550
pH [H2O][1]		5.11	5.86	7.37
EC [dS m^{-1}]		96.9	85.4	91.65
Ultimate analysis[2]				
Molar O/C		0.660	0.330	0.180
BET surface area[2,3]	[m^2 g^{-1}]	-	<1	189 ± 3.2

[1] pH determined in 1:20 soil-water suspension
[2] adopted from (Lou et al., 2016a)
[3] according to (Brunauer–Emmett–Teller) BET method

3.2.4.2 Experiment under Pre-Set Redox Conditions

To simulate different redox conditions under flooding, an automated biogeochemical microcosm system (MC) was used in this study. Technical details are provided by Yu and Rinklebe in 2011, and successfully applications of this microcosm system can refer to the previous publications (Antić-Mladenović et al., 2010; Frohne et al., 2011; Frohne et al., 2015; Rinklebe et al., 2016). Flooding conditions in MCs were prepared with 210 g of incubated control soil (CS) and soil with different amendments (S&BM, S&BC300, and S&BC550) which were sieved < 150 µm to prevent the damage of the glass container of MCs and 1680 mL tap water. Four MCs for each treatment were used as replicates; thus, 16 MCs were used in total. Data of E_H and pH values, which measured every 10 min, are given as averages in this study. Ten defined E_H windows were examined (from -300 to 250 mV) which were set 24 h before sampling and maintained by the automated flushing of N_2 and synthetic air/O_2. The maximum, minimum and average E_H values of 6 hours before sampling were listed in Table 6-3 for each defined E_H window. Redox potential of soil suspension was allowed to decline for a prolong period of time and then, accelerated by continuously flushing the MCs with N_2. The deepest E_H value was around -200 mV for S&BM. The pattern of E_H and pH, as well as each sampling point, are presented in Fig. 6-2. The initial sampling was conducted after one-hour stirring in the MCs. Slurry samples (65 mL) were collected by a syringe, centrifuged for 15 min at 5000 rpm and then filtered by a 0.45-µm Millipore filter membrane (Whatman Inc., Maidstone, UK) immediately under N_2-atmosphere. To avoid any effect of oxygen, the entire sample separation was carried out in a glove box (MK3 Anaerobic Workstation Model MARK3, UK) which maintained the oxygen concentration within (0.0 – 0.1 %). The soil samples were kept at 4 ˚C before the phytoavailability and mobility test was conducted.

TABLE 3-6 The definition of E_H windows for contaminated soil (CS), and soils treated with pine sawdust biomass (S&BM), biochar produced at 300 ^oC (S&BC300) and biochar produced at 550 ^oC (S&BC550) under various E_H conditions. (200 and 100 redox windows were reached twice after 250 mV, while the second time were presented as 200’ and 100’, respectively).

Defined E_H Window	**E_H 6 h Before Sampling (mV) Control**			**E_H 6 h Before Sampling (mV) Biomass**			**E_H 6 h Before Sampling (mV) Biochar300**			**E_H 6 h Before Sampling (mV) Biochar550**		
	Min.	**Max.**	**AVG.**	**Min.**	**Max.**	**AVG.**	**Min.**	**Max.**	**AVG.**	**Min.**	**Max.**	**AVG.**
Initial	307	323	317	225	283	257	263	302	282	186	223	206
-300	-334	-238	-294	NA	NA	NA	-335	-182	-295	-362	-315	-333
-200	-253	-186	-220	-213	-160	-202	-323	-156	-240	-265	-187	-242
-100	-130	-83	-107	-157	-97	-132	-163	-103	-132	-139	-68	-126
0	-20	-6	-12	-55	0	-24	-20	19	-1	-11	17	-5
100	79	82	80	93	120	107	80	120	98	89	105	93
200	216	220	218	212	219	216	200	219	210	189	214	198
250	253	259	255	239	254	248	213	257	241	220	247	234
200’	187	245	214	179	184	180	173	230	199	154	183	169
100’	129	226	178	107	124	113	109	165	148	89	110	73

Min. = Minimum, Max. = Maximum, AVG. = Average, and NA = Not Applicable

In total, 16 MCs were used in this study, which allowed for 4 replicate samples for each type of treatments (CS, S&BM, S&BC300 and S&BC550). To reach the deepest redox value, extra carbon source (15 g wheat straw (34.6 % carbon) and 5 g glucose) were added to the soil samples to provide an additional carbon source for microorganisms which consume the oxygen, while the dosage was decided according to our preliminary experiment. The straw contained 49.8, 1.6, 63.3, 4.5, 268.8 and 11.8 mg kg^{-1} of Al, Fe, Cu, Mn, S, and Zn respectively. Concentrations of As and Pb were below the detection limits. Flushing with N_2 was also conducted to decrease the E_H. After reaching the lowest E_H (defined E_H windows: -300 mV), the E_H was controlled by flushing synthetic air and/or oxygen to increase the E_H. Nitrogen gas was also used to decrease the E_H automatically to reach the next window and maintain the E_H value 24 h before sampling. The E_H, pH, and temperature in the MCs were recorded at every 10 min and stored in a data logger.

The average of 4 replicate MCs was calculated for the CS and each treatment; the number of measurements of E_H and pH was 3,121, 3,109, 3,156 and 3,115 for CS, S&BM, S&BC300 and S&BC550 respectively. The pH electrode had a technical error for one of the four MCs in S&BM and S&BC300 respectively; therefore, pH was measured manually during sampling. The total incubation period in MCs lasted for approximately 22 days (530 hours).

Figure 3-2 shows the basic setup of MCs. The detailed components includes: (1) thermometer, (2) pH electrode, (3) E_H electrode, (4) dispersion tube for nitrogen (N_2), (5) dispersion tube for oxygen (O_2), (6) sampling tube, (7) overhead stirring system, (8) double-hull incubation vessel, (9) temperature control system (not using in this section), (10) data loggers for recording pH, E_H, and temperature every 10 min, (11) automatic E_H controlling system by N_2 and O_2 valves; (12) a control computer for data loggers, pump, and E_H controlling system.

3.2.4.3 Metal(loid) Phytoavailability and Mobility

The phytoavailability and mobility of metal(loid)s under varied EH conditions of CS, S&BM, S&BC300, and S&BC550 were studied by methods described in Section 3.3.2 and 3.3.5 respectively. To maintain the samples in a stable EH condition, all the samples were collected under oxygen-avoiding conditions. Also, the extraction solutions of these two tests were added to the soil under an anoxic condition in the glove box (nitrogen gas was used to control the oxygen content to 0.1%).

3.2.4.4 Scanning Electron Microscopy and Elemental Dot Mapping

To study the morphological and elemental composition of pine sawdust biomass and biochar produced at different temperature, scanning electron microscopy (Hitachi S-4800 with ISIS 310, Japan) images and elemental dot mapping were operated at 15 keV with energy dispersive X-ray spectroscopy (SEM-EDX) (Ahmad et al., 2014a).

3.2.4.5 Statistical Analysis

Duncan’s multiple range tests (SPSS, 22.0) were used to determine the significance levels ($p < 0.05$) for each treatment (Figs 6-3&4&6&7), within the modified sequential extraction results (Table 6-4), and the defined E_H windows for various treatments (Table 6-6). Two-factor ANOVA was studied to determine the effects of amendments and E_H conditions on metal phytoavailability and mobility (Table 6-5).

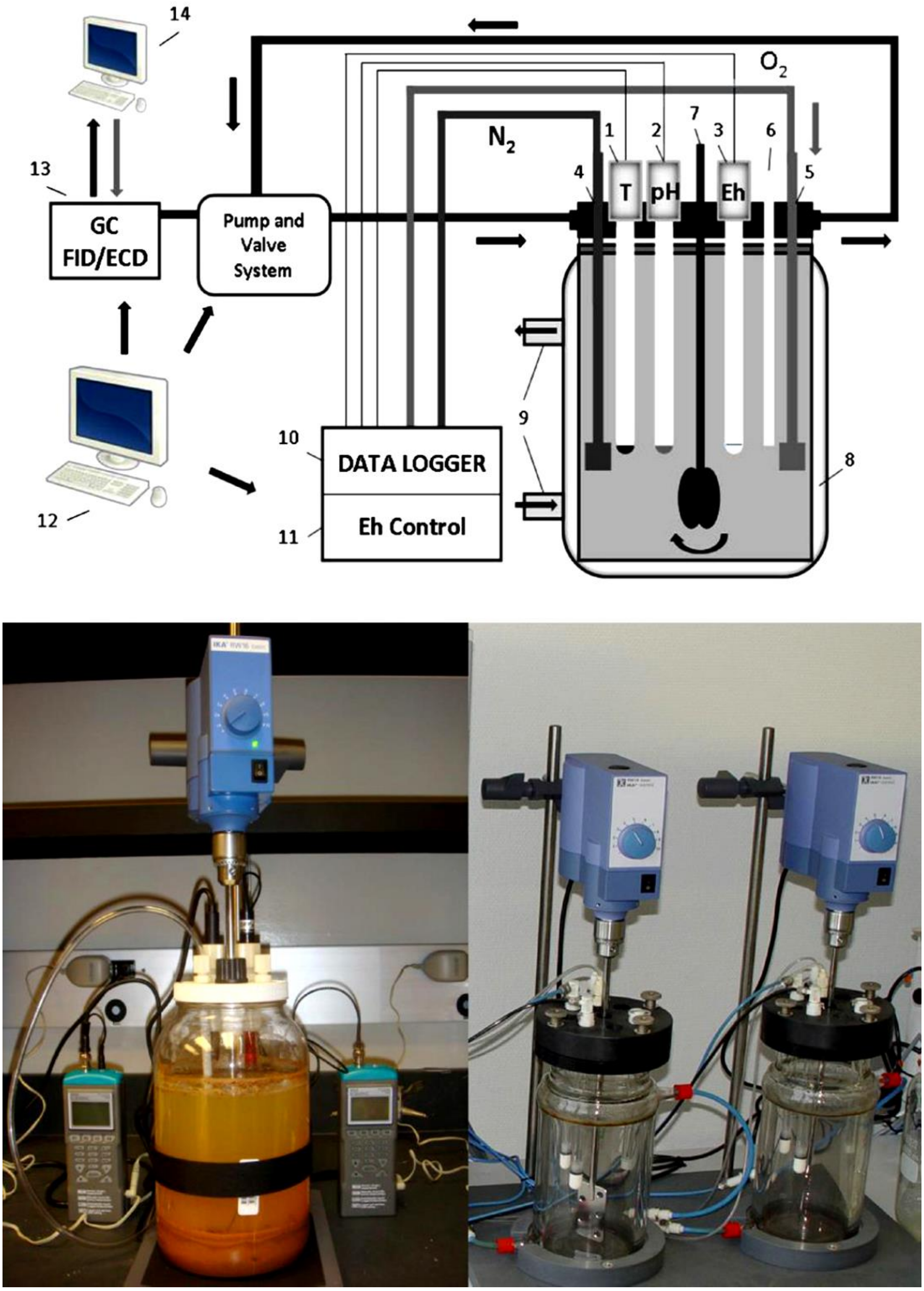


FIGURE 3-2 A schematic of a soil microcosm (above), and photos of a microcosm with automatic E$_H$ and pH measuring system (bottom left) and microcosms with temperature control system (bottom right) (Yu and Rinklebe, 2011).

3.2.5 Integrating EDDS-Enhanced Washing with Low-Cost Stabilization of Metal-Contaminated Soil from an E-Waste Recycling Site

3.2.5.1 Amendment Materials

Two types of biochar were produced at the Central Laboratory of Kangwon National University using the same feedstock (soybean stover collected from Chungju-city, Korea) at different temperatures (300 ^{o}C and 700 ^{o}C, referred to as SBC300 and SBC700). The production details were reported in our previous study (Ahmad et al., 2016b). The BET surface areas were 5.61 m^2 g^{-1} for SBC300 and 420 m^2 g^{-1} for SBC700, whereas the pH at 1:5 biochar/water suspension were 7.27 for SBC300 and 11.32 for SBC700, respectively. Biochar production and characterization were performed at the Central Laboratory of Kangwon National University, the Korea Basic Science Institute and the National Center for Inter-University Research Facilities of Seoul National University in Korea. As our biochar samples were produced from clean cellulosic biomass in uncontaminated agricultural soils, they contained negligible amounts of metals and complied with the IBI Biochar Standards (IBI Biochar Standards, 2015). Coal fly ash was obtained from a sub-bituminous coal combustion plant in the Southland Region of New Zealand. Previous results showed that CFA provided a large surface area (212 m^2 g^{-1}) and was composed of 12% merwinite ($Ca_3Mg(SiO_4)_2$), 4% calcite ($CaCO_3$), and 2% portlandite ($Ca(OH)_2$). It also contained a large quantity of poorly crystalline (amorphous) Fe and Al oxides (5700 and 6760 mg kg^{-1}, respectively), which are equivalent to an acid neutralizing capacity of 54.3% $CaCO_3$ (Wang et al., 2013; Tsang et al., 2014)

3.2.5.2 Batch Experiments

Soil washing was conducted at a soil-to-solution ratio of 1:10 g mL^{-1} in an end-over-end rotator (30 rpm) for two hours only, which could reduce costs and facilitate a high throughput rate for industrial applications. The EDDS concentration was two times of the total concentration of target metals in the contaminated soil, i.e., EDDS-to-metal molar ratio was equal to 2, which was selected in view of our previous findings (Tsang et al., 2009b; Yip et al., 2009). Hence, 6.67 mM EDDS solutions were prepared with 10 mM electrolyte $NaNO_3$ and 2 mM MES at pH 5.5. L^{-1}, where NaN_3 (0.2 g) was added to avoid potential biodegradation and the container was wrapped in foiled paper to prevent photodegradation. After 2-h washing, samples separated by centrifugation at 4000 rpm for 10 min followed by filtration through 0.45-μm filters. To eliminate the effect of entrapped and loosely bound metal-chelant complexes, the soil samples were rinsed with DI water by manual shaking for 1 min at a 1:10 g mL^{-1} ratio before subsequent experiments. In the control experiments of 2-h washing with deionized water, there was the negligible extraction of target metals from the soil (not shown) because the soil had been contaminated and aged in field before this study.

Biochar and CFA were added to the untreated and EDDS-washed soil samples at 10% by weight as follows: CFA, SBC300, SBC700, and mixture of CFA and SBC300/SBC700 at a 1:1 weight ratio (referred to as SBC300-CFA and SBC700-CFA). The water content was maintained at 70% of water holding capacity at room temperature. The amended soils were stabilized for 2 months in a box wrapped in foiled paper at room temperature (20 ± 2°C). The soil samples were weighed weekly and DI water was added to maintain the moisture content. At the end of two-month incubation, the soil samples were dried in a 60°C oven.

3.2.5.3 Leachability, Mobility, Phytoavailability, and Bioaccessibility of Residual Metals

The leachability, mobility, phytoavailability and bioaccessibility of the residual metals in the soil before and after stabilization and EDDS-extraction followed by stabilization. The detailed methods can refer section 3.3.1, 3.3.2, 3.3.3, and 3.3.4 respectively.

3.2.5.4 Statistical Analysis

Duncan's multiple range tests were performed using SPSS 22.0 for Windows (SPSS, USA) to determine the significance levels ($p < 0.05$) of differences in the results after EDDS washing and/or soil amendments.

3.2.6 Permeable Reactive Barriers for Groundwater Pollution Control at E-Waste Recycling Sites

3.2.6.1 Low-cost adsorbents

Six adsorbents were investigated in this study: limestone, apatite, acid mine drainage sludge (AMDS), CFA, biochar, and food waste compost (FWC). Apatite and limestone were purchased from Ward's Natural Science in Australia and China respectively, and then ground manually and sieved to a particle size between 0.15 and 1.18 mm. AMDS was collected from the coal processing areas of the Blackwater Treatment Plant at Stockton Mine on the west coast of New Zealand. Before the collection of sludge by sedimentation using a lamella clarifier, the AMDS was neutralized by adding hydrated lime ($Ca(OH)_2$) and then flocculated with a polymer. CFA, a fine combustion residue, was obtained from a thermal power plant in Southland, New Zealand. AMDS and CFA are naturally large in size; therefore, both were sieved to 2.00 mm before use. Biochar and FWC were donated by the Kadoorie Farm of Hong Kong and the Kowloon Bay Pilot Composting Plant, respectively, and were sieved to a particle size between 0.15 and 1.18 mm before use due to their smaller initial sizes.

3.2.6.2 Batch Sorption and Column Leaching Tests

To investigate the adsorption ability of these six materials, adsorption isotherm batch tests were conducted. Three metals, Cu, Pb and Zn, were selected given the original composition of the e-waste soil used in this study. The initial concentrations of the metals ranged from 2 to 50 mg L^{-1} (five points were chosen: 2, 5, 10, 30, and 50 mg L^{-1}); depending on the adsorption ability of each material and the results of adsorption isotherm experiments, additional metal concentrations of 100 and 500 mg L^{-1} were added when appropriate (i.e., when the material had a strong adsorption ability and the use of low metal concentrations yielded insufficient data). A solid-to-liquid ratio of 0.1 g: 40 mL was used in a 50 mL centrifuge tube, which was rotated in an end-over-end rotator at a speed of 30 rpm for 24 h at room temperature (20 ± 1 ºC) to reach equilibrium. Batch experiments were performed in duplicate, and the results are shown as averages.

Small-scale column tests were used to study the materials' adsorption ability as permeable reactive barriers. The column was 6.75 ± 0.05 cm in height, with a diameter of 1.5 cm. All adsorbents were mixed with clean sand which acted as an inert medium and had been previously screened between 0.15 and 1.18 mm, at a ratio of 1:10 by dry weight and then packed into the plastic column. Filter papers (Whatman, No. 42) were placed at the top and bottom of the column to prevent the loss of particles greater than

2.5 µm. The pore volumes (PVs) of different mixtures were determined by weighing the unsaturated and saturated columns with deionized water in the absence of air bubbles before performing the column experiments. To expel the majority of the air bubbles, all of the columns were fully saturated with a 10 mM $NaNO_3$ (Riedel-de Haën) solution at pH 5.5 ± 0.5, which was pumped at a slow flow rate of 0.25 mL min^{-1} for 60 PV using a peristaltic pump (Watson Marlow, 505S). Simulated contaminated groundwater was pumped into the columns from bottom to top at a flow rate of 1.30 mL min^{-1} during sample collection. The solutions were prepared at a pH of 4.2 ± 0.5 using $Cu(NO_3)_2$ (Scharlau), $Zn(NO_3)_2$ (Wako), and $Pb(NO_3)_2$ (Acros Organics) at concentrations determined by the results of the initial SPLP tests. For AMDS, CFA, biochar and FWC, effluent from the tops of the columns was collected for analysis every 30 PVs until 435 PVs had passed through the system. However, because the adsorption abilities of limestone and apatite had been determined in advance to be lower, the column tests for these two materials were only conducted for a total of 160 PVs by collecting samples every 10 PVs.

3.3 Leachability, Mobility, Phytoavailability, and Bioaccessibility of Residual Metal(loid)s in the Soil

3.3.1 Toxicity Characteristic Leaching Procedure (TCLP) for Leachability

Toxicity Characteristic Leaching Procedure (TCLP; USEPA Method 1311) was used to simulate the condition after decomposing in a landfill. The soil was mixed with acetic acid solution whose pH was adjusted to 4.93 ± 0.05 by 1 N NaOH at a soil-to-solid ratio of 20 L kg^{-1} and rotated in an end-over-end rotator at 30 rpm for 18 h.

3.3.2 Synthetic Precipitation Leaching Procedure (SPLP) for Mobility

The Synthetic Precipitation Leaching Procedure (SPLP; USEPA Method 1312) is simulating slightly acidic rainwater used sulfuric and nitric acid at a weight ratio of 60/40 and pH 4.2 (± 0.05). It was performed at a liquid-to-solid of 20 L kg-1 and rotated in a 30-rpm end-over-end rotator for 18 hours. It is used to show how contaminated soil could be affected by acidic rainwater.

3.3.3 Simplified Test of Physiologically-based Extraction (SBET) for Bioaccessiblility

Simplified test of physiologically-based extraction (SBET) can be used to assess the human bioaccessiblity of metals in soils. It simulates the bioaccessiblity of metals in the stomach of people using 0.4 M glycine adjusted to pH 1.5 with concentrated HCl, and the soil-to-solution ratio is 50 L kg-1, the mixture was rotated at 100 rpm at 37 ^{o}C for 1 h. The orally ingested bioaccessible fraction (BAF%) was calculated as the percentage of the solute fraction by simulative stomach solution directly from the SBET result ($C_{\text{bioaccessible}}$, mg kg^{-1}) over pseudo-total concentration in the soil (C_{total}, mg kg^{-1}) as the followed equation showed (Luo et al., 2012b):

$$\text{BAF\%} = \frac{C_{bioaccessible}}{C_{total}} \times 100 \qquad (3\text{-}1)$$

3.3.4 Phytoavailability Test by DTPA Extraction

DTPA extraction of micronutrient metals which available for plants were studied (Lindsay and Norvell, 1978). It was carried out by shaking 1 g soil sample with 2 ml of a solution of 0.005 M DTPA, 0.1 M triethanolamine and 0.01 M $CaCl_2$ at pH 7.3 in an end-over-end shaker for 1 h.

3.3.5 A Rhizosphere-Based Phytoavailability Test

A rhizosphere-based extraction that developed by Fang et al. (2007) was employed to study the metal(loid) phytoavailability. The extraction solution was prepared by 10 mM combined organic acid of acetic, lactic, citric, malic and formic acid at a molar ratio of 4:2:1:1:1. The soil samples collected at each defined E_H window were washed at a soil-to-solution ratio of 1:10 g mL^{-1} by an end-over-end rotator for 16 hours.

3.4 Cytotoxicity

To assess the acute cytotoxicity, Microtox® (AZUR Environmental Microtox® Model 500) was employed to determine the reduction in bioluminescence of a marine bacterium (*Vibrio fisheri*) after sample exposure, in which modified Basic Solid Phase Test was used (Campisi et al., 2005). Before and after treatments, the soil samples were mixed with diluent (35% NaCl solution) at 1:5 g mL^{-1}, adjusted to pH 6-8 using 0.1 N NaOH and HNO_3, and diluted to a series of nine concentrations. The immediate light emission by *Vibrio fisheri* from 510 µL reagents with 500 µL sample was recorded as initial light output (I_0) to minimize the interference of turbidity. The EC_{50} values (at which ecological process was reduced by 50%) were calculated based on the 30-min light reading under a log-linear model using the software MicrotoxOmni^{TM} (Azur Environmentals, USA) (Moreno et al., 2001).

3.5 Enzyme Activity

All the soils to determine enzyme activity tests were dried with desiccator before or after treatment without any temperature change to cut down the potential change of enzyme activities as low as possible.

3.5.1 Dehydrogenase Activity

The method to detect dehydrogenase activity is based on the colorimetric determination of 2,3,5-triphenyl formazan (TPF) as the reduction product of 2,3,5-triphenoltetrazolium (TTC) and dehydrogenase (Casida et al., 1964). Mixed 10 g soil and 0.1 g $CaCO_3$, and then weighted 3 g this mixture as one sample; three samples in total. Added 0.5 mL TTC solution with 1.25 mL DI water, and then capped and put them in an incubator at 37°C for 24 hour. All the samples were extracted with methanol and filter with funnel and filter paper (Whatman No. 40) quantitatively till the reddish color disappeared from the filter paper into a 100 mL volumetric flask. The extractant were measured spectrophotometrically at 485 nm. The results were expressed as TPF (μg) g^{-1} of dry soil.

3.5.2 Urea Remaining Test

To evaluate the urease, a urea remaining test was used based on determining the loss of urea by adding a certain amount of urea beforehand (Tabatabai, 1994). A 5 mL of urea solution was added to 5 g of soils as one sample. Samples were capped and incubated at 37°C for 5 hours. 50 mL of 2 M KCl-PMA (phenylmercuric acetate) solution was added into the soil samples and shook in an end-over-end rotator in 30 rpm for 1 hour. The suspensions were filtered by funnel with Whatman No.40 filter paper. Thus, an 1 mL the extractants, 10 mL KCl-PMA solution and 30 mL color reagent which prepared by the diacetylmonoxime, thiosemicarbazide were added into a 50 mL volumetric flask. Besides, an 85% phosphoric acid and concentrated sulfuric acid freshly with the above mixture of extractants and placed in a boiling water bath for 30 min, and then immediately cooled down with cold water. The volume of the mixture was adjusted to 50 mL with DI water and measured at 527 nm by a spectrophotometer.

3.5.3 Acid Phosphatase Activity Test

The acid phosphatase activity test is based on a colorimetric estimation of the *p*-nitrophenol released by phosphatase activity when soil is incubated at pH 6.5 (Tabatabai and Bremner, 1969; Eivazi and Tabatabai, 1977; Tabatabai, 1994). A soil sample of 1 g was placed in tube with 0.2 mL toluene, 4 mL of modified universal buffer (MUB) prepared by tris(hydroxymethyl)aminomethane, maleic acid, citric acid, boric acid, and sodium hydroxide at pH 6.5 (adjusted with 0.1 M HCl) and 1 mL of *p*-nitrophenyl phosphate solution made in the same buffer. After incubating at 37^{o}C for 1 hour, 1 mL 0.5 M $CaCl_2$ and 4 mL 0.5 M NaOH were added to the mixture to stop the formation of *p*-nitrophenol and then filtered the sample by Whatman no.40 filter paper. Lastly, the *p*-nitrophenol was determined by spectrophotometer at 400 nm. The results were present as *p*-nitrophenol of dry soil.

3.6 Sequential Extraction

3.6.1 Five-Step Tessier's Sequential Extraction

The distribution of metals in the untreated/treated soil was assessed using five-step Tessier sequential chemical extractions, which were operationally defined yet indicative of binding strength as shown in Table 3-6 (Tsang et al., 2009; Tsang and Hartley, 2014).

TABLE 3-7 Tessier's sequential extraction procedure.

Extraction	Fractionation	Extracting Solution	Extraction Condition
1	Exchangeable	1 M $MgCl_2$, pH 7	2 h, 20 ^oC
2	Weakly complexed and bound to carbonate	1 M $NaCH_3CO_2$, pH 5	5 h, 20 ^oC
3	Bound to Fe oxides of low crystallinity and Mn oxides	0.04 M NH_2OH-HCl in 25 % (v/v) CH_2CO_2H	6 h, 96 ^oC
4	Bound to organic matter and sulphides	30 % H_2O_2 + HNO_3 (pH 2), 3.2 M $CH_3CO_2NH_4$ in 20 % (v/v) HNO_3	5 h, 85 ^oC
5	Residual	HNO_3 (69%) and $HClO_4$ (70%)	Digestion[a]

[a] The residue of soil followed the total digestion method by Wong et al. (2002)

3.6.2 Modified Seven-Step Sequential Extraction

In chapter six, a modified sequential extraction method was adopted to study the specific geochemical fractions of As and Pb in soil. The detailed fractions were listed in Table 3-7. The amorphous Fe oxide part were replaced by sulfide part according to Ma and Rao (1997), due to the importance of sulfur under various redox conditions. 2

g of air-dried soil and 50 mL extractant were mixed by an end-over-end rotator at a speed of 20 rpm. The mixed samples were centrifuged and followed the methods described in section 3.8.2 to measure the metal(loid)s inside.

TABLE 3-8 Seven-step modified sequential extraction

Extraction	Fractionation	Extracting Solution	Extraction Condition
1	Soluble + Exchangeable	1 M NH_4NO_3	24 h, room temperature
2	Sorbed and bound to carbonate	1 M NH_4OAc (pH 6.0)	24 h, room temperature
3	Manganese oxide fraction	0.1 M NH_2OH-HCl + 1 M NH_4OAc (pH 6.0)	0.5 h, room temperature
4	Organic fraction	0.025 M NH_4EDTA (pH 4.6)	1.5 h, room temperature
5	Sulfide fraction	3 mL 0.02 M HNO_3 + 5 mL 30% H_2O_2 (H_2O_2 pH=2.0 with conc. HNO_3)	2 h, 85°C in a water bath
		3 mL 30% H_2O_2 (H_2O_2 pH=2.0)	3 h, 85°C in a water bath
		5 mL 3.2 M NH_4OAc in 20% HNO_3 after cooling and dilute to 20 mL with DI water	
6	Crystalline iron oxide fraction	0.1 M Ascorbic acid in 0.2 M NH_4-Oxalate buffer (pH 3.25)	0.5 h, 96 $^{\circ}$C at a water bath
7	Residue	Aqua regia (HCl : HNO_3 = 1:3 mL)	Microwave digestion

3.7 Available Nitrogen, Phosphorus and Organic Carbon in Soil

Available nitrogen was extracted by 2 M KCl at 1:8 g mL^{-1} and 1-h shaking at 180 rpm. After centrifugation and filtration, the samples were analyzed for both N-NH_3 and NO_3 (while N-NO_2 was negligible) as the available nitrogen by a portable colorimeter (DR890, Hach). Organic carbon of the soil was evaluated by total organic carbon analyzer (Shimadzu TOC-L). Available phosphorus was determined using the Bray-1 method that applied 0.03 M ammonium fluoride (NH_4F) and hydrochloric acid (HCl) to the soil samples at 1:7 g mL^{-1} (Bray and Kurtz, 1945). After 20-min centrifugation at 4000 rpm, 2 mL supernatant was mixed with 0.5 mL Bray-1 reagent (i.e., ammonium molybdate $[(NH_4)_6Mo_7O_{24}.4H_2O]$, antimonyl tartrate ($KSbO{\cdot}C_4H_4O_6$) and L-ascorbic acid ($C_6H_8O_6$) that gave blue colour). The solution was analyzed at 882 nm after 30 minutes using a UV/Vis spectrometer and compared to a standard curve prepared by potassium dihydrogen orthophosphate (KH_2PO_4).

3.8 Metal Determination

3.8.1 *Liquid Samples*

At the end of the aforementioned batch tests of extraction, aqueous samples were separated by centrifugation at 4000 rpm for 10 min followed by filtration through 0.45-μm nylon membrane filter (MCE) and stored at 4 ^{o}C in a refrigerator. Liquid samples (Chapter 4, 5, 7, and 8) subjected to an acid digestion with concentrated nitric acid at a volume ratio of 2:5, and then analyzed by ICP-OES (Perkin Elmer Optima 3300DV). For the liquid samples in Chapter 6, concentrated nitric acid was used to acidify the samples at a dosage of 1% of the sample volume before analysis by the ICP-OES (Ultima 2, Horiba Jobin Yvon, Unterhaching, Germany).

3.8.2 Soil Samples

The total metal content in soils or the residue fraction of the sequential extraction (both Tessier five-step and modified seven-step method) were undergone acid digestion or microwave digestion. An acid digestion is prepared by concentrated HNO_3 and $HClO_4$ at a volume ratio of 4:1 and gradient heating process to the maximum temperature of 105 °C (Wong et al., 2002). Microwave digestion was followed the USEPA Method 3051a.

3.9 Risk Assessment

Human health risks were calculated using the potential for groundwater contamination from the SPLP results, to indicate the risk associated with untreated or treated soil under acid rain precipitation. Humans can be exposed to groundwater contaminated by Cu, Zn and Pb via (a) direct oral ingestion (CDI_i); and (b) dermal absorption via showering (CDI_d) (USEPA, 2010; Luo et al., 2012). Among the three target metals in this study, Cu and Zn are considered class D (not classifiable as to human carcinogenicity) and Pb B2 (probable human carcinogen based on carcinogenicity in animals) according to the Integrated Risk Information System of the USEPA. Eqs. 3-2&3 were used to calculate the CDI of the above exposure pathways; the parameters used are shown in Table 3-8 (USEPA, 2004). The non-cancer risks of individual metals via various routes of exposure ways calculated as hazard quotients (HQ, Eq. 3-4), and total cumulative risks were calculated as hazard indices (HI, Eq. 3-5). Due to its carcinogenicity, the lifetime cancer risk of Pb is calculated by multiplying the exposure dosage by both routes of exposure by the corresponding slope factor (Eq. 3-

6).

Table 3-8:

$$CDI_{ingestion} = \frac{C_W \times IR \times EF \times ED}{BW \times AT} \tag{3-2}$$

$$CDI_{dermal} = \frac{C_W \times SA \times K_P \times ET \times EF \times ED \times CF}{BW \times AT} \tag{3-3}$$

$$HQ_{i\ or\ d} = \frac{CDI_{i\ or\ d}}{RfD_{i\ or\ d}} \tag{3-4}$$

Non-cancer risk: HI = ΣHQ $= HQ_i + HQ_d$ (3-5)

Lifetime cancer risk $= CDI_i \times SF_i$ (3-6)

TABLE 3-9 Definition and values of the variables for the risk assessment

	Definition	Unit	Value	References
CDI_i	Chronic daily intake by oral ingestion	mg kg^{-1} d^{-1}	(Eq. 3-2)	(USEPA, 2011)
CDI_d	Chronic daily intake by dermal absorption	mg kg^{-1} d^{-1}	(Eq. 3-3)	(USEPA, 2011)
IR	Ingestion rate	L d^{-1}	2	(USEPA, 2011)
EF	Exposure frequency	d yr $^{-1}$	350	(USEPA, 2004)
ED	Exposure duration	yr	30	(USEPA, 2011) (USEPA, 2011)
BW	Average body weight	kg	70	(USEPA, 2011)
AT	Average time	d	10,950 (non-carcinogens)	(USEPA, 2011) (USEPA, 2004)
SA	Exposed skin area	cm^2	25,550 (carcinogens)	(USEPA, 2004)
SA	Exposed skin area	cm^2	18,000 (adult) 6,560 (children)	(USEPA, 2004) (USEPA, 2004) (ECYWA, 2004)
K_p	Dermal permeability coefficient	cm h^{-1}	Cu: 0.001 Zn: 0.0006 Pb: 0.0001	(USEPA, 2004)
ET	Exposure time during bathing/shower	h d^{-1}	0.25	(USEPA, 2004)
CF	Unit conversion factor	L cm^{-3}	0.001	(USEPA, 2013b) (WHO, 2011; USEPA, 2013b)
SF	Slope factor (carcinogens)	(mg kg^{-1} d^{-1})$^{-1}$	Pb: 8.5×10^{-3} (oral)	(USEPA, 2013a)
RfD_i	Chronic oral reference dose	mg kg^{-1} d^{-1}	Cu: 0.04 Zn: 0.3 Pb: 2.74×10^{-4}	(USEPA, 2004)

NA=Not Applicable

3.10 MINTEQ Setup

To calculate the solution speciation of metals and chelants in each step of different soil washing schemes with individual and mixed chelants, the programme Visual MINTEQ version 3.0 (Gustafsson, 2012) was employed with the measured metal concentrations (Cu, Zn, Pb, Al, Fe, and Ca), concentrations of EDDS and/or EDTA, DOM concentrations, solution pH, and background ions (Na and NO_3^-). The DOM concentrations were assumed to be two-fold of dissolved organic carbon (DOC) concentrations, which were measured using TOC analyzer (Shimadzu TOC-5000A) and carbon concentration resulting from EDDS and buffer was subtracted. The composition of DOM was assumed to be 50% fulvic acid and 50% humic acid, where metal-DOM binding was modeled using the NICA-Donnan model with generic parameters of the program. Possible precipitation of $Al(OH)_3$ and amorphous $Fe(OH)_3$ was considered in the speciation calculation. The stability constant of metal-chelant complexation and EDDS protonation were summarized in Table 3-9 according to the previous studies (Tsang et al., 2009b; Yip et al., 2009; Lo et al., 2011b).

TABLE 3-10 Stability constants of metal-chelant complexes at an ionic strength of 0.1 M.

Metal-chelant complexes	**Log K**
$AlEDDS^-$	12.9
$CaEDDS^{2-}$	4.72
$FeEDDS^-$	22.0
$CuEDDS^{2-}$	18.5
$CuHEDDS^-$	12.0
CuH_2EDDS	4.15
$ZnEDDS^{2-}$	13.4
$ZnHEDDS^-$	6.68
ZnH_2EDDS	2.48
$PbEDDS^{2-}$	12.7
$PbHEDDS^-$	5.90
$HEDDS^{3-}$	10.1
H_2EDDS^{2-}	6.95
H_3EDDS^-	3.85
H_4EDDS	3.00

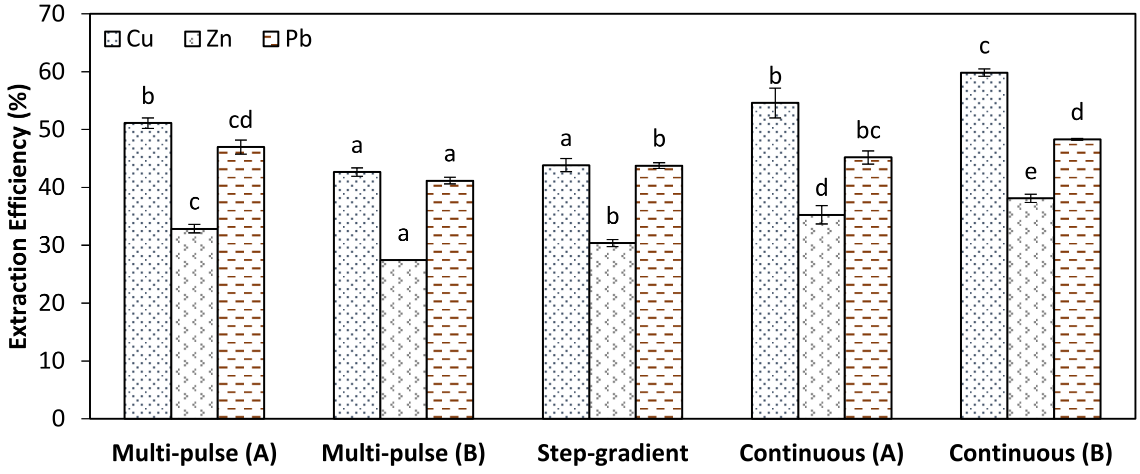
CHAPTER 4. Multiple Washing Schemes and Combined Application of EDDS and EDTA for Soil Washing of an E-Waste Contaminated Site

4.1 Water-Assisted Washing

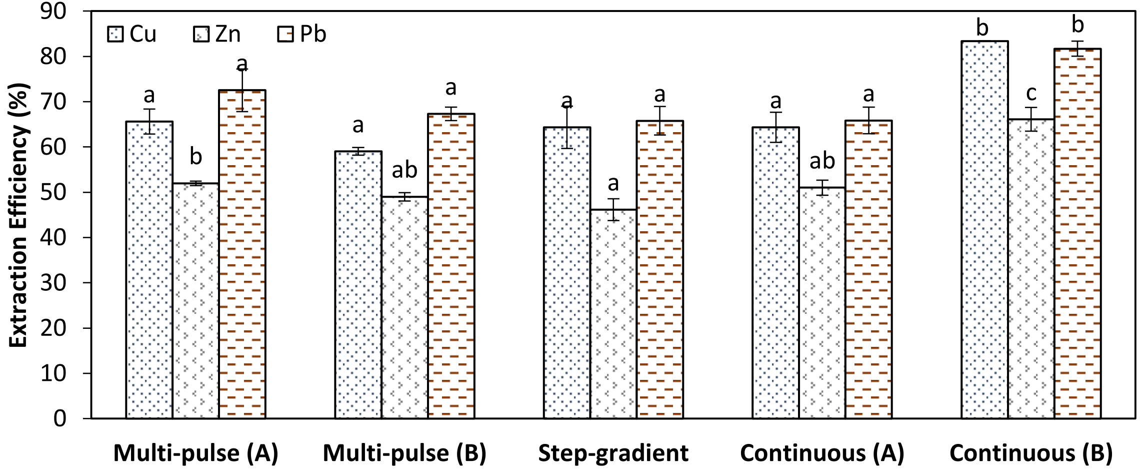
Figure 4-1 compares the metal extraction efficiencies achieved by the various washing schemes considered in this study. As shown, the subsequent use of water rinsing after the chelant washing, slightly enhanced the extraction efficiencies of target metals were by about ~10% (Fig. 4-2a&c). The enhancements in total metal removed achieved by water washing relative to multi-pulse washing scheme B that were conducted without water washing (Fig. 4-2b&d) are from 10.27 – 13.78 % for Cu, 6.98 – 11.02 % for Pb, and 8.25 – 12.48% for Zn (Fig. 4-3a&c). This may be due to the ability of water rinsing to desorb trapped and adsorbed chelant or metal-chelant complexes on the soil surface and/or alternatively desorb chelant may have extracted the labile metals from the soil (Komárek et al., 2009; Tsang et al., 2009; Lo et al., 2011b). This suggests that a water washing section in the last step of soil washing may assist in further increasing the removal of easily mobilized metals in chelant-washed soils. This can reduce the potential human health risk from remobilizing the hazardous metals from the refilled soil from residual chelant and/or metal-chelant complexes after soil washing. Slightly higher water extraction of Cu and Zn over Pb may be due to the different metal speciation and chemical fractions in soils. The additional benefit of water washing is the lower cost of water when compared to chelating agents.

In the early phase of the water rinsing, greater amounts of metals were extracted; the extraction then decreased with time. Similar behavior was observed in chelant extraction. The reduction in the removal of metals indicated fewer metals exist in the labile fraction (exchangeable and carbonated fraction) after several short-term washing (Yip et al., 2009). It also suggested the first washing step is the most crucial step since it extracted over 2/3 of the total extractable metals. Similar behaviors were observed in multi-pulse washing scheme B (Fig. 4-2b&d). Thus an increasing dosage of chelant in the first washing step was recommended. To keep the same total amount of chelant, a step-gradient washing scheme was proposed as in Fig. 3-1c.

(a) EDDS



(b) EDTA



(c) 1:1 EDDS-EDTA mixture

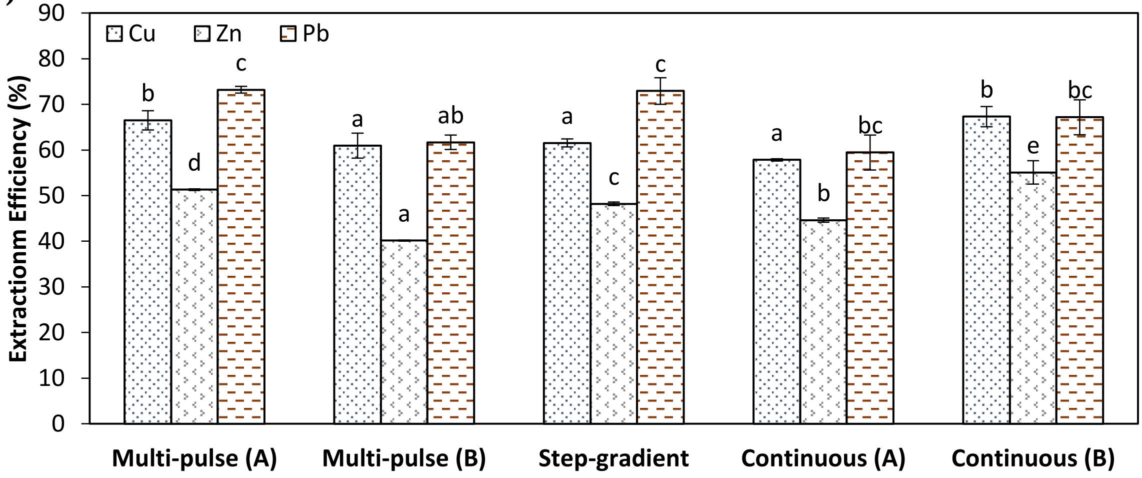


FIGURE 4-1 Extraction efficiency of target metals by different soil washing schemes: (a) EDDS; (b) EDTA; (c) EDDS-EDTA mixture (letters a-e denote statistical differences of different washing schemes, according to the Duncan's test ($p < 0.05$); multi-pulse (A): with water rinsing; multi-pulse (B): without water rinsing; continuous (A): MR 2; continuous (B): MR 6).

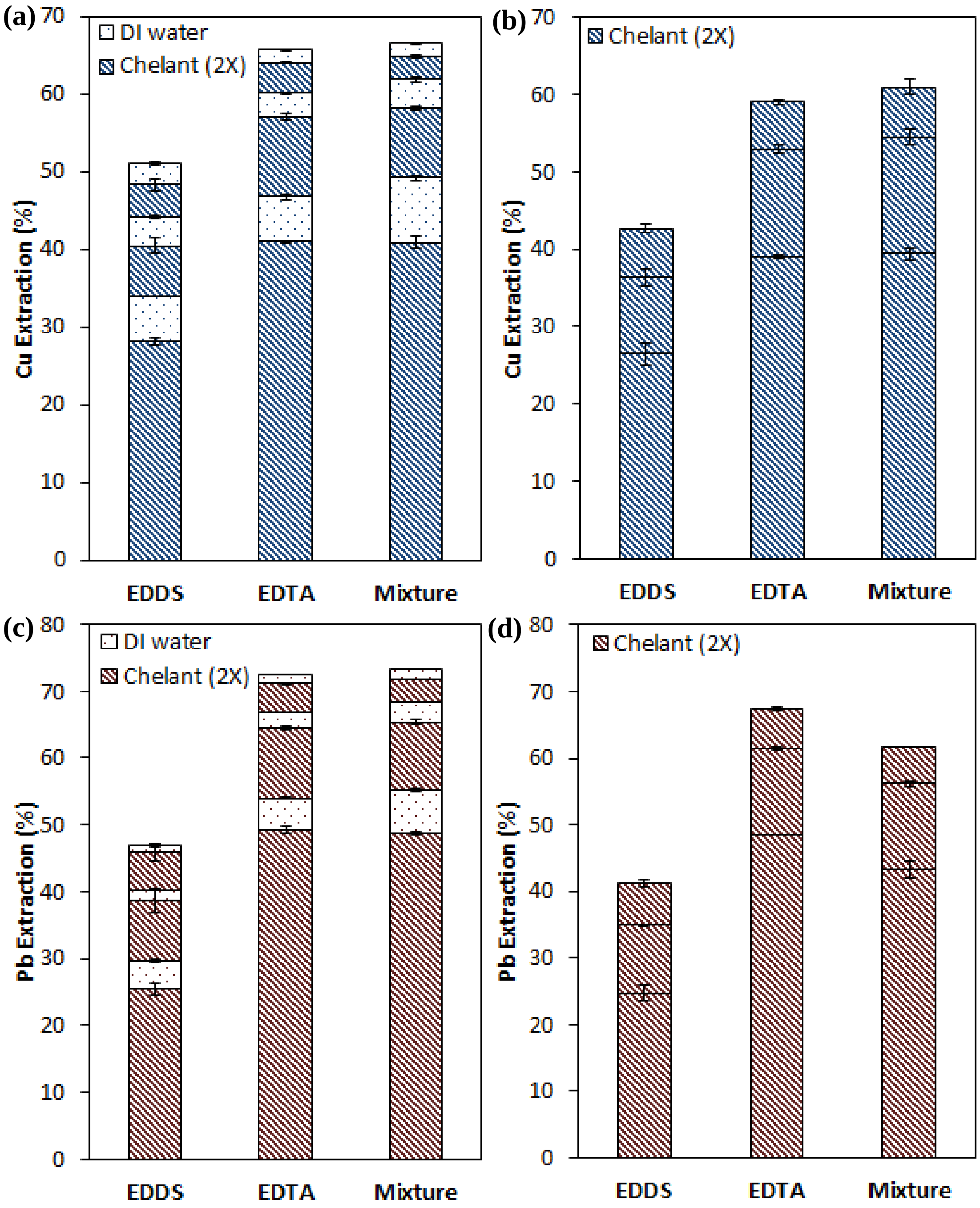


FIGURE 4-2 Extraction efficiency of Cu (a&b) and Pb (c&d) by multi-pulse washing scheme: (a&c) with intermittent water washing; (b&d) without intermittent water washing.

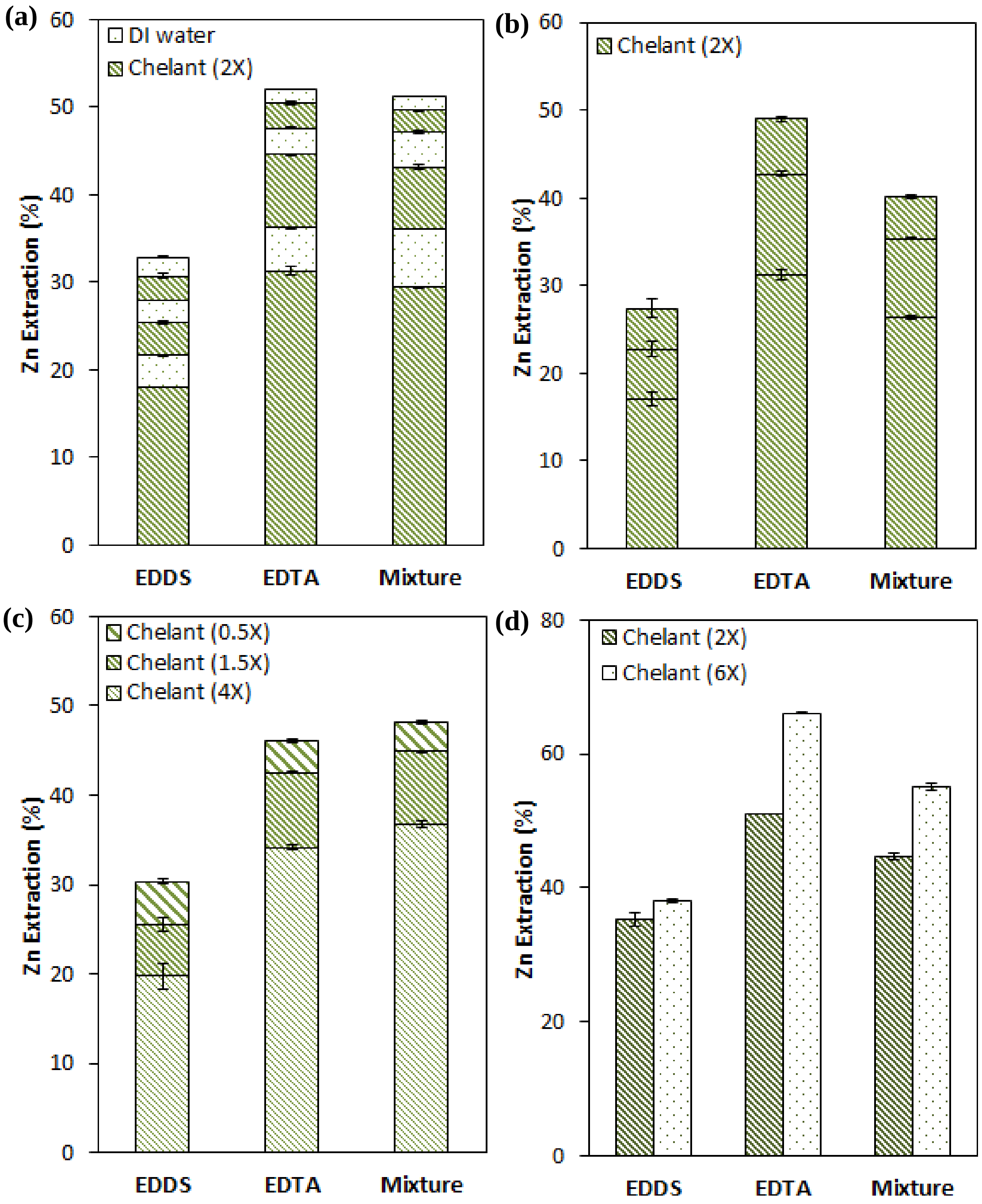


FIGURE 4-3 Extraction efficiency of Zn: (a) multi-pulse washing with intermittent water rinsing; (b) multi-pulse washing without intermittent water rinsing; (c) step-gradient washing; (d) continuous washing.

4.2 Effects on Gradient Dosage of Chelant

Interestingly, the metal extraction achieved by the use of three gradient dosages (MR 4, MR 1.5, and MR 0.5) of chelants (Fig. 4-4a&c) were limited in comparison to multi-pulse washing scheme B which used constant concentration (MR 2) of chelants but three times. This suggested the use of the same dosage of chelants, which is easier, would be preferrable in practical application because of its greater efficiency. The 3-h step-gradient washing scheme, using a mixture of EDTA and EDDS, extracted comparable Cu and slightly higher Pb than the continuous washing for 24 h. The higher removal efficiency could be because the step-gradient washing extracted less elements (Fe, Ca, Al, and Mg) that can compete with the trace elements dissolved in the first chelant washing, as well as the metal-chelant complexes formed (Polettini et al., 2006; Polettini et al., 2007). In addition the use of low concentration of single EDTA washing for a short time (less than 1 h) may only destabilize the metals instead of detaching the metals thus increasing their mobility in the soils (Zhang et al., 2010). Multiple washing steps like step-gradient washing and multi-pulse washing may assist in relieving the above problems.

The extraction efficiencies of the 24-h continuous washing with EDDS/EDTA removed higher quantities of Cu and Pb than the step-gradient washing with both MR 2 and MR 6 (Fig. 4-4b&d). Continuous washing scheme B removed the greatest amount of all three metals, due to a high concentration of chelant and duebto the extended washing period applied. The industrial application of a long washing time (24 h) and use of high dosage of chelant may not be beneficial because of the cost involved. In addition the EDTA induced two-stage extraction process that involved fast complexation within 1-2 hours and a slow mineral dissolution suggest that a longer reaction time of over 2 h with EDTA washing would have little benefit (Zou et al., 2009). Prolonged washing time leads to limited improvement in the extraction efficacies of metals by EDDS, especially for Pb. This could be attributed to preferential unwanted EDDS-induced dissolution of Ca and Al containing minerals in soil (Lo et al., 2011b). EDTA is also able to dissolve the Fe and Mn oxides minerals that binds metals. The binding properties of these oxides are evident from the sequential extraction results (Fig. 5-2a), especially after a long period of washing (Nowack and Sigg, 1997; Nowack et al., 2001). This is consistent with the higher metal extraction achieved by EDTA in this study. In addition, using high dosages (MR 6 for continuous washing) of chelant could be phytotoxic (decreasing plant dry mass), as well as adverse for inducing change of soil physical and chemical properties (strong mineral dissolution and pore clogging) (Nowack et al., 2006; Tsang et al., 2007).

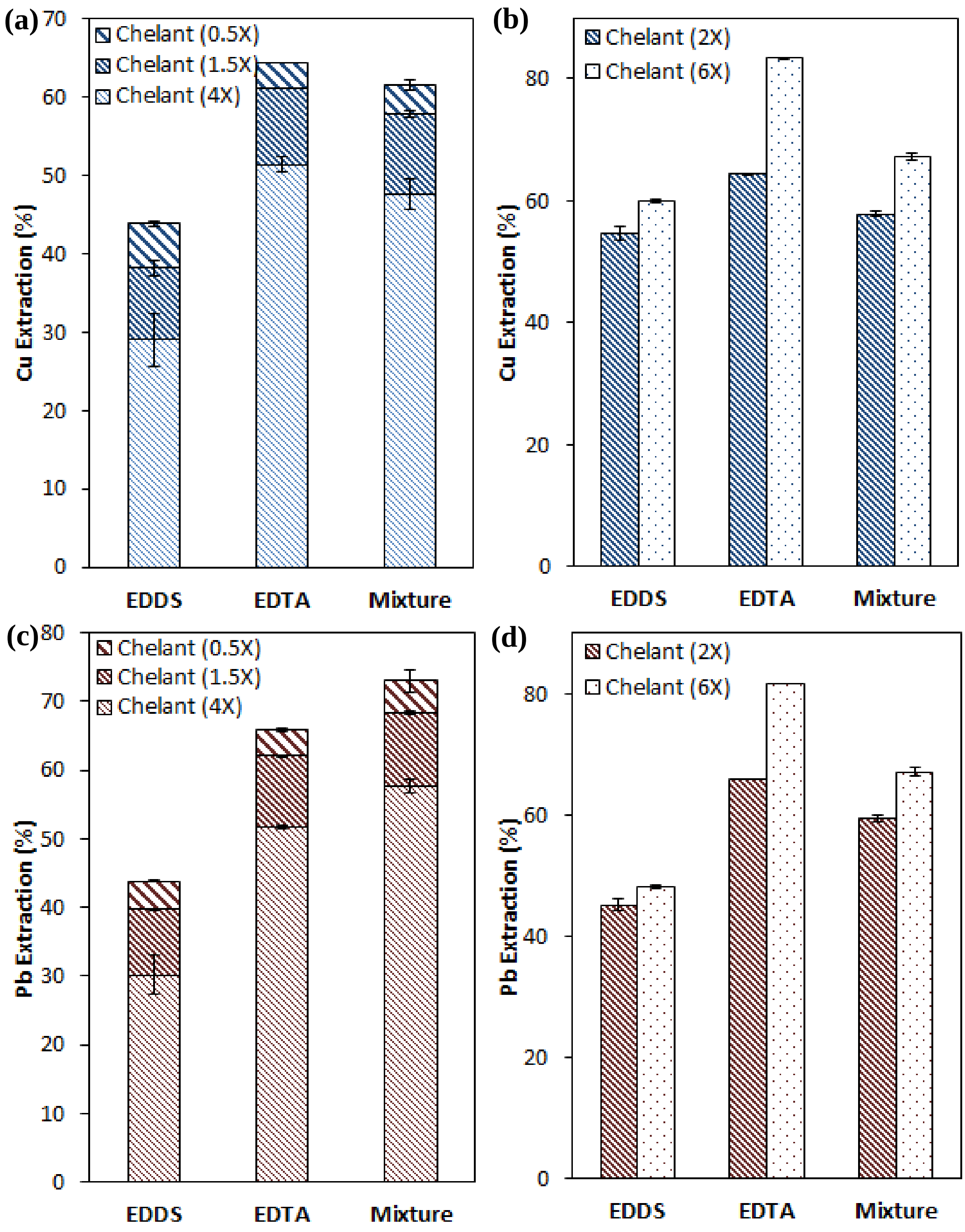


FIGURE 4-4 Extraction efficiency of Cu (a&b) and Pb (c&d): (a&c) step-gradient washing; (b&d) continuous washing.

4.3 Benefits of Combined Use of Chelants

Previous studies reveal that EDDS showed low extraction of Cu and Zn, in particular the extractable Cu in comparison to EDTA. This is despite the similarity in the stability constants of Cu-EDDS^{2-} (log K = 18.4) and Cu-EDTA^{2-} (log K = 18.8) (Luo et al., 2011). The maximum Zn extracted by EDDS achieved though washing continuously for 24 at a high dosage of 20 mM (MR 6) was only 40% (Fig. 4-1). The Pb extraction was even lower at 20%. The Pb extraction was 20% lower than that achieved by EDTA. The low extraction efficiencies was believed to related to the difference in the stabilities of metal-chelant complexes, especially for Pb-EDDS, and the metal geochemical distribution in soil (Yip et al., 2010; Lo et al., 2011b). The sequential extraction result showed that only around 20% of Cu and Zn and almost no Pb exists in the exchangeable and carbonate fractions of the soil; these fractions are believed to be easily extracted by EDDS (Fig. 5-2a). The results also revealed that around 60% of Cu and Zn and 75% of Pb are bound to the Fe/Mn oxide fraction. Though both of EDDS and EDTA can dissolve minerals longer washing periods appear to be necessary. EDDS is only able to slightly dissolve Fe/Mn oxide in comparison with EDTA particularly for short periods of washing (Tandy et al., 2004; Komárek et al., 2009).

Our results showed that higher concentration of EDDS (MR 6) and a longer continuous washing time (24 h) only achieved 60 % metal extraction (Fig. 4-2&4). Also, the difference between continuous washing by EDDS at MR 2 and MR 6 is not significant, which indicated that increasing the washing time and dosage offered limited benefit (Fig. 4-4b&d). A prolonged period of washing did lead to a higher extraction efficiency, however, greater quantities of free EDDS also remained in the washing solution. As a result a large amount of Ca and Al mineral dissolution also occurred

(Fig. 4-5c&f).

An integrated use of EDDS and EDTA enhanced the metal extraction efficiencies significantly, particularly of Pb and Zn in the short-term washing schemes (multi-pulse washing scheme A and B and step-gradient washing scheme). Some extractions were comparable with EDTA extraction or were even higher (Fig. 4-(2-4)). This is possibly due to the better use of both chelants, which allowed EDTA to selectively extract Pb and Zn while EDDS dissolved Cu. This hypothesis is supported by our modeling results performed in Visual MINTEQ. The results suggested that Cu and Pb complexed with EDDS and EDTA respectively at the first washing step with mixed chelant of the multi-pulse washing scheme A, while Zn complexed chiefly to EDDS (Fig. 4-6a). After the removal of Pb, EDTA began forming metal-chelant complexes with Cu and Zn after the first washing step, while more EDDS remained as free ions in the solution (Fig. 4-6c). The significant amount of uncomplexed EDDS in the washing system could potentially adsorb and complex with metal on the soil surface resulting in unwanted mineral dissolution. An additional feature revealed by our modeling is the preferential complexation of mineral cations (e.g. Fe, Al, and Ca) with EDTA rather than EDDS (Fig. 4-6b). This indicated a stronger capacity for EDTA to complex with mineral cations, which is consistent with previous studies (Polettini et al., 2006).

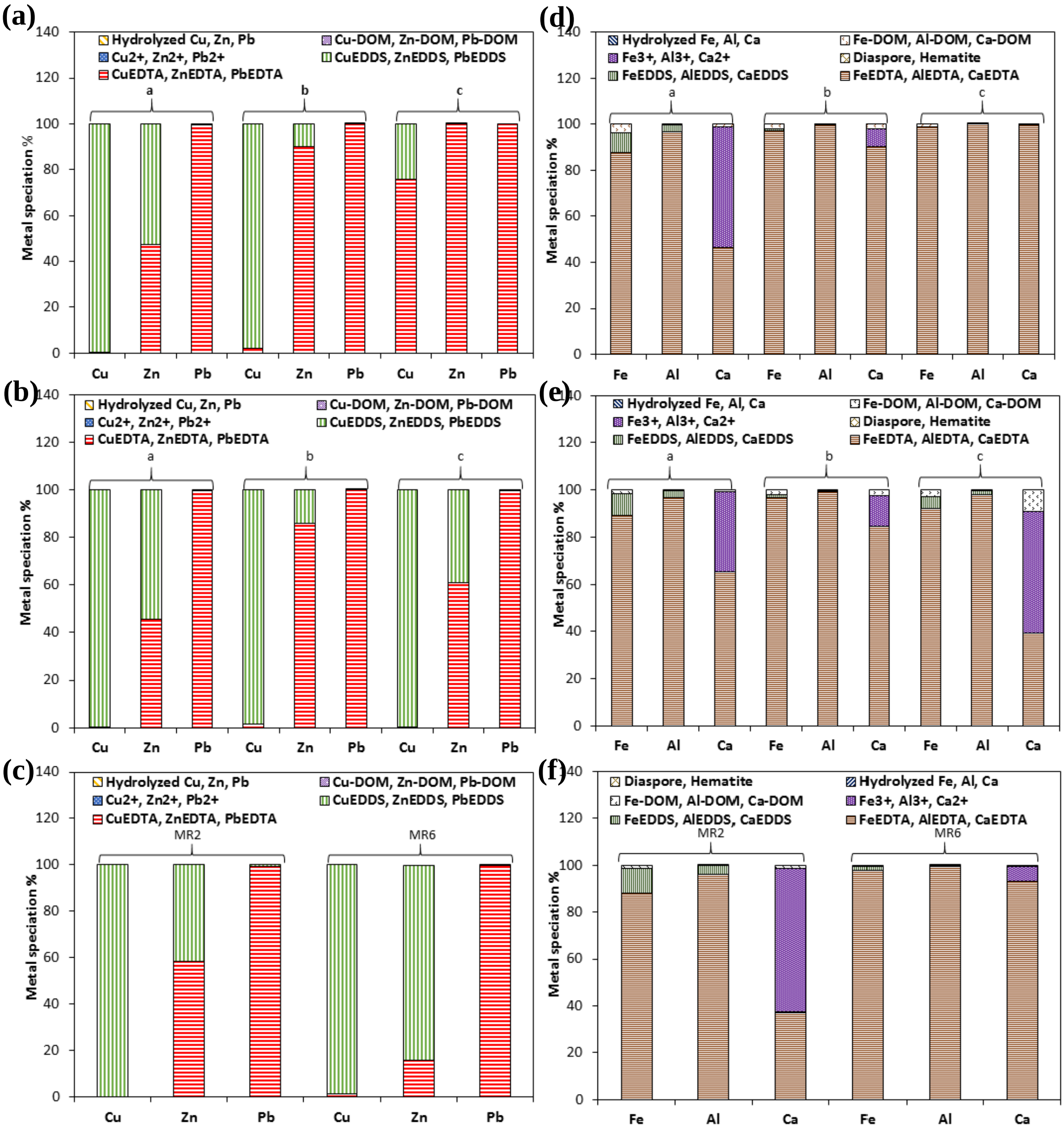


FIGURE 4-5 Solution speciation of target metals (a-c) and mineral cations (d-f) using mixed chelant under different washing schemes: (a&d) multi-pulse washing without intermittent water rinsing; (b&e) step-gradient washing; (c&f) continuous washing (letters a, b, c denote chelant-enhanced washing steps).

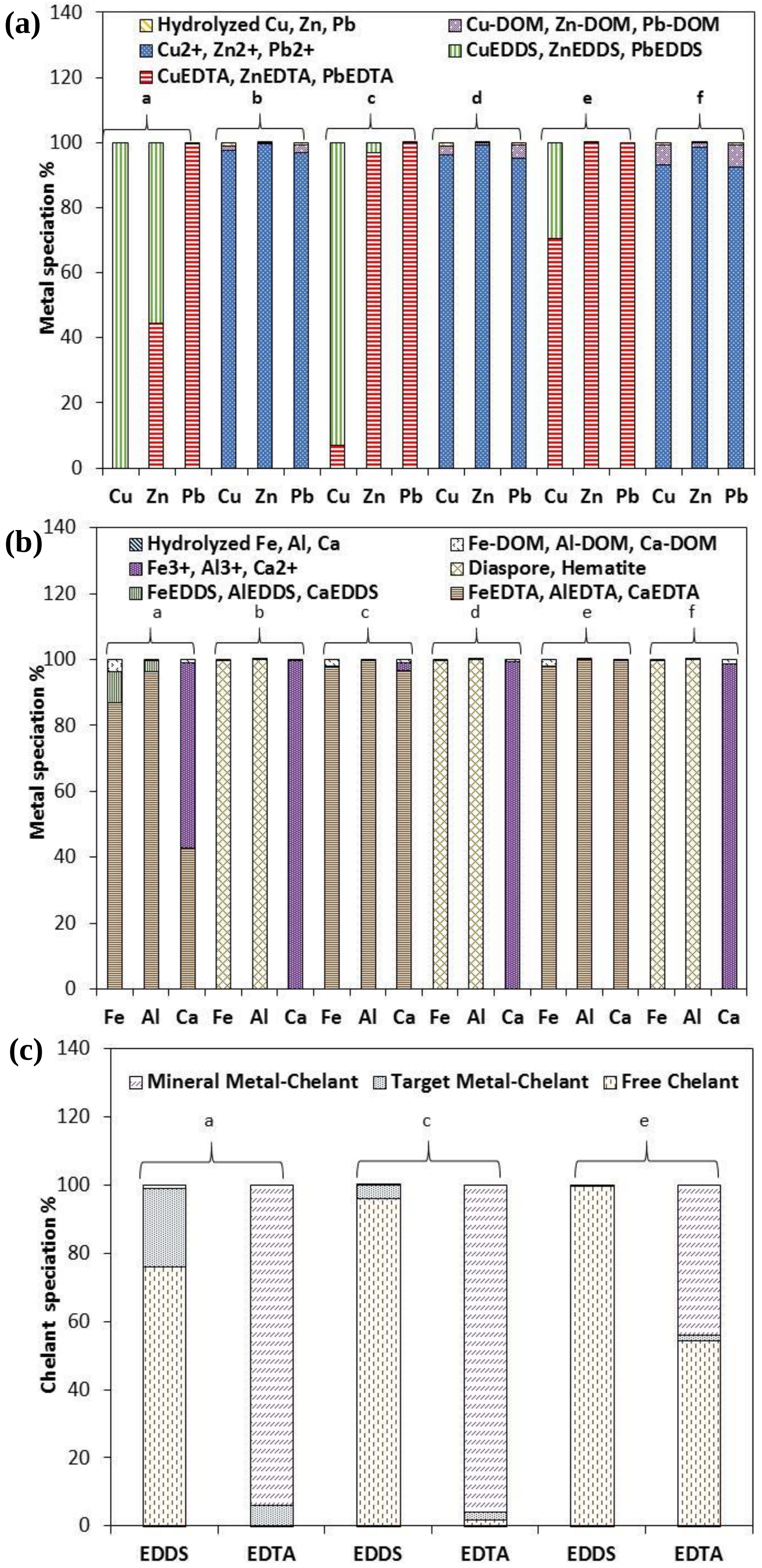


FIGURE 4-6 Solution speciation in multi-pulse soil washing scheme using mixed chelant: (a) target metals; (b) mineral cations; (c) chelant speciation (letters a, c, e denote chelant-enhanced washing steps, whereas letters b, d, f denote water rinsing steps).

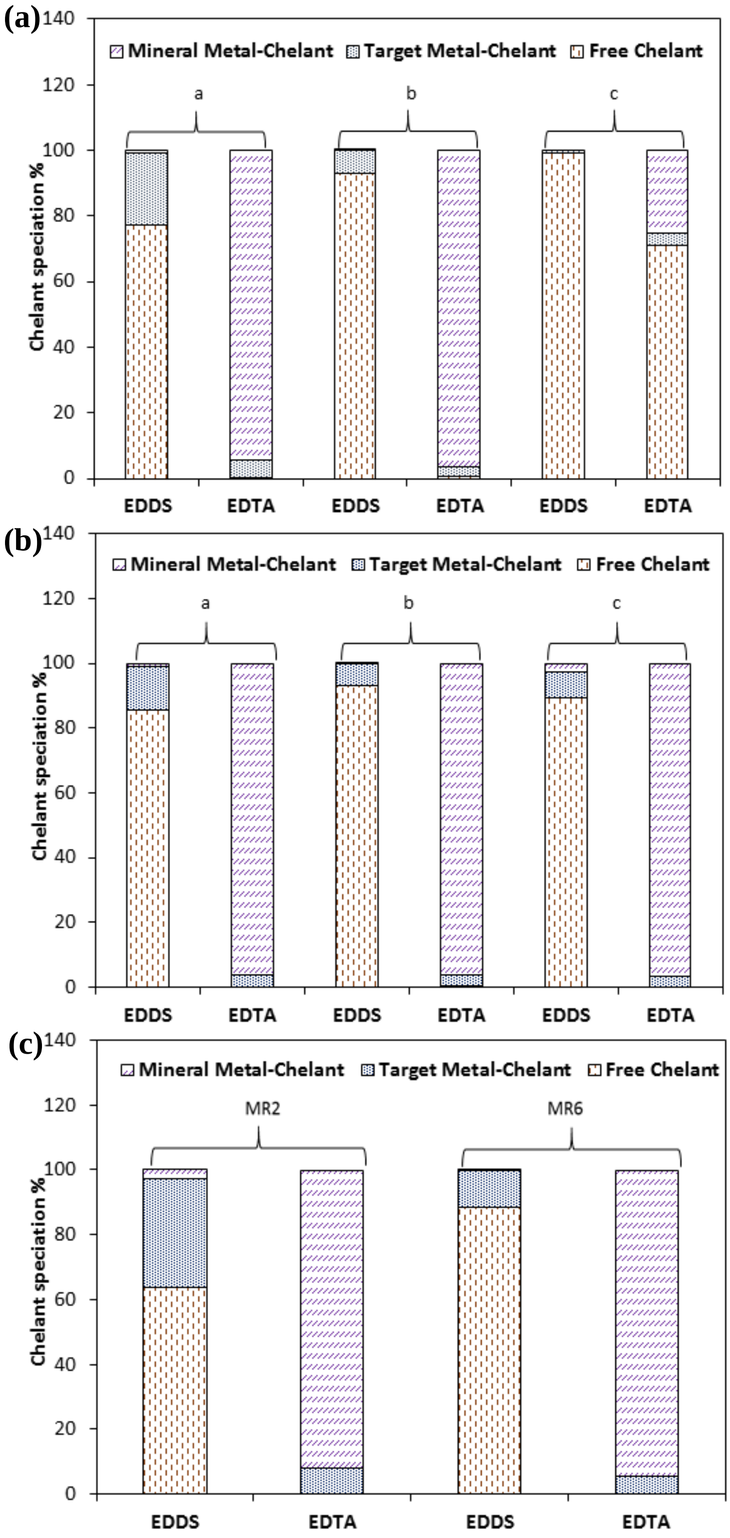


FIGURE 4-7 Speciation of mixed chelant under different washing schemes: (a) multi-pulse washing without intermittent water rinsing; (b) step-gradient washing; (c) continuous washing (letters a, b, c denote chelant-enhanced washing steps).

4.4 Leachability, Bioaccessibility and Mitigation of Human Risk of Residual Metals

After the extractions by various washing schemes, the leachability of residual Cu, Zn, and Pb decreased significantly in comparison to the untreated soil (Fig. 4-8). It should be noted that higher leachability of Cu were observed in both long-term washings under two concentrations of chelants especially for EDDS only. While the Cu leachability significantly decreased after EDTA extraction regardless of the washing method; 24-h continuous washing or 2-h chelant or three successive washing. A re-adsorption of the Cu-EDDS complexes on the oxides surface in the treated soil may have contributed to the high leachability of Cu (Tsang et al., 2009). Also, the destabilized but un-detached Cu from EDDS extraction may have also lead to the high leachable Cu. This might due to the metal redistribution that led to less labile fractions (exchangeable and carbonate) after washing (Lei et al., 2008). A previous study by Zhang et al. (2010) also suggested that a short-time (half-hour) and low concentration of chelant extraction may destabilize but not necessarily detach the metals. Thus, a subsequent washing by water or chelant as the last washing step is suggested to remove these undetached Cu and would be helpful in minimizing their potential risk to human health.

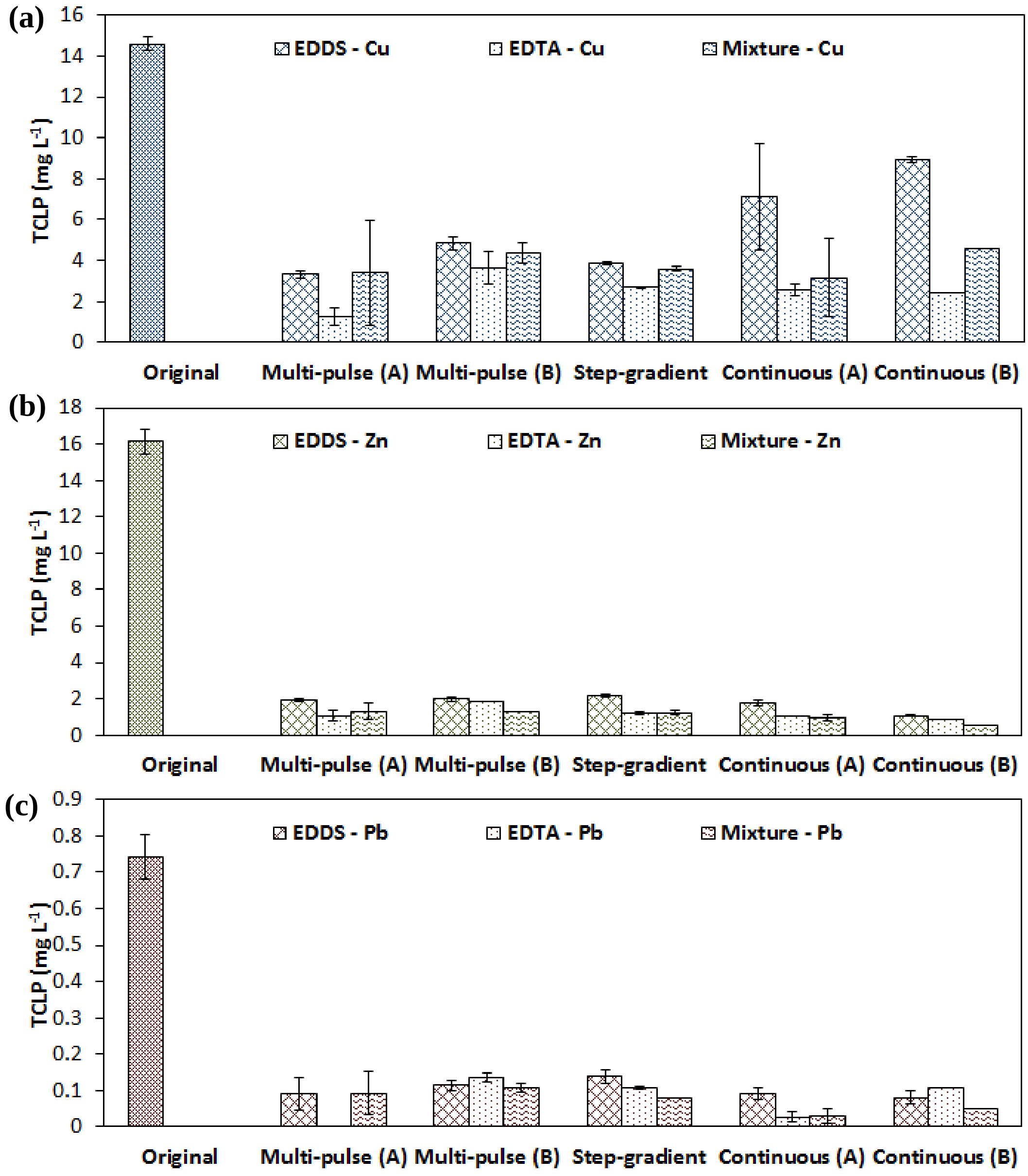


FIGURE 4-8 Residual leachability by TCLP tests: (a) Cu; (b) Zn; (c) Pb.

The bioaccessible factor BAF% of Cu and Zn in chelant washed soil were reduced to (by?) around 20% and 40% respectively, in comparison with the untreated soil (78% and 73% for Cu and Zn, respectively) (Fig. 4-9). While bioaccessible Pb (originally 83%) were reduced by 20 – 40%, except in soil washed by step-gradient washing using EDDS and mixed chelant (Fig. 4-9c). Lead and zinc in the residual soil were possibly shifted by EDDS washing into more labile fractions resulting in higher bioaccessible Pb and Zn in comparison with soil washed with EDTA (Lei et al., 2008). This is prevalent in the step-gradient washing scheme that used a high concentration (MR 4) of chelant at the first washing step. These results suggest that successive EDDS washings in MR 2 was more effective than step-gradient washing. It appears short and use of high concentration of EDDS extraction may not be able to remove the target metals but instead enhance their bioaccessibility. Additionally, it should be noted that BAF% represent only the bioaccessible fraction rather than the concentration of bioaccessible metals, and the bioaccessible metals were successfully minimized by the washing. According to the statistical results, continuous washing using a higher dosage of chelant reduced the greatest amount of both the BAF% and bioaccessible metals (data not shown).

The calculated human health risk based on the bioaccessible metal results showed significant reduction in the risk was achieved as a result of most of the washing schemes, with the exception of the step-gradient washing by EDDS (Fig. 4-10). Besides the 24-h EDTA washing, most of the children non-cancer risks were still unacceptable due to the low extraction efficacy of Pb that is the most poison metal in the study. It can damage the human nervous system, brain, and kidney, especially for the children (ATSDR, 2015). This approximate risk calculation revealed the importance of reducing bioaccessible Pb in preference to other metals in the soil. The results emphasized the significance and importance of Pb removal as a criteria in the selection of suitable washing method. The children lifetime cancer risk based on bioaccessible Pb after washing is considered minor (~10^{-6}, Fig. 4-10d).

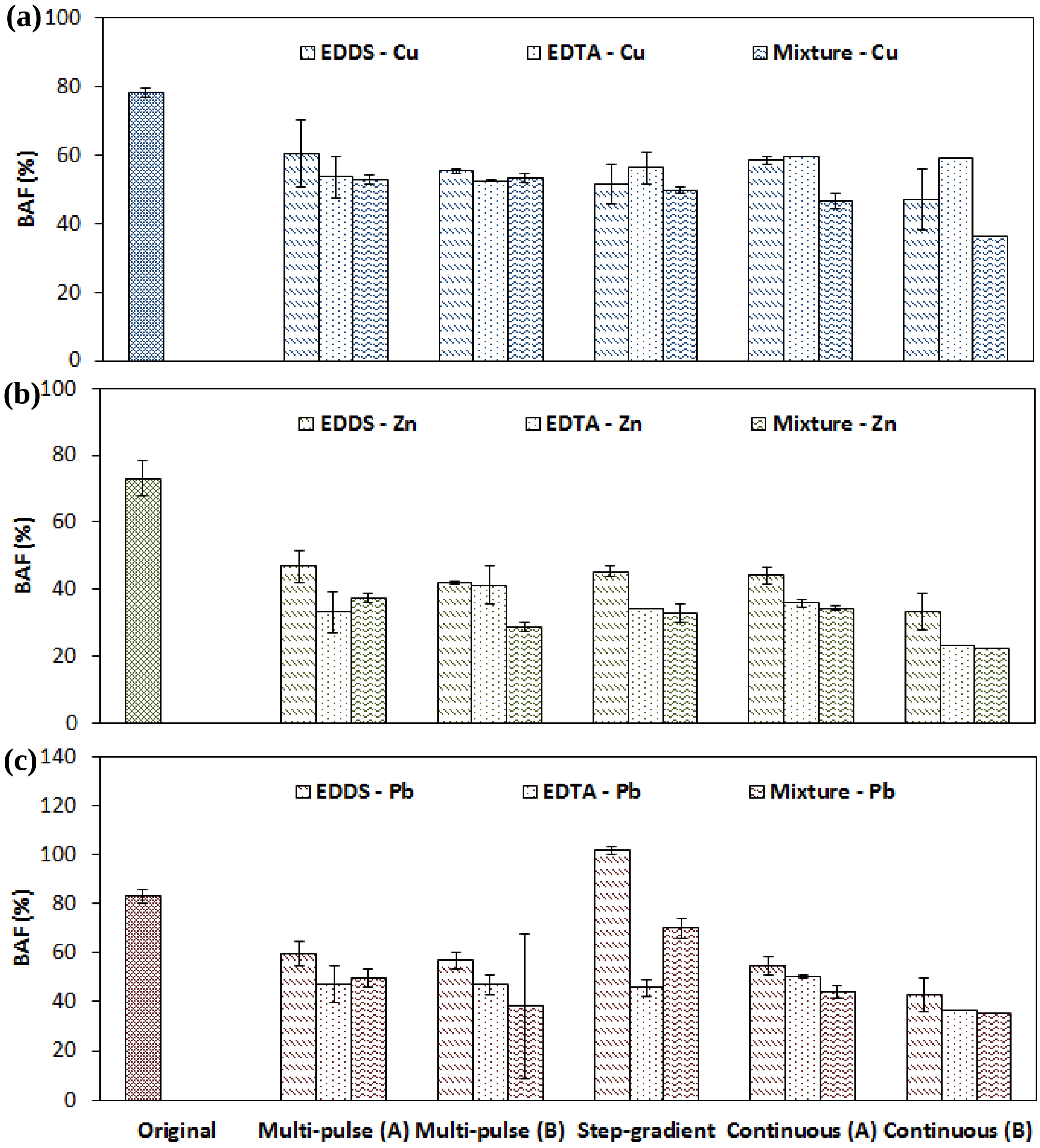


FIGURE 4-9 Residual bioaccessibility by SBET tests: (a) Cu; (b) Zn; (c) Pb (BAF%: bioaccessible fraction).

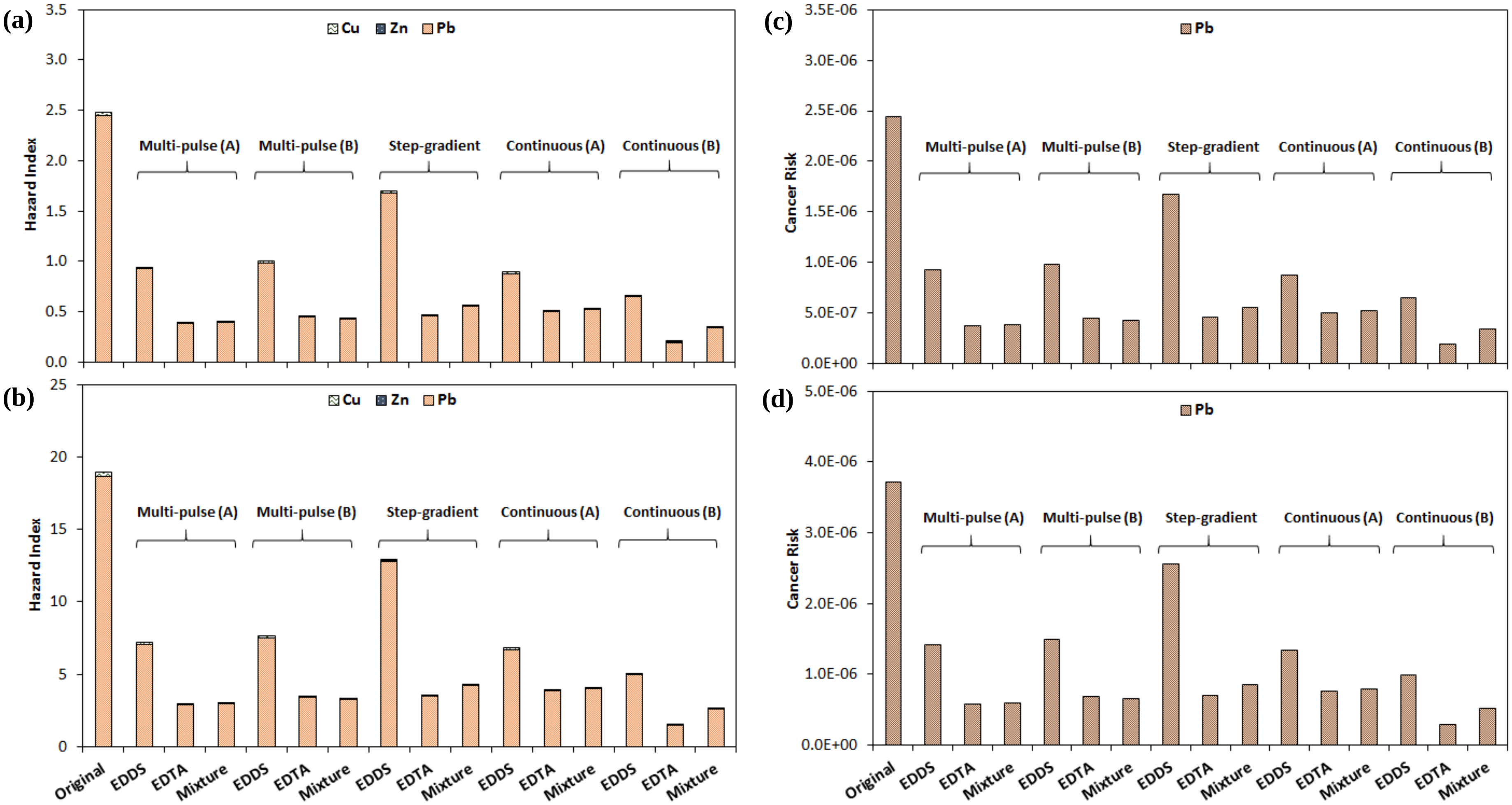


FIGURE 4-10 Human health risks before and after different washings schemes: (a) non-cancer risk to adults; (b) non-cancer risk to children; (c) cancer risk to adults; (d) cancer risk to children (chronic daily intake adjusted by considering bioaccessible fraction).

4.5 Summary

Different types of designed soil washing schemes by chelants successfully enhanced the extraction efficiencies of target metals of an e-waste contaminated soil in this study. The results revealed that low-cost final water washing could remove adsorbed metal-chelants after the last chelant washing step. This resulted in further reduced metal leachability and bioaccessibility of metals in treated soil. Enhanced removal of metals was prominent in soils washed with mixtures of EDDS and EDTA followed by water washing. Marginal increments were found in using step-gradient washing scheme in comparison with multi-pulse washing scheme B using a constant concentration of chelant. The long-term continuous washing for 24 h removed the highest amount of target metals, but multi-pulse washing scheme with a mixture of chelant and water rinsing removed comparable amounts of metals while also reducing residual EDTA. The use of EDDS and EDTA enhanced the extraction of both Cu and Pb and overcame the limited complexation of EDDS with Pb. The long-term EDDS washing led to higher leachability of Cu, which indicated that Cu-EDDS complexes easily adsorbed on the soil after a long-term washing. While short-term washing schemes using EDDS alone only reached low metal extraction. The step-gradient washing by EDDS solely led to a high BAF% of Pb. This was possibly because the high concentration of EDDS only shifted the Pb to more labile fractions within the 1-h washing in the first step. The human risk assessment results suggested the key of remediation factor for this soil is the removal of Pb. This is due to its high toxicity and potential carcinogenicity. Therefore the use multi-steps of washing by chelants and the mixed application of EDDS and EDTA should be further investigated in an industrial scale since they achieved comparable extraction efficiencies while delivering soils with low metal leachability and bioaccessibility.

CHAPTER 5. Selective Dissolution Followed by EDDS Washing of an E-Waste Contaminated Soil: Extraction Efficiency, Fate of Residual Metals, and Impact on Soil Environment

5.1 EDDS washing

Relatively low extraction efficiencies of Cu (31.2%), Zn (14.6%), and Pb (13.5%) were achieved by 2-h soil washing with EDDS (Fig. 5-1). The observed extraction efficiencies resembled the order of the stability constants of metal-EDDS complexes: $CuEDDS^{2-}$ (log K = 18.5) > $ZnEDDS^{2-}$ (log K = 13.0) > $PbEDDS^{2-}$ (log K = 12.7) (Tsang et al., 2009). This was also in line with the metal distribution (Fig. 5-2a), where the labile fractions (i.e., exchangeable and carbonate) only accounted for approximately 30% of Cu, 15% of Zn, and 24% of Pb. Thus, selective dissolution prior to EDDS washing could facilitate the extraction of strongly bound metals from minerals and organic matter in the soil. Figure 5-1 illustrates the extracted amounts of Cu, Zn, and Pb after sequential washing by various chemical reagents and EDDS, while Table 5-1 summarizes the extraction efficiencies of all extraction methods.

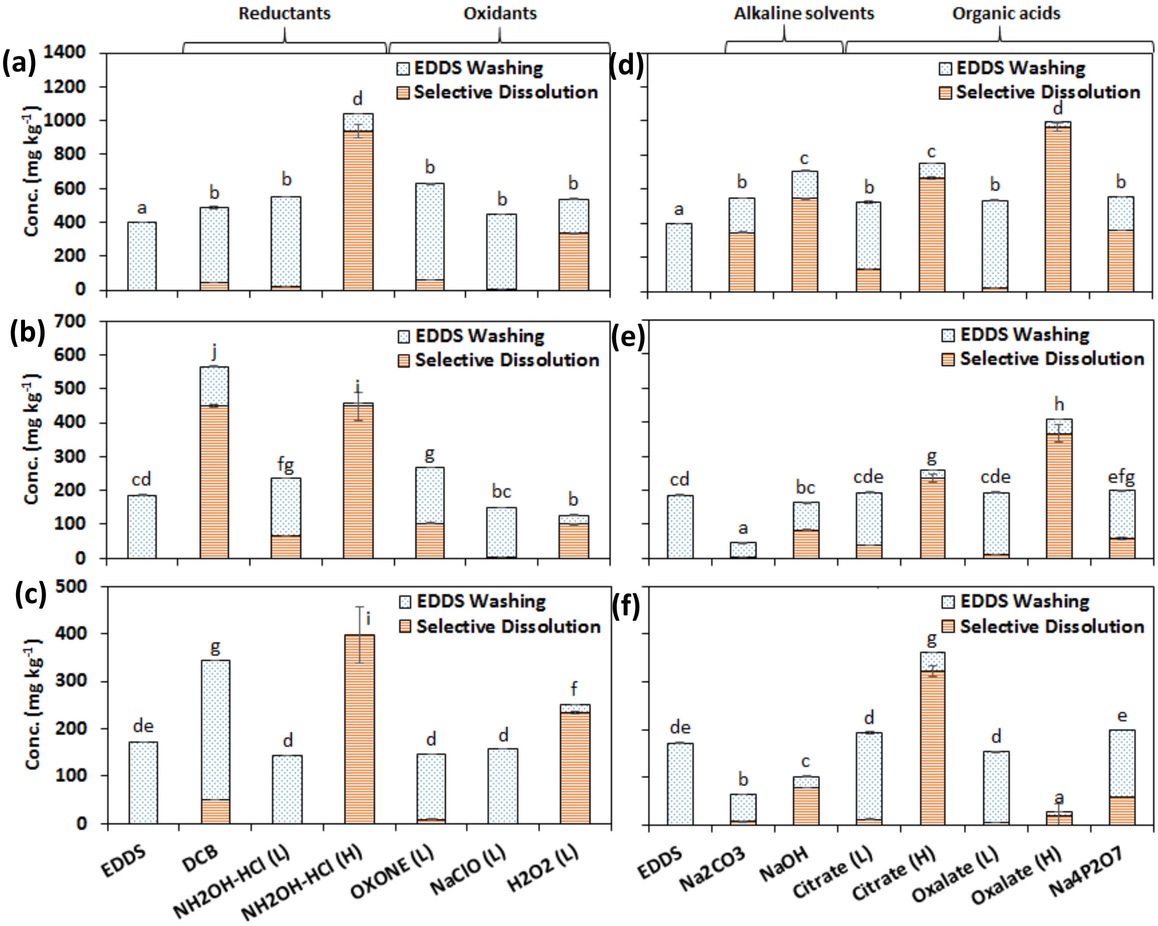


FIGURE 5-1 Extraction of Cu (a&d), Zn (b&e) and Pb (c&f) after 2-h selective dissolution followed by 2-h EDDS washing. (Same letters above the bar indicate that the results are not significantly different according to the Duncan's test ($p < 0.05$)).

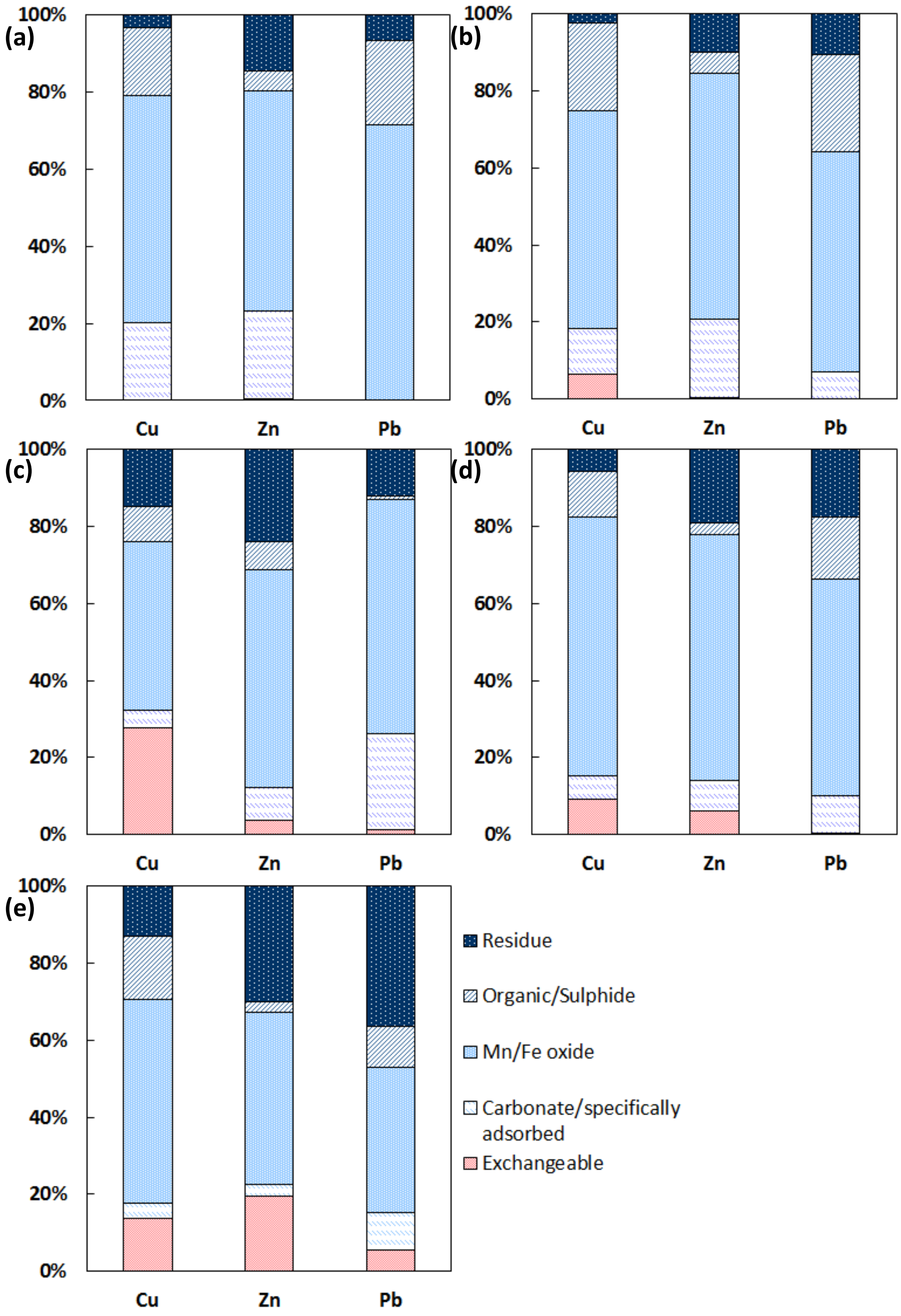


FIGURE 5-2 Sequential extraction results of field-contaminated soil: (a) before washing, (b) EDDS washing only, (c) oxalate+EDDS washing, (d) citrate+EDDS washing, and (e) NH_2OH-HCl+EDDS washing.

TABLE 5-1 Extraction efficiency of selective dissolution prior to EDDS washing.

		Concentration and pH	Extraction Efficacy (%)		
			Cu	Zn	Pb
	EDDS Extraction only	3.34 mM	31.2	14.5	13.5
Reductant	DCB (sodium dithionite buffered with citrate and bicarbonate)	0.4:1:10 g:g:mL at pH 7.3	38.2	44.4	26.9
	Hydroxylamine hydrochloride	Low dosage (L): 1 × $[Me]_{Fe/Mn\ Ox}$ (2.2 mM) High dosage (H): 0.25 M	43.2	18.5	11.1
			81.5	35.9	31.0
Oxidant	OXONE	1 × $[Me]_{OM}$ (0.45 mM)	49.0	21.0	11.4
	Sodium hypochlorite	1 × $[Me]_{OM}$ (0.45 mM)	34.9	11.8	12.3
	Hydrogen peroxide	1 × $[Me]_{OM}$ (0.45 mM)	42.1	9.90	19.6
Alkaline solvent	Sodium carbonate	0.5 M	43.1	3.60	5.10
	Sodium hydroxide	0.5 M	55.5	12.8	8.00
Organic acids	Ammonium citrate	Low dosage (L): 1 × $[Me]_{Fe/Mn\ Ox}$ (2.2 mM) High dosage (H): 0.3 M	41.1	15.2	15.2
			58.8	20.2	28.9
	Ammonium oxalate	Low dosage (L): 1 × $[Me]_{Fe/Mn\ Ox}$ (2.2 mM) High dosage (H): 0.2 M	42.0	15.2	12.0
			78.0	31.9	2.20
	Sodium pyrophosphate	0.1 M at pH 10	43.4	15.5	10.8

5.2 Reductive and Oxidative Dissolution Followed by EDDS Washing

As shown in Fig. 5-1(a-c), DCB extracted about 85% of Zn and 67% of Pb from the e-waste contaminated soil, while there was a little enhancement in the Cu removal, reflecting the difference in metal distribution and binding affinity. It was interesting to note that certain amounts of metals were extracted by subsequent EDDS washing. Dithionite in citrate solution at a buffered pH (optimal at 7.3) could substantially dissolve the iron and manganese oxides (Shang and Zelazny, 2008), as evidenced by Fig. 5-3, which facilitated the release of metals in the first stage of washing. The DCB method dissolved the largest amounts of Fe and Mn at the first washing step among all the methods. However, the dissolved metals may have been re-adsorbed or re-precipitated on the soil surfaces, as revealed in a recent study (Kim et al., 2015). Hence, this study illustrated the significance of EDDS washing for complexing with readily available target metals that were destabilized by prior DCB extraction.

The high concentration of acidified NH_2OH-HCl dissolved 83% of Cu, 70% of Zn, and 80% of Pb in the first stage of washing, whereas the second stage of EDDS washing was found unnecessary (Fig. 5-1(a-c)). It was probably the result of strongly acidic condition (pH ~ 0.4) in this method that favoured nearly complete mineral dissolution. In comparison, the low concentration of acidified NH_2OH-HCl (2.2 mM, equivalent to the amount of oxide fraction in Fig. 5-2) showed moderate enhancement (~20%) for Cu and Zn extraction compared to that of EDDS washing only. Such increment could be attributed to the selective dissolution of amorphous iron and manganese oxides/hydroxides (Im et al., 2015; Kim et al., 2015), because the low concentration of acidified NH_2OH-HCl dissolved significantly smaller amounts of Fe and Mn (Fig. 5-3). Among the reductants, DCB displayed a stronger ability for mineral dissolution than hydroxylamine hydrochloride, which was in agreement with previous findings of sequential extraction procedures (Hass and Fine, 2010).

For the selected oxidants (Fig. 5-1(a-c)), the low dosages were studied (0.45 mM) based on the amount of organic matter fraction in the sequential extraction results (Fig. 5-2). Persulfate in OXONE along with successive EDDS washing was shown to enhance extraction of Cu and Zn by about 30%. This could be attributed to the oxidation of soil organic matter by $SO_4^{2-\bullet}$ radicals generated in the presence of transition metals (Yan and Lo, 2012; Liu et al., 2014; Nalliah, 2015). On the other hand, it was interesting to note that hydrogen peroxide showed a higher extraction on Cu and Pb while sodium hypochlorite was ineffective. It was probably because H_2O_2 reacted with amorphous Fe oxides and produced $OH^{-\bullet}$ radicals via Fenton-like reaction (Mikutta et al., 2005; Lee and Sedlak, 2009; Zhu et al., 2014), which oxidized the organic components and dissolved more Cu and Pb in the first stage of washing. However, the oxidation by hydrogen peroxide was found to result in a loss of 60-80% of organic carbon, total nitrogen, and water retention (Sirguey et al., 2008). Hence, the fate of residual metals and the associated impact of soil properties were investigated in the subsequent sections.

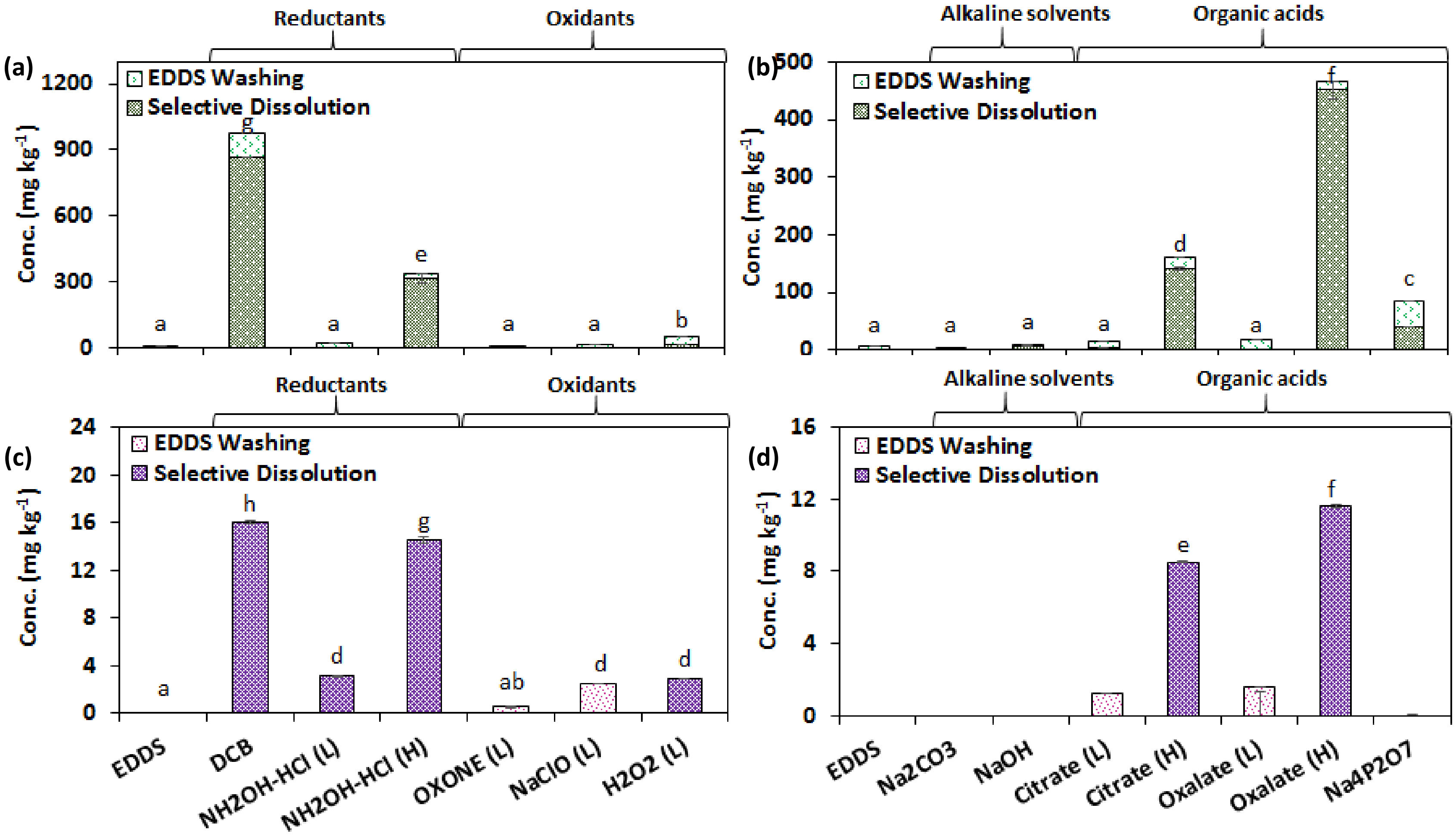


FIGURE 5-3 Dissolved concentrations of Fe (a&b) and Mn (c&d) after 2-h selective dissolution and 2-h EDDS washing. (Same letters above the bar indicate that the results are not significantly different according to the Duncan's test ($p < 0.05$)).

5.3 Alkaline Solvents and Organic Acids Followed by EDDS Washing

Both carbonate and hydroxide were observed to enhance Cu extraction by 45% and 88% (Fig. 5-1(d-f)), because the strongly alkaline medium could dissolve aluminosilicates by forming soluble Al-hydroxyl complexes (Wang et al., 1981) while there was trivial dissolution of Fe and Mn by alkaline solutions (Fig. 5-3). However, the successive extraction of Zn and Pb by EDDS was hampered, which was probably due to the formation of precipitates after the use of alkaline solvents (K_{sp} of $Zn(OH)_2$, $ZnCO_3$, $Pb(OH)_2$ and $PbCO_3$ are $3.0 \times 10^{-16}, 1.4 \times 10^{-11}, 1.4 \times 10^{-20}$ and 1.4×10^{-14}, respectively (Haynes, 2015)).

During the first stage of washing at the high dosage of low-molecular-weight organic acids, citrate enhanced the extraction of all metals by 60-80% while oxalate increased the extraction of Cu and Zn by approximately 80% (Fig. 5-1(d-f)). This reflected the efficacy of citrate and oxalate for promoting the oxide dissolution via surface protonation and Fe-O bond destabilization in the solid lattice (Blesa et al., 1994). However, the high dosage of oxalate suppressed the extraction of Pb, where the supernatant samples turned darker and more precipitates were filtered out. This was indicative of the formation of lead-oxalate precipitates (PbC_2O_4) that have a low solubility product ($K_{sp}=2.74\times10^{-11}$) (Qiu et al., 2009). In contrast, the extraction efficiency by the high dosage of pyrophosphate was relatively low, where only the extraction of Cu was enhanced by 30%. This signified the limited ability of pyrophosphate when compared to citrate and oxalate in the first washing stage, although it was also useful for facilitating mineral dissolution (Yan and Lo, 2012).

However, the low dosage of citrate and oxalate (2.2 mM) only extracted a limited amount of metals in the first stage of washing and slightly enhanced subsequent EDDS extraction (Fig. 5-1(d-f)). These results indicated that prior washing by citrate and oxalate was effective only when a high dosage was applied for Fe and Mn dissolution (Fig. 5-3), because of the relatively low stability constants of metal-citrate complexes (log $K_{Cu\text{-}citrate}$=7.6, log $K_{Zn\text{-}citrate}$=6.1, log $K_{Pb\text{-}citrate}$=5.7 (Gustafsson in 2008)) and metal-oxalate complexes (log $K_{Cu\text{-}oxalate}$=4.5, log $K_{Zn\text{-}oxalate}$=3.4, and log $K_{Pb\text{-}oxalate}$=4.2 (Qiu et al., 2009)) compared to those of metal-EDDS complexes (log $K_{Cu\text{-}EDDS}$=18.5, log $K_{Zn\text{-}EDDS}$=13.4, log $K_{Pb\text{-}EDDS}$ =12.7 (Tsang et al., 2009)). However, citrate and oxalate have a lower price in the market (USD 600-800 per tonne of citrate/oxalate compared to USD 2000-5000 per tonne of EDDS (Alibaba, 2016)), and they naturally exist in the soil resulting from root excretion, microbial metabolism and organic decomposition that induce less residual impact (Perez-Esteban et al., 2013), which could be an advantage of their application.

5.4 Leachability, Bioaccessibility, and Risk Mitigation of Residual Metals

After the two stages of selective dissolution and EDDS washing, the leachability of residual metals were significantly reduced in comparison to that of the contaminated soil in most of the cases, as indicated by the TCLP results (Fig. 5-4). However, it should be noted that the reductants on their own, DCB in particular, substantially increased the leachability of Cu and Pb, as indicated by the statistical analysis of Duncan’s test. This clearly demonstrated the importance of subsequent EDDS washing, otherwise after dithionite-promoted oxide dissolution (Fig. 5-3), the released metals probably re-adsorbed on the soil surfaces and became readily mobile. On the other hand, prior application of oxidants and organic acids increased the leachability of Cu when compared to the samples only washed by EDDS, although the leachability of Zn and Pb was further reduced. This was corroborated by the increase in the exchangeable fraction of Cu after sequential washing (Fig. 5-2), possibly due to loosely bound Cu complexes (with EDDS, citrate/oxalate, and dissolved organic matter) on the soil surfaces. Recent studies also revealed that the residual metal-chelant complexes led to the increase in leachability and exchangeable fraction (Jelusic et al., 2013; Tsang and Hartley, 2014). Hence, an additional washing step with water may be recommended before on-site backfilling of the treated soil.

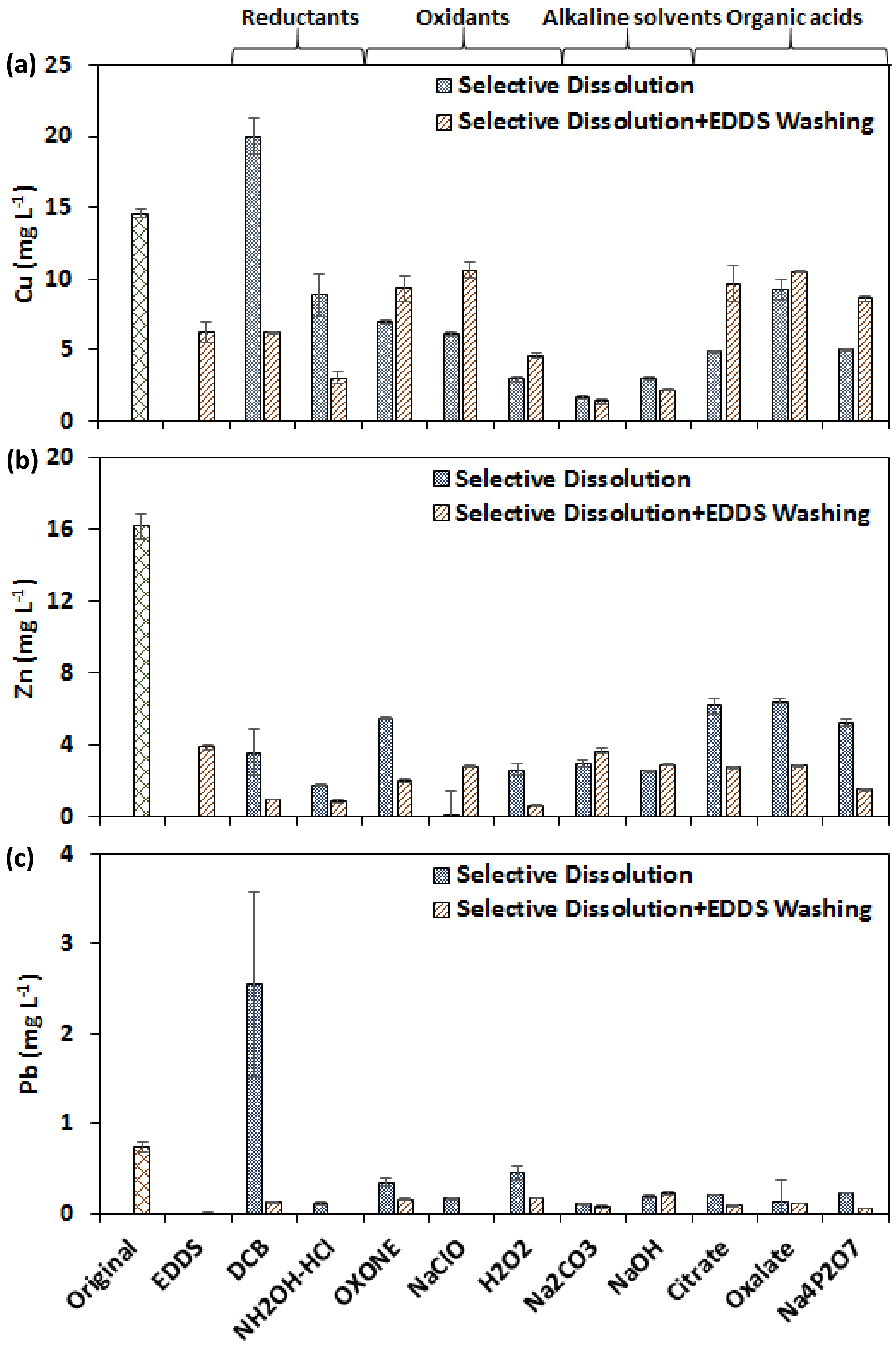


FIGURE 5-4 Leachability of (a) Cu, (b) Zn, and (c) Pb after 2-h selective dissolution followed by 2-h EDDS washing.

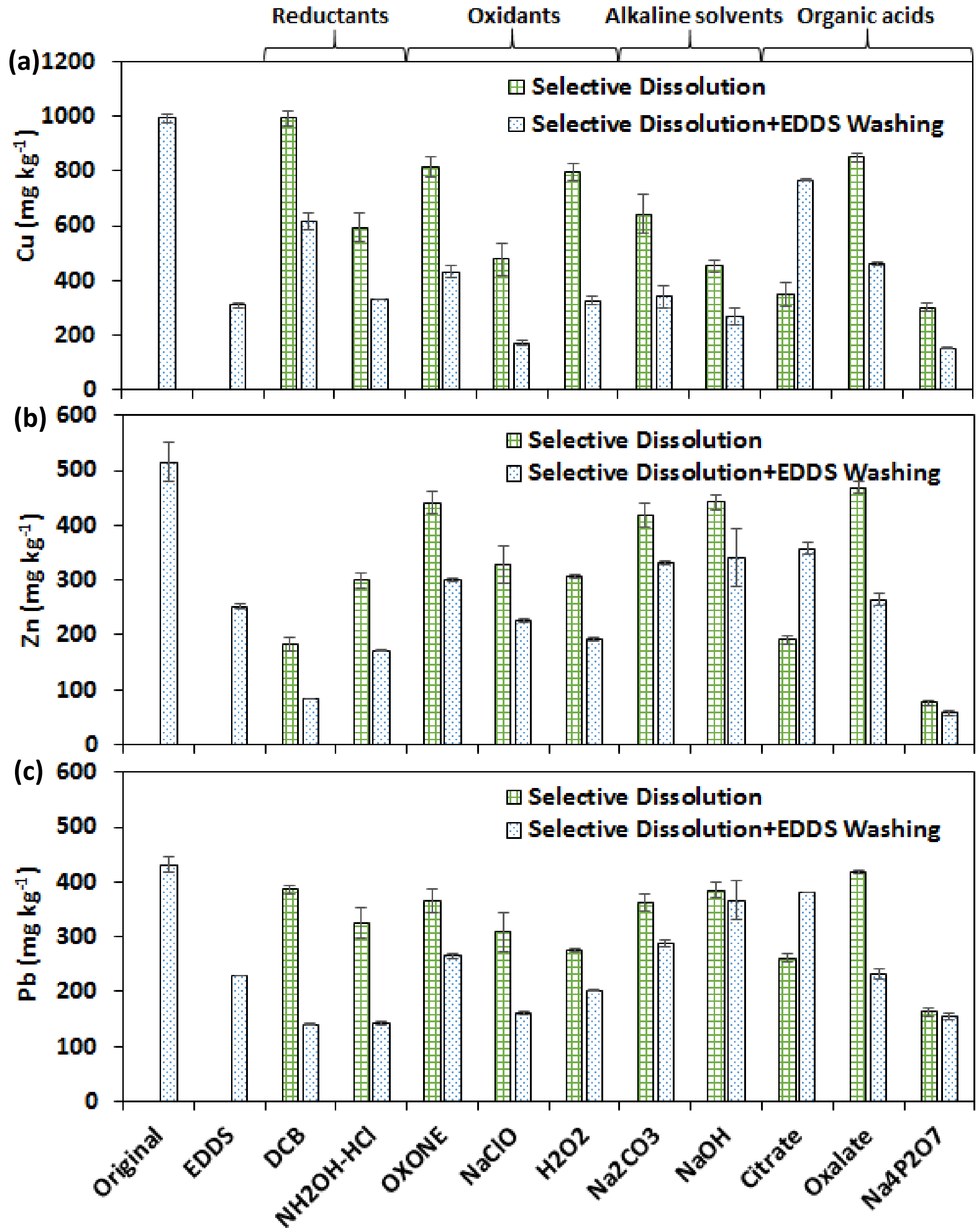


FIGURE 5-5 Bioaccessibility of (a) Cu, (b) Zn and (c) Pb after 2-h selective dissolution followed by 2-h EDDS washing.

In contrast, while the bioaccessibility of Cu, Zn, and Pb (as indicated by SBET results) was reduced by EDDS washing only (Fig. 5-5), it was unfavourably elevated after the first stage of washing by most of the reagents (*e.g.*, DCB, hydroxylamine hydrochloride, sodium hypochlorite, alkaline solvents, and organic acids). Although subsequent washing by EDDS notably decreased the metal bioaccessibility, only a few of them were lower than that of EDDS washing solely. It should, therefore, be reminded that the intense reactions by strongly reductive/oxidative/alkaline agents involved in these selective dissolution steps would shift the metals from the Fe/Mn oxide, organic matter and residue fractions to more labile and bioaccessible fractions.

The influence of the change of bioaccessibility (despite the reduction of total concentration) was then evaluated by means of non-site-specific calculation for human health risks. Despite higher Pb extraction by DCB, hydroxylamine hydrochloride, and citrate after the sequential washing (Fig. 5-1), the non-cancer risk of children in the treated soil was still unacceptable (hazard index > 1, Fig. 5-6a), which was predominantly due to residual Pb. The lifetime cancer risk of Pb (probable human carcinogen) for children was considered minor (~ 10^{-6}, Fig. 5-6b). Both non-cancer and cancer risks were less severe for adults and thus not shown. Such approximate risk calculation illustrated the significance of minimizing the bioaccessibility of residual Pb (Fig. 5-4), which was found insufficient for children, in consideration of the toxic effects of Pb including damage on the nervous system, brain, and kidneys (ATSDR, 2015).

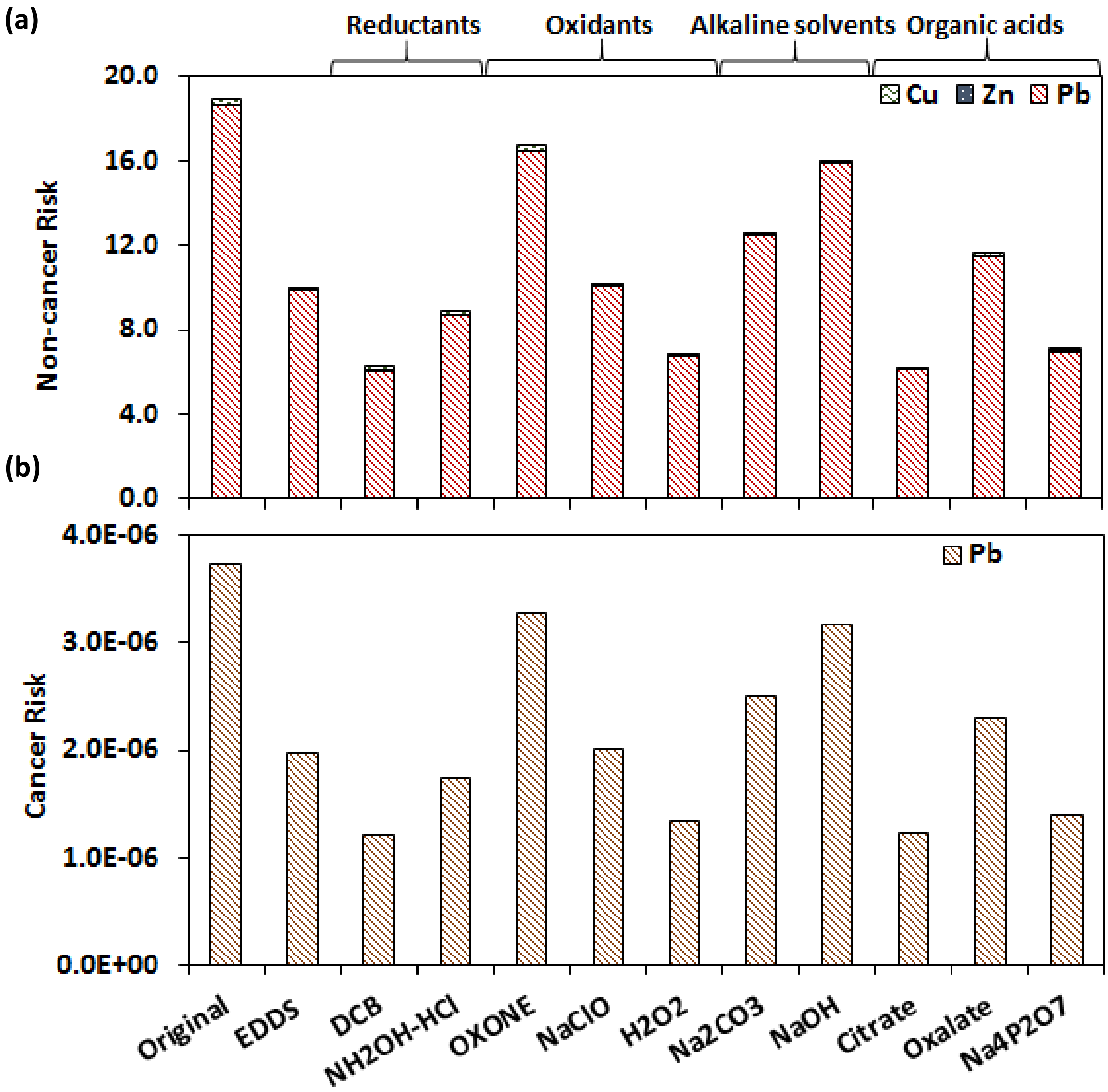


FIGURE 5-6 Non-cancer (a) and cancer (b) risks of children exposed to the field-contaminated soil before and after sequential washing (taking into account the SBET results).

5.5 Cytotoxicity, Enzyme Activities, and Available Nutrients of the Treated Soil

Before any treatment, the field-contaminated soil showed hormesis phenomenon in the Microtox analysis (Table 5-2), which was also observed when the luminescent bacteria (*V. fischeri*) was exposed to a low concentration of toxins or stressors such as metals (Damelin et al., 2000; Shen et al., 2009). This indicated that in spite of the high total concentrations, these metals were not readily bioaccessible to microbes in the aged soil samples. After washing by EDDS only, the EC_{50} value could not be calculated by the MicrotoxOmni^{TM} software because the toxicant concentration was too low, confirming that EDDS washing on its own was able to minimize the cytotoxicity of metals in the soil. This was corroborated by the marginal amount of exchangeable fraction of the metals (Fig. 5-2), which might be too low to be toxic to *V. fischeri*. Another possible reason was the reduction of metal toxicity by metal-ligand complexation (Sillanpää and Oikari, 1996). In contrast, the EC_{50} values for the soils first washed by hydroxylamine hydrochloride, citrate, and oxalate were 341, 516, and 1313 g L^{-1}, respectively (Table 5-2). The results indicated that prior washing with these reagents increased the cytotoxicity when compared to EDDS washing alone. The toxicity of hydroxylamine hydrochloride-treated soil could be attributed to the extremely low pH used (Maisto et al., 2011).

TABLE 5-2 Microtox results and organic carbon of field-contaminated soil before and after washing by EDDS, oxalate+EDDS, citrate+EDDS, and NH_2OH-HCl+EDDS.

Soils	EC_{50} (g L^{-1})[a]	OC (%)
Before Treatment	Hormesis	4.81
After EDDS Washing	N/A[b]	5.29
After Oxalate+EDDS Washing	1310	6.18
After Citrate+EDDS Washing	516	5.47
After NH_2OH-HCl+EDDS Washing	314	7.85

[a] Average results;
[b] Negligible cytotoxicity that cannot be calculated by the MicrotoxOmni™ software.

Washing by EDDS alone reduced the dehydrogenase activity by 30% while enhancing the acid phosphatase and urease activities, according to the statistical analysis of Duncan’s test (Fig. 5-7(a-c)). The dehydrogenase activity of untreated and EDDS-washed soils might be hampered by residual Cu, which was signified by the notable colour development of formazan (Mora et al., 2005). Oxalate enhanced both dehydrogenase and urease activities by more than 50%, while citrate promoted acid phosphatase activity. This was consistent with previous findings that low-molecular-weight organic acids could stimulate enzyme activities (Renella et al., 2007). In contrast, hydroxylamine hydrochloride significantly compromised both acid phosphatase and urease activities due to the low pH and reductive condition. These results indicated that prior washing with strong reductants may significantly disturb the soil properties and lead to unrecoverable damage.

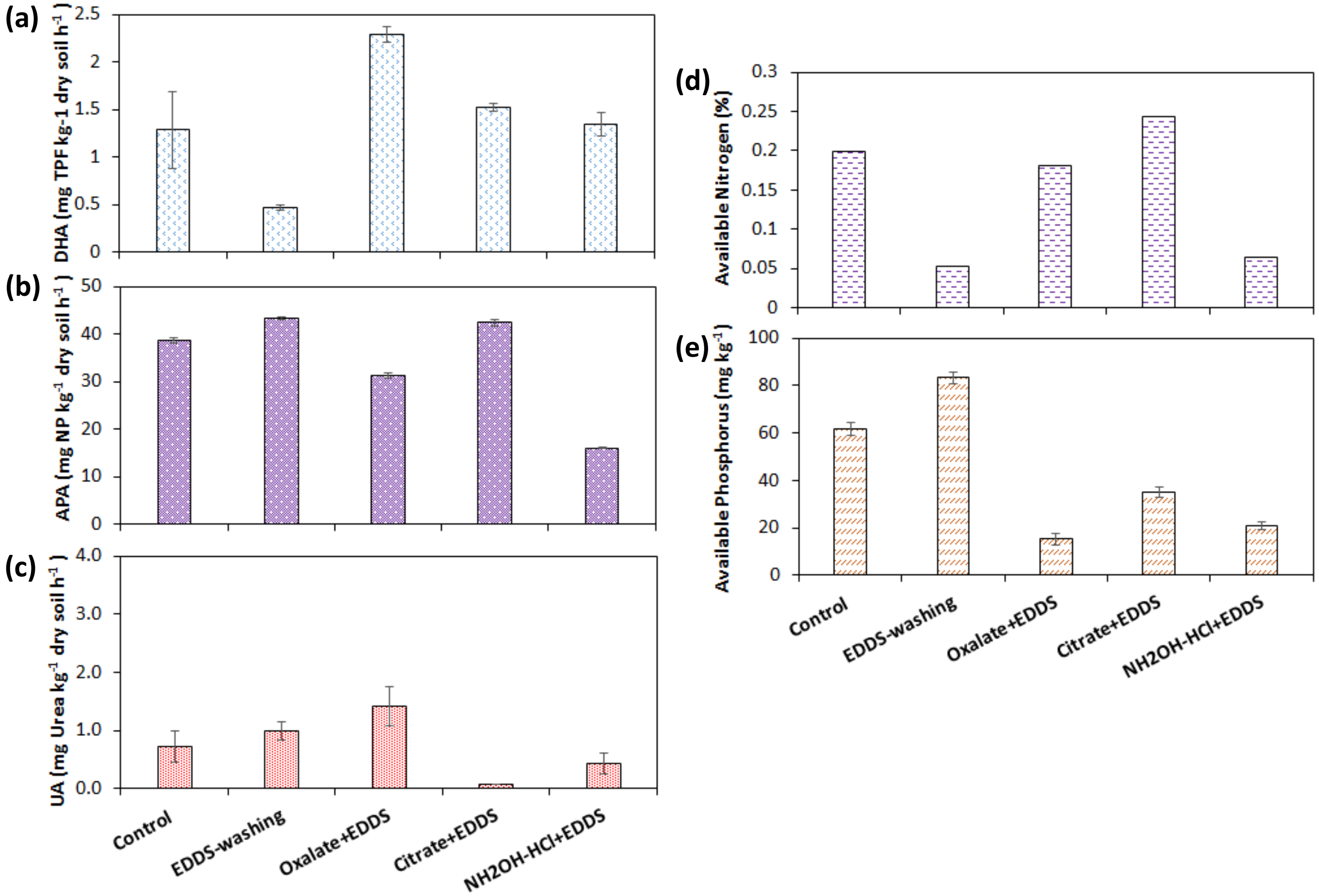


FIGURE 5-7 Dehydrogenase activity (a), acid phosphotase activity (b), urease activity (c), available nitrogen (d), and available phosphorus (e) in the soil before and after sequential washing by EDDS, oxalate+EDDS, citrate+EDDS, and NH_2OH-HCl+EDDS.

Available nitrogen in the soil was decreased by EDDS washing (Fig. 5-7d), which was in agreement with previous findings (Liu and Lin, 2013) and related to solubilization of oxides and organic matter. Prior washing by hydroxylamine hydrochloride also extracted available nitrogen, hindering nitrogen mineralization and uptake by crops from the treated soil. In contrast, prior washing by weak organic acids did not cause a significant change in available nitrogen, possibly because the release of available nitrogen was facilitated by Fe/Al complexation with citrate and oxalate (Matsumoto et al., 2005). On the other hand, EDDS washing itself slightly increased the available phosphorous (Fig. 5-7e), probably by enhancing the solubility of Fe-/Al-bound phosphate in the soil. Nonetheless, two-step washing of oxalate, citrate, and hydroxylamine hydrochloride followed by EDDS washed off the available phosphorus. The leaching of phosphorus could be due to continuous mobilization of soil colloids and organic matter by chelating agent and organic acids (Jalali and Ostovarzadeh, 2009). In contrast, the content of organic carbon increased after sequential washing (Table 5-2), indicating the presence of residual EDDS in the soil. Therefore, this study indicated the need for replenishment of nitrogen and phosphorus to enhance the soil quality after sequential washing.

5.6 Summary

To remediate the e-waste contaminated soil, this study employed various selective dissolution methods to extract strongly bound metals and facilitate subsequent EDDS washing. In general, higher extraction efficiencies were accomplished by reductants and organic acids than oxidants and alkaline solvents, probably because of a larger amount of metals bound to Fe/Mn oxides in this study. After the two-stage washing, the leachability and bioaccessibility of the residual metals were significantly decreased, where subsequent EDDS washing was responsible for removing the metals re-adsorbed on the labile fractions. However, compared to EDDS washing only, sequential washing was found to increase the cytotoxicity and suppress the enzyme activities and available nutrients in the treated soil. LMWOAs were preferred over strong reductants as the former imposed less adverse ecological impact. This study showed that, besides extraction efficiency, the fate of residual metals and impact on soil quality should be considered to enhance the possibility of reusing and backfilling the treated soil.

CHAPTER 6. Phytoavailability and Mobility of Lead and Arsenic in a Contaminated Soil after Stabilization by Pine Sawdust Biochar under Dynamic Redox Conditions

6.1 Characterization of Soil and Amendments and the Effect of pH and E_H

The soil has high total contents of As (2050 mg kg^{-1}) and Pb (1680 mg kg^{-1}) which is about 80 times higher than the permitted value for As (25 mg kg^{-1}) and 8 times higher for Pb (200 mg kg^{-1}) according to the Korea Ministry of Environment (Table 3-2 & 6-1). After 105-day incubation with BM, BC300, and BC550 respectively, the pH of the soil increased from 4.24 (CS) to 4.42 (S&BM), 4.48 (S&BC300), and 5.66 (S&BC550) respectively, which was most probably due to the application of BM or biochars. Besides, modified sequential extraction results indicated the geochemical distribution of As and Pb changed after amendment (Fig. 6-1). Arsenic is bound to crystalline Fe and residue fractio n, and Pb is chiefly bound to the residue fraction, sorbed and carbonate and crystalline Fe in the CS soil after incubation, which indicated that the potential of phytoavailability and mobility of As and Pb were low. Also, As shifted slightly from sorbed and carbonate, manganese and organic to sulfide fraction in S&BM, from organic to sulfide fraction in S&BC300, and from sorbed and carbonate and organic to sulfide fraction in S&BC550, according to Duncan's multiple range test (Table 6-4). BC550 reduced Pb from soluble and exchangeable, manganese, and organic fraction significantly, whereas BM reduced it slightly. BC300 decreased the Pb bound to manganese and organic fraction. These suggested that BM and biochars reduced the mobility of trace elements by shifting them to the less mobile fraction in various degrees after incubation.

TABLE 6-1 Physiochemical properties of contaminated soil (CS), and soils treated with pine sawdust biomass (S&BM), biochar produced at 300 °C (S&BC300), and biochar produced at 550 °C (S&BC550) after 105-day incubation.

	Unit	CS	S&BM	S&BC300	S&BC550
Basic properties					
pH[1]		4.24	4.42	4.48	5.66
EC	µS/cm	223	72.2	164	156
Total carbon	%	1.28	2.19	6.69	7.53
Concentrations[2]					
As	mg kg^{-1}	2050	1950	1680	1910
Pb		1680	1640	1460	1590
Al	g kg^{-1}	46.2	39.3	51.0	58.2
Fe		46.9	44.4	40.0	44.3
Mn		0.72	0.70	0.57	0.63
S		0.48	0.46	0.41	0.45

[1] pH determined in in a 1:5 soil-$CaCl_2$ suspension according to DIN EN 15933 (2012)
[2] According to USEPA 3051a (2007)

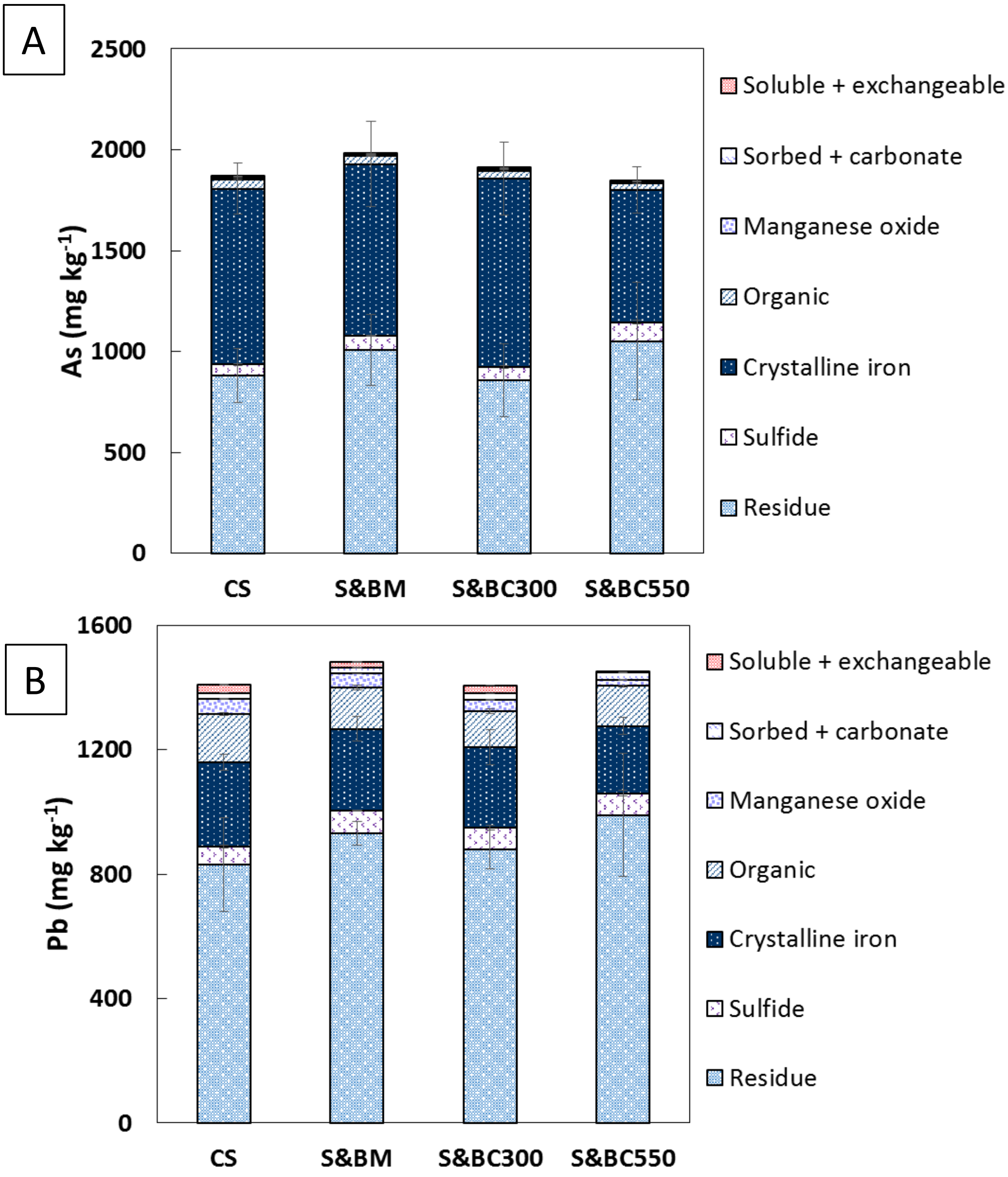


FIGURE 6-1 Sequential extraction results of As and Pb in the untreated contaminated soil (A: CS), and soils treated with pine sawdust biomass (B: S&BM), biochar produced at 300 oC (C: S&BC300), and biochar produced at 550 oC (D: S&BC550) after 105-day incubation.

During the microcosm experiment with controlled pre-set redox conditions, the pH values ranged from 4.5 to 5.5 for CS, S&BM, and S&BC300 and from 5.0 to 6.75 for S&BC550 under various E_H conditions (Fig. 6-2). The pH of the slurry increased when E_H decreased, which is most probably due to the consumption of protons by the reductions of Fe^{3+}, Mn^{4+} and NO_3^- for CS (for the whole period) and soil samples with amendments (before the 100 mV defined E_H window) (Yu et al., 2007; Frohne et al., 2011; Rinklebe et al., 2016). After the 100 mV E_H window, the pH fluctuation became stronger, especially for BC550. Biochar produced at higher pyrolysis temperature (550 ºC) leads to higher pH value. This might be due to the removal of functional groups that can provide protons and the accumulations of inorganic minerals on the surface of biochar. It is noteworthy that pH is suggested to be one of the key factors affecting As and Pb fractions in CS, S&BM, S&BC300 and S&BC550. The higher pH condition affects the mobility and phytoavailability of As and Pb by influencing the competition between H^+ ions and metal(loid) ions, which will be discussed in detailed in the following sections 3.2-3.4 (Beesley et al., 2011).

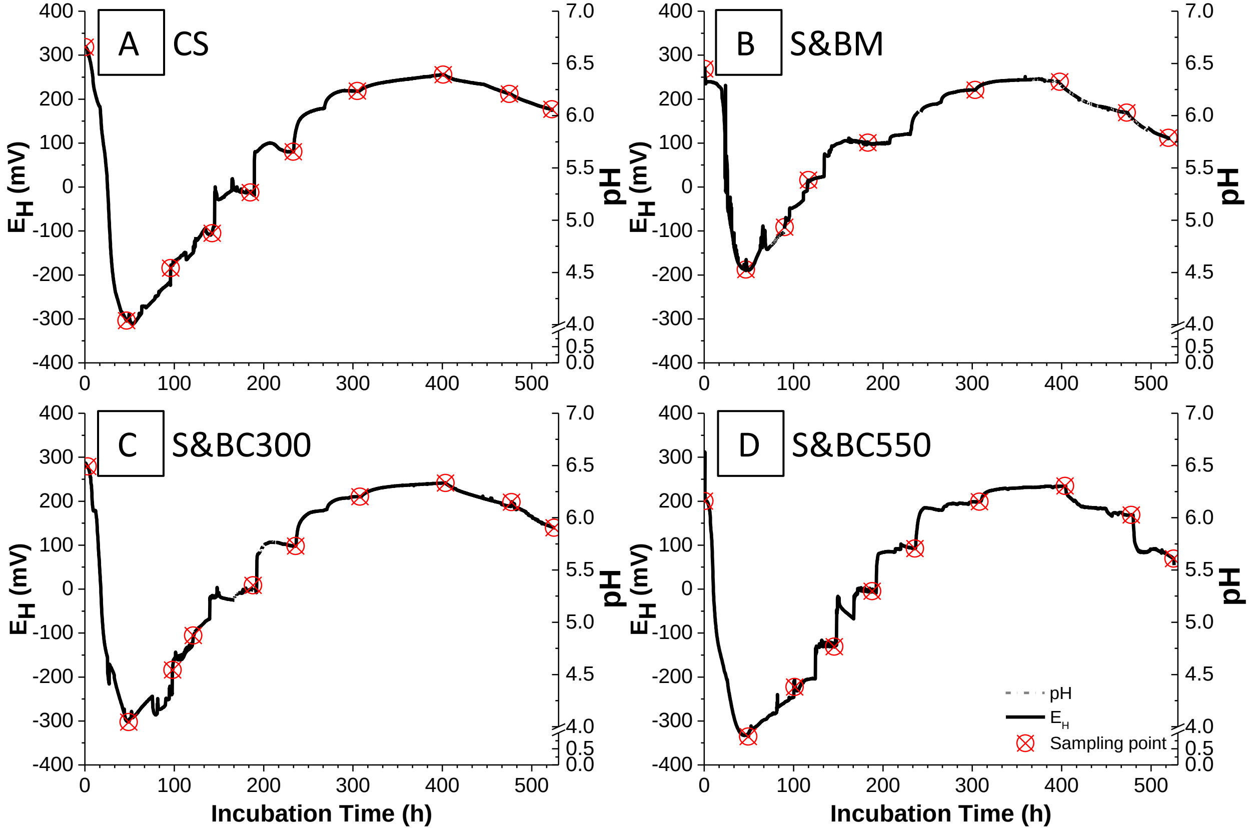


FIGURE 6-2 Development of redox potential (EH: solid line), pH (dash line) and sampling time (cross) in soil slurry (data every 10 min, n= 3,121, 3,109, 3,156, and 3,115 for A, B, C and D respectively which were averages based on an underlying dataset (n ≈ 12,000) of four reduplicate samples) in the microcosms of untreated contaminated soil (A: CS), and soils treated with pine sawdust biomass (B: S&BM), biochar produced at 300 oC (C: S&BC300), and biochar produced at 550 oC (D: S&BC550). The lines represent the average of the four microcosms (replications).

TABLE 6-2 Duncan's multiple range tests results for the modified sequential extraction of As and Pb in the contaminated soil (CS), and soils treated with pine sawdust biomass (S&BM), biochar produced at 300 ºC (S&BC300), and biochar produced at 550 ºC (S&BC550) after 105-day incubation.

Different treatments	**Sequential extraction**						
	Soluble + exchangeable	**Sorbed +carbonate**	**Manganese**	**Organic**	**Crystalline iron**	**Sulfide**	**Residue**
				As content (mg kg^{-1})			
CS	2.27^{ab}	4.45^{b}	8.95^{c}	47.2^{c}	871^{ab}	54.7^{a}	882^{a}
S&BM	2.12^{a}	4.05^{a}	7.64^{b}	39.7^{b}	851^{ab}	70.9^{b}	1010^{a}
S&BC300	2.67^{c}	4.43^{b}	8.42^{c}	39.3^{b}	933^{c}	66.3^{b}	858^{a}
S&BC550	2.13^{a}	4.78^{c}	6.51^{c}	31.2^{a}	655^{a}	93.9^{c}	1050^{a}
				Pb content (mg kg^{-1})			
CS	26.8^{c}	19.8^{a}	48.7^{d}	155^{c}	272^{a}	58.2^{a}	830^{a}
S&BM	18.9^{b}	19.5^{a}	43.0^{c}	135^{b}	263^{a}	71.9^{a}	932^{a}
S&BC300	26.4^{c}	19.9^{a}	37.8^{b}	116^{a}	258^{a}	69.4^{a}	880^{a}
S&BC550	2.83^{a}	24.0^{b}	19.3^{a}	129^{b}	215^{a}	69.9^{a}	991^{a}

* Duncan's multiple range tests (SPSS, 22.0) were used to determine the significance levels ($p < 0.05$) within one washing step for various treatments.

TABLE 6-3 Two-factor ANOVA showing the effect of amendments and EH conditions on the tested variables.

Source	***df***	**As Mobility**	**Pb Mobility**	**As Phytoavailability**	**Pb Phytoavailability**
				P > F	
Amendments	3	< 0.0001***	< 0.0001***	< 0.0001***	< 0.0001***
E_H conditions	9	< 0.0001***	< 0.0001***	< 0.0001***	< 0.0001***
Error *MS*		1.5	0.049	2.284	0.033
R^2		0.874	0.749	0.922	0.940

*P <0.05, **P <0.01, and ***P <0.001

6.2 Mobility of As under Various E_H Conditions

Statistical analysis by two-factor ANOVA (Table 6-5) showed that the mobility of As in CS, S&BM, S&BC300, and S&BC550 was significantly affected by the E_H conditions and various amendments used ($p < 0.05$), as well as phytoavailability of As and Pb. The mobility of As for CS, S&BC300, and S&BC550 was higher from reducing conditions (-300 to 100 mV E_H window) than oxidizing conditions (100 to 250 mV E_H window) excluding the fluctuation at -100 (S&BC300) and 0 mV (CS and S&BC500) (Fig. 6-3). In general, the results were consistent with our previous studies of As concentration in the liquid phase under various E_H conditions (Frohne et al., 2011). However, the mobility of As was controlled well for S&BM, under both anoxic and oxic conditions (the reason will be discussed in the following paragraphs). Many factors affect the mobility of As in the flooded soils, such as metal concentration, adsorption/desorption processes, pH, redox condition, organic matter, Fe, Mn, and S chemistry under flooded conditions (Takahashi et al., 2004; Gorny et al., 2015). Sequential extraction results showed that there were still over 50% of As bound to the Fe/Mn oxide part for CS, S&BM, and S&BC300, after 105-day incubation of this soil (Fig. 6-1). That indicated an enormous amount of As might be mobilized under anaerobic conditions (E_H < -100 mV) for all treatments. Two major reasons are possible for the pattern of mobility of As under varied E_H conditions: a) the reduction of Fe/Mn (hydr)oxides under the anoxic condition which leads to the release of As which co-precipitate or adsorbe on the Fe/Mn (hydr)oxides, and b) the shift from arsenate to arsenite which also contributed to an increased mobility of As (Du Laing et al., 2009a; Borch et al., 2010; Gorny et al., 2015). It is noteworthy that pH is suggested to be one of the key factors affecting the mobility and phytoavailability of As and Pb fractions in CS, S&BM, S&BC300 and S&BC550. The higher pH condition affects the mobility and phytoavailability of As and Pb by influencing the competition between H^+ ions and metal(loid) ions. However, Mn hydr(oxide) could not be the major reason, since it exits mostly as Mn^{2+} due to the slightly acidic condition (pH 4.5-6) in our study (Takeno, 2005).

The mobility of As ranged from 5-12.5 mg kg^{-1} in CS (Fig. 6-3), it became lower when treated with BM and BC300 to around 5 mg kg^{-1} and 5-10 mg kg^{-1}, respectively. With the amendment of BC550, the mobility of As ranged around 5-15 mg kg^{-1}. BM has a lignocellulosic surface which also offers significant amounts of hydroxyl and phenol functional groups, which can bind trace elements by forming stable complexes and precipitations and facilitating the sorption of metal(loid)s on its surface (Kurniawan et al., 2006). Besides that, less dissolved Fe and Mn were found and matched the variation of As mobility by SPLP extraction (Fig. 6-4&6-5), which indicated a suspected suppression of dissolution of Fe and Mn oxides with the help of BM. One of the possible reasons could be the DOC provided by BM served as electron accepters and hamper the oxide dissolution (Dong et al., 2014). Also, increased DOC with the addition of BM may also enhance the oxidation of As^{III} in the liquid phase and the oxidation efficacy was increased with the slight increasing of pH as reported in a study by Dong et al. (Dong et al., 2014). Hence, the mobility of As might be reduced for the oxidation to As^{V} which has a lower mobility. The SEM-EDX result also showed that BM has a higher O/C ratio (0.66) than BC300 and BC550, which indicate it is more hydrophilic. Biochar produced under low temperatures, like BC300, offered abundant oxygen-containing carboxyl, hydroxyl and phenolic functional groups (Uchimiya et al., 2011b; Ahmad et al., 2014b; Gorny et al., 2015; Stuckey et al., 2015). 300 ˚C is not high enough for a complete decomposition of carbohydrates, cellulose, hemicelluloses, lignin which are the common components for pine sawdust, while for 550 ˚C could be sufficient for the carbohydrates, cellulose, and hemicelluloses (Yang et al., 2007; Wei et al., 2015). BC550 produced at a higher temperature was considered with a highly aromatic structure and carbonized. Thus it was suspected that the useful oxygen-containing function groups for stabilizing As were removed mostly (Rajapaksha et al., 2014). The SEM-EDX result also showed that BC300 has a higher O/C ratio (0.32) than BC550 (0.18), which indicate it is more hydrophilic (Ahmad et al., 2012b). On the other hand, BC550 offered a higher surface area (189.2 m^2 g^{-1}) than BC300 (< 1 m^2 g^{-1}) (according to BET method) (Lou et al., 2016a).

The mobility of As increased dramatically from -300 to 100 mV for S&BC550 condition, except the fluctuation at 0 mV. Those values are even higher than in CS as well as in comparison with S&BM and S&BC300. We believe that the high mobility of As in the BC550 treatment resulted from a slightly higher pH (~5.0 to 5.25) than the other amendments during the microcosm experiment (pH ranged 4.5 to 4.75) (Fig. 6-2) (Almaroai et al., 2013b; Ahmad et al., 2014b). Soil pH plays a major role in controlling the mobility of As, which due to the reduced adsorption effect on Fe oxide surfaces when the pH become higher (Madejon and Lepp, 2007; Hartley et al., 2009). The pH of the extractant of SPLP is 4.2, which is not strong enough to buffer the soil-solution system. Another possible reason could be the increasing released phosphorus (P) which released from biochar under a higher soil pH replaced the As sorbed on the biochar surface because of the chemical similarity of As and P (Hartley et al., 2009). Though after 105-day incubation by BC550, there was a small amount of As binding to the from sorbed and carbonate and organic shifted to sulfide fraction according to the result of sequential extraction (Fig. 6-1 and Table 6-4).

The dramatic decrease of As mobility at -100 (S&BC300) to 0 mV (CS and S&BC550) and 200 mV (CS, S&BC300, and S&BC550) could be strongly related to the redox chemistry of S, Fe, and Mn oxide under the changing E_H. High concentrations of Fe and Mn acting similar pattern with As were found in the mobility test at -100 mV to 0 mV and 200 mV (Fig. 6-4&6-5). When E_H began to reduce to the area around -100 mV to 0 mV, pyrite (FeS_2, $k_{sp} = 10^{-16.4}$) forms possibly, therefore the mobility of As reduced greatly potentially by forming arsenian pyrite or adsorption on the pyrite (Tao et al., 1994; Farquhar et al., 2002). When E_H raised to around 200 mV, pyrite dissolves and SO_4^{2-} forms. The oxidation of Fe^{2+} and Fe^{3+} also could be one of the reasons making the situation complicated.

6.3 Phytoavailability of As under Various E_H Conditions

Although the initial E_H value was high (317, 257, 382 and 206 mV for CS, S&BM, S&BC300, and S&BC550 respectively), the phytoavailable As was lowest under various treatments (Fig. 6-6). One of the possible reason is the equilibrium have not been reached at the beginning of the experiment. The 6-h average pH values before the initial sampling were 6.27 for S&BC550, 5.38, 5.58, and 5.56 for CS, S&BM, and S&BC300, respectively. They were the highest values for CS, S&BM, and S&BC300 during the whole experiment (Fig. 6-2), while the water-soluble As is believed that strongly related to the pH condition (Beesley and Marmiroli, 2011).

In general, the phytoavailable As showed an increasing trend with enhanced E_H, which is particularly obvious after the 0-100 mV E_H window where the phytoavailability of As rose from 20 to 35 mg kg^{-1}. These general patterns were significantly different from the fluctuation pattern of the mobility As in this study which was even higher when E_H was < 0 mV and previous studies (Fig. 6-3) (Frohne et al., 2011). After 100 mV E_H window, more phytoavailable As released under all amendments. It could be resulted from extractant used to evaluate the As phytoavailability which included organic acids like acetic, lactic, citric, malic and formic acid. Carboxylic acids (such as citric and malic acid) is able to capture P though chelation, due to the physicochemical similarity between P and As, citric and malic acid could have better extraction ability with As than HNO_3 and H_2SO_4 in SPLP extractant (Fitz and Wenzel, 2002). At pH 4.5-5 (slurry pH for S&CS, S&BM, and S&BC300), As exists as As(S) mostly when E_H < - 200 mV, while Fe and Mn exist as Fe^{2+} and Mn^{2+}, respectively, according to the FACT database (Takeno, 2005). When E_H > -200 mV, As exists as As^{III} ($HAsO_2$) mainly, which indicated an increase of mobility. The phytoavailability change pattern of As could be affected by the interactions of the As speciation under such E_H and pH conditions in sampling and the acidic extractant (pH = 1.6) which favors immobilizing the As under a higher E_H (< 0 mV).

Slight suppresses of the phytoavailability of As were observed with the help of BM and BC300 in comparison with CS (Table 6-6), which is similar to the results of As mobility. BC550 released more phytoavailable As particularly after the 100 mV E_H window. The possible reasons could be similar to the increased mobility of As with the assistant of BC550.

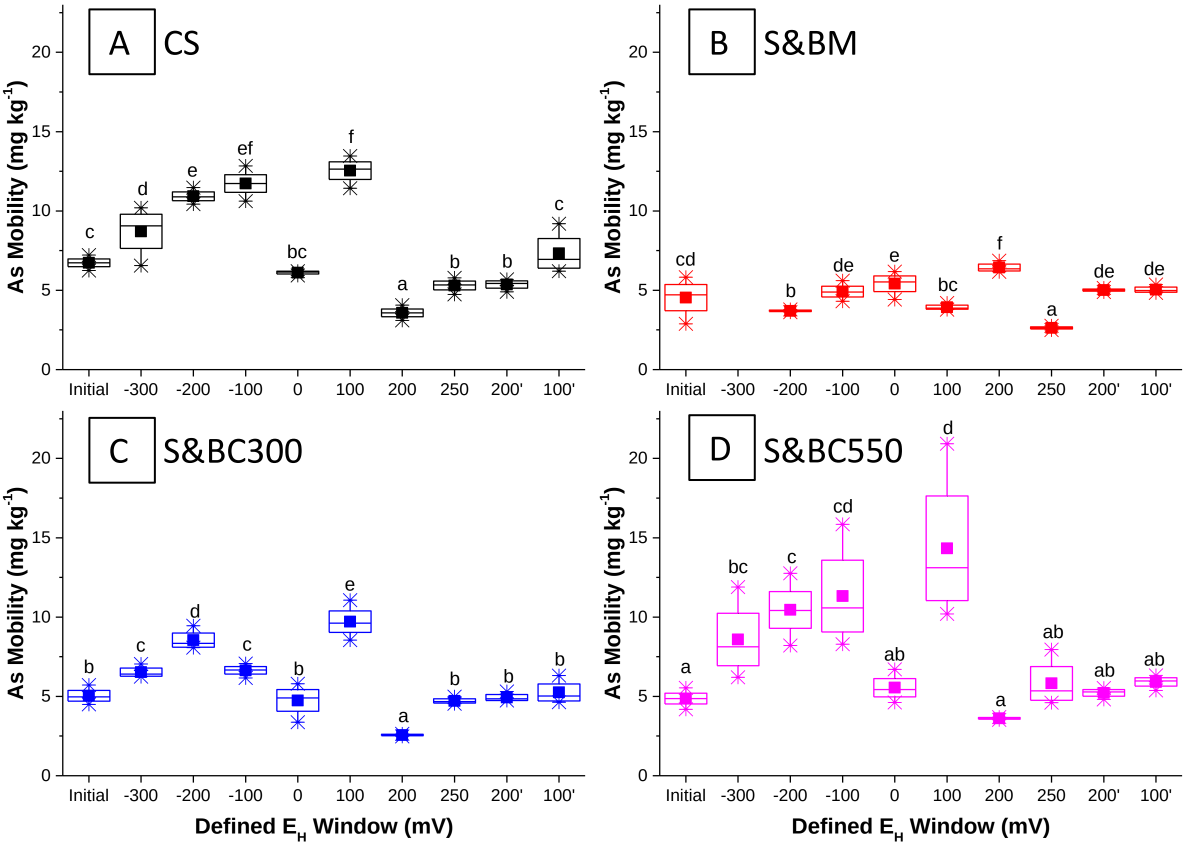


FIGURE 6-3 Mobility of As in the untreated contaminated soil (A: CS), and soils treated with pine sawdust biomass (B: S&BM), biochar produced at 300 ºC (C: S&BC300), and biochar produced at 550 ºC (D: S&BC550) under various E$_H$ conditions.

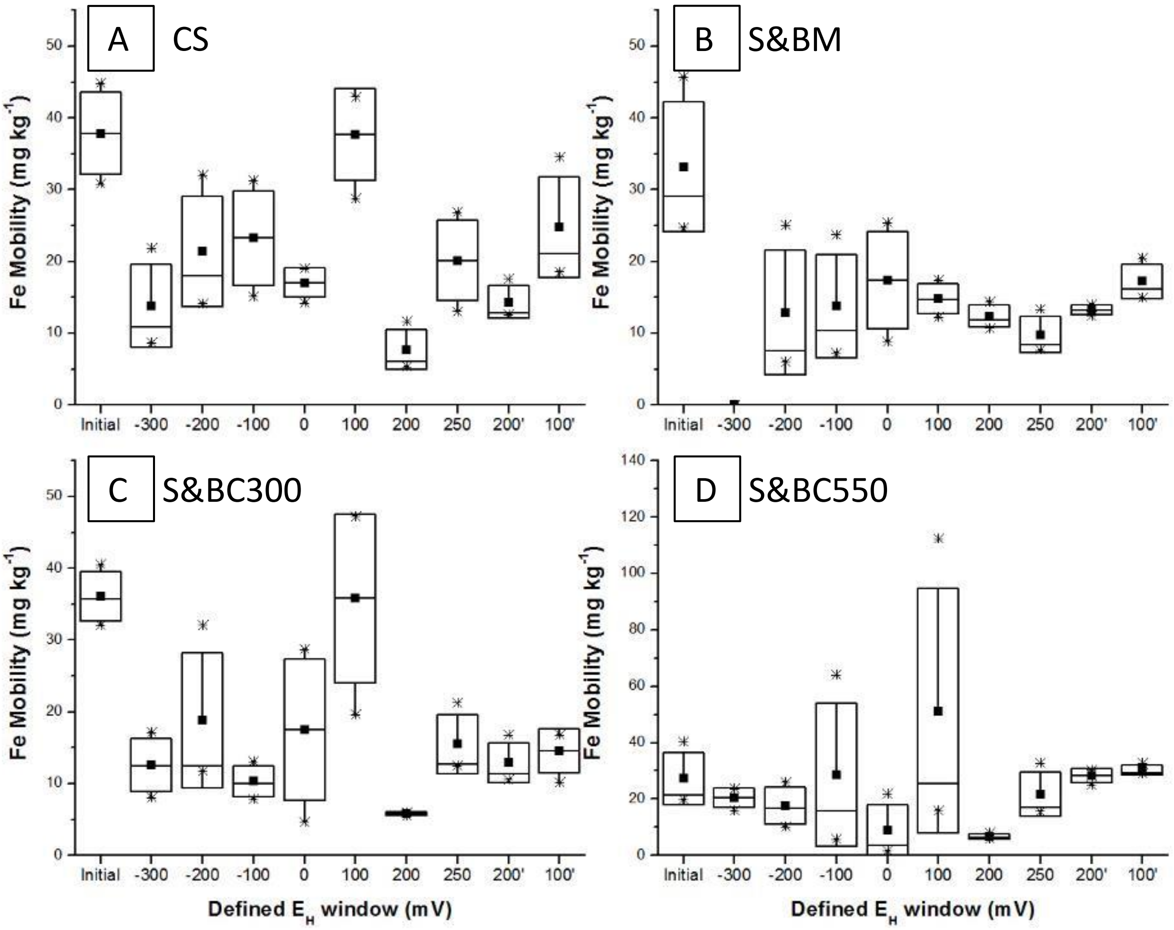


FIGURE 6-4 Mobility of Fe in the untreated contaminated soil (A: CS), and soils treated with pine sawdust biomass (B: S&BM), biochar produced at 300 °C (C: S&BC300), and biochar produced at 550 °C (D: S&BC550) under various E_H conditions.

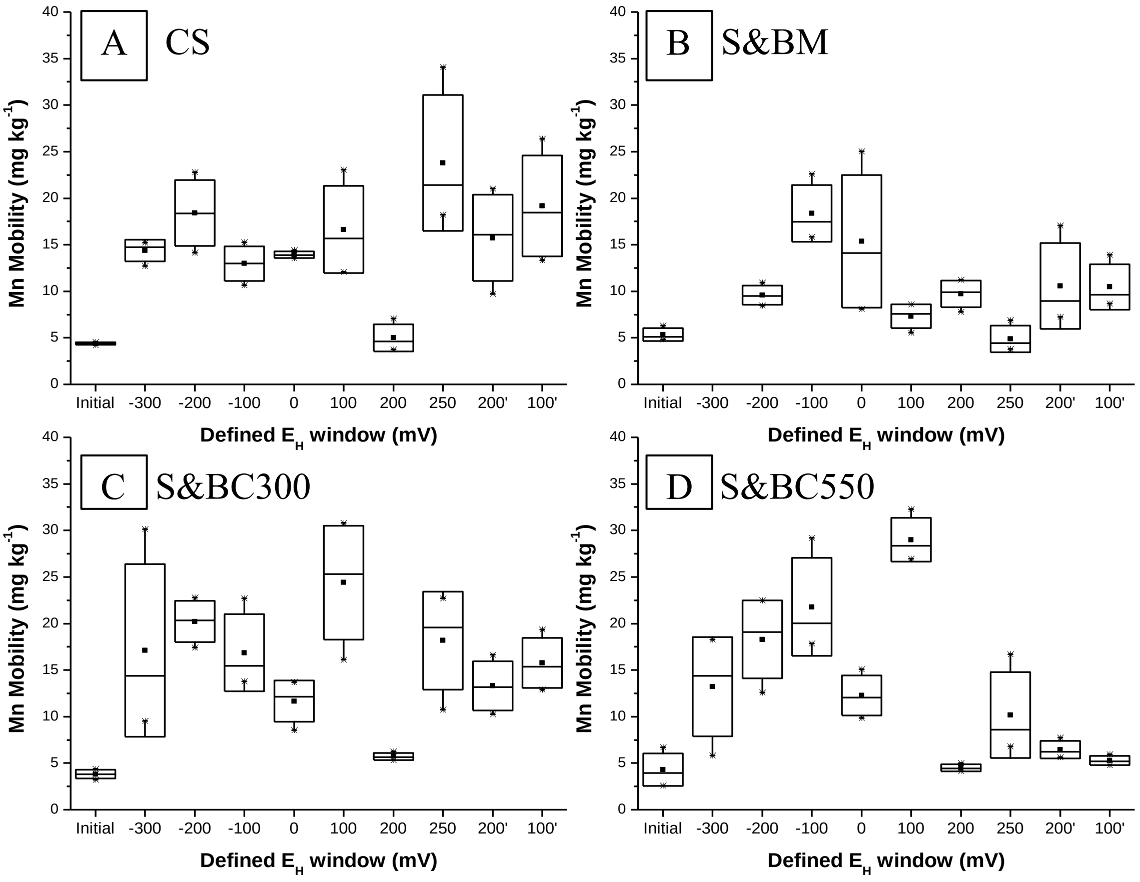


FIGURE 6-5 Mobility of Mn in the untreated contaminated soil (A: CS), and soils treated with pine sawdust biomass (B: S&BM), biochar produced at 300 °C (C: S&BC300), and biochar produced at 550 °C (D: S&BC550) under various E_H conditions.

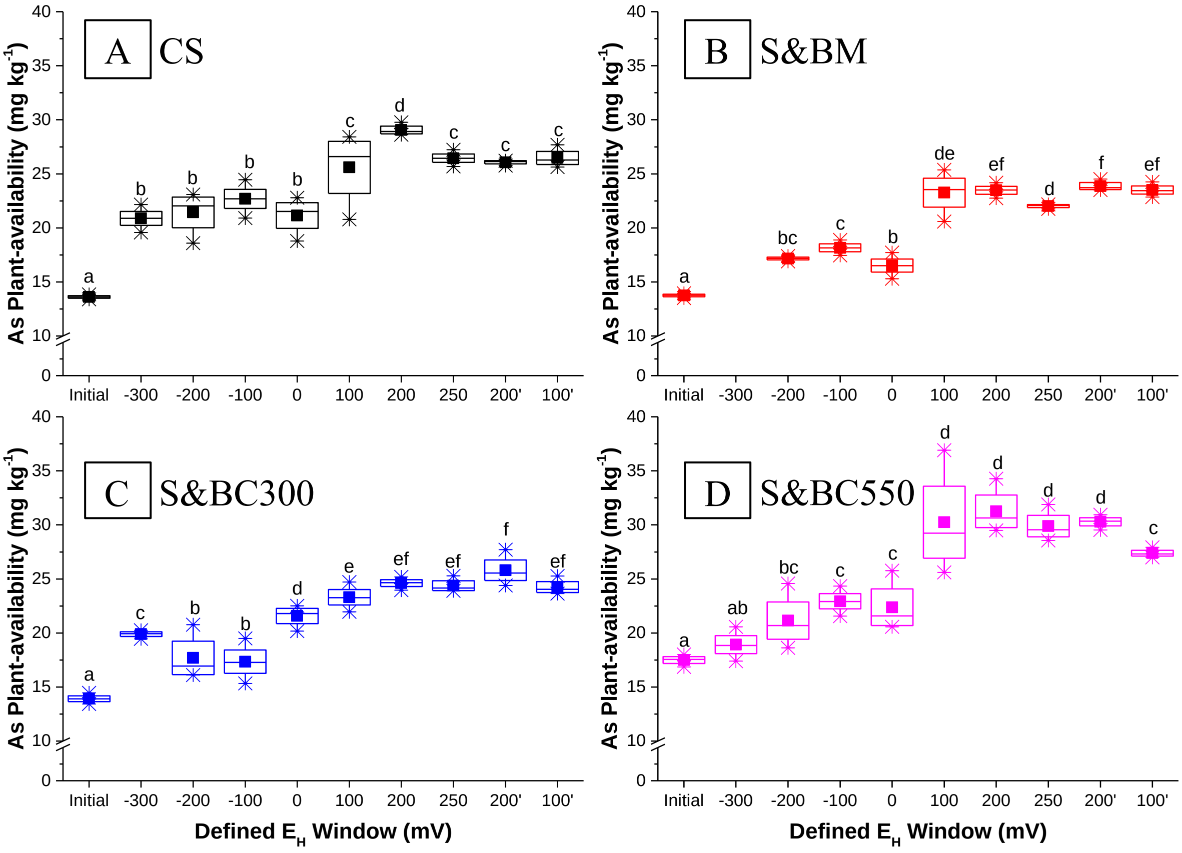


FIGURE 6-6 Phytoavailability of As in the untreated contaminated soil (A: CS), and soils treated with pine sawdust biomass (B: S&BM), biochar produced at 300 °C (C: S&BC300), and biochar produced at 550 °C (D: S&BC550) under various E$_H$ conditions.

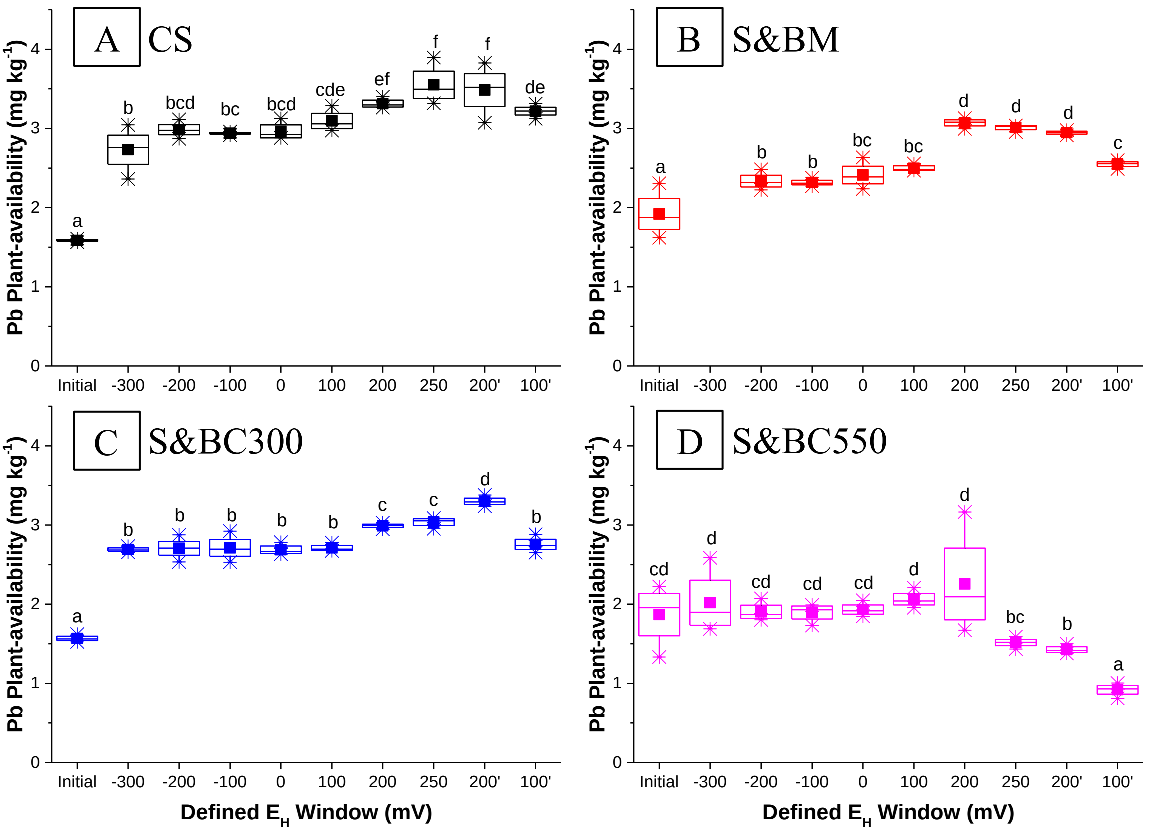


FIGURE 6-7 Phytoavailability of Pb in the untreated contaminated soil (A: CS), and soils treated with pine sawdust biomass (B: S&BM), biochar produced at 300 °C (C: S&BC300), and biochar produced at 550 °C (D: S&BC550) under various E_H conditions.

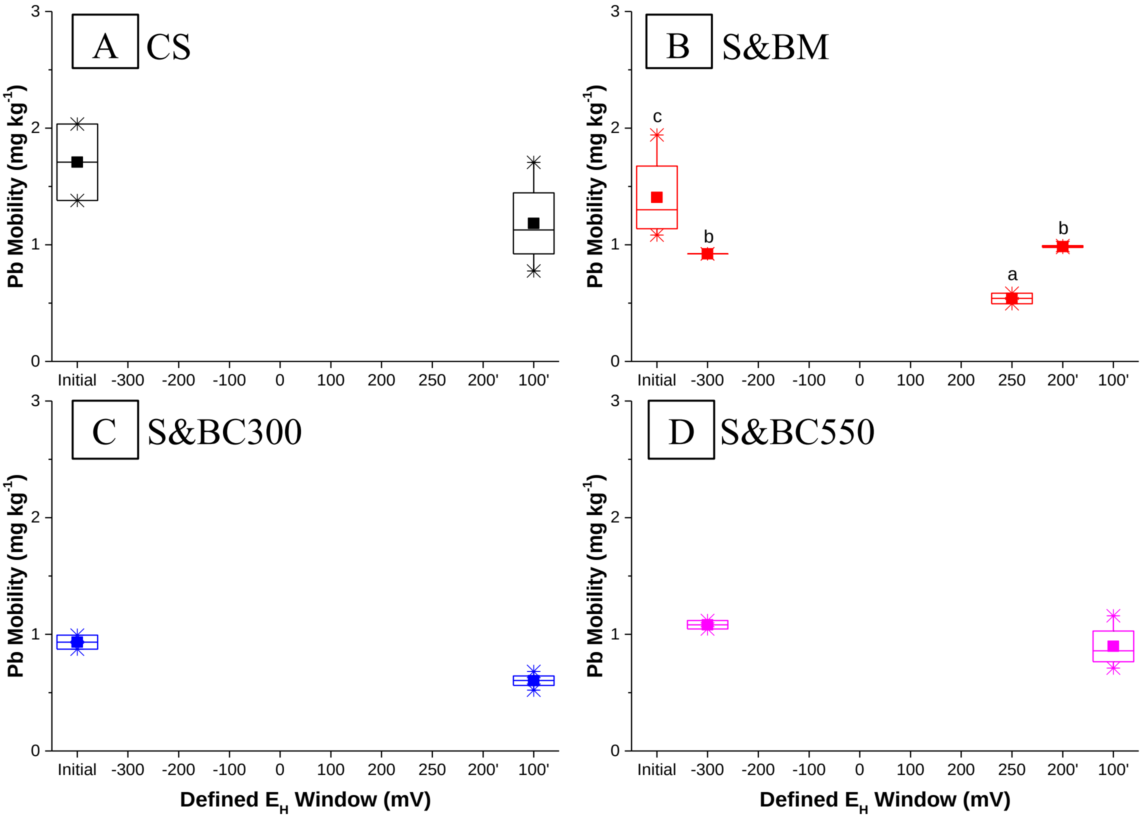


FIGURE 6-8 Mobility of Pb in the untreated contaminated soil (A: CS), and soils treated with pine sawdust biomass (B: S&BM), biochar produced at 300 °C (C: S&BC300), and biochar produced at 550 °C (D: S&BC550) under various E_H conditions.

TABLE 6-4 Duncan's multiple range tests results for phytoavailability and mobility of As and Pb within the defined E_H windows for various amendments. (All metal data were presented in average).

Different treatments	Defined E_H windows								
	Initial	**-300**	**-200**	**-100**	**0**	**100**	**200**	**250**	**200'**	**100'**
As Plant-availability (mg kg^{-1})									
CS	13.6^{a}*	20.9^{b}	21.4^{b}	22.7^{b}	21.2^{b}	25.6^{ab}	29.1^{b}	26.4^{c}	26.1^{b}	26.5^{b}
S&BM	13.8^{a}	NA**	17.2^{a}	18.2^{a}	16.5^{a}	23.3^{a}	23.5^{a}	22.0^{a}	23.9^{a}	23.5^{a}
S&BC300	13.9^{a}	19.9^{ab}	17.7^{a}	17.3^{a}	21.6^{b}	23.3^{a}	24.6^{a}	24.4^{b}	25.8^{b}	24.3^{a}
S&BC550	17.5^{b}	18.9^{a}	21.1^{b}	22.9^{b}	22.4^{b}	30.2^{b}	31.3^{c}	29.9^{d}	30.3^{c}	27.4^{b}
Pb Plant-availability (mg kg^{-1})									
CS	1.59^{a}	2.73^{b}	2.98^{d}	2.94^{d}	2.96^{d}	3.09^{d}	3.31^{b}	3.55^{c}	3.48^{c}	3.22^{d}
S&BM	1.92^{a}	2.69^{b}	2.34^{b}	2.32^{b}	2.41^{b}	2.50^{b}	3.07^{b}	3.01^{b}	2.95^{b}	2.55^{b}
S&BC300	1.57^{a}	NA	2.71^{c}	2.71^{c}	2.69^{c}	2.71^{c}	2.99^{b}	3.04^{b}	3.30^{c}	2.75^{c}
S&BC550	1.87^{a}	2.02^{a}	1.90^{a}	1.89^{a}	1.93^{a}	2.06^{a}	2.26^{a}	1.52^{a}	1.43^{a}	0.92^{a}
As Mobility (mg kg^{-1})									
CS	6.73^{d}	8.71^{a}	10.9^{c}	11.7^{c}	6.11^{c}	12.5^{bc}	3.58^{b}	5.30^{b}	4.93^{a}	7.33^{b}
S&BM	4.53^{a}	NA	3.70^{a}	4.92^{a}	5.41^{ab}	3.93^{a}	6.43^{c}	2.63^{a}	5.01^{a}	5.04^{a}
S&BC300	5.04^{c}	6.53^{a}	8.55^{b}	6.64^{b}	4.75^{a}	9.72^{b}	2.57^{a}	4.71^{b}	5.22^{a}	5.25^{a}
S&BC550	4.86^{b}	8.58^{a}	10.5^{c}	11.3^{c}	5.55^{ab}	14.3^{c}	3.62^{b}	5.82^{b}	5.37^{a}	5.91^{a}
Pb Mobility (mg kg^{-1})									
CS	1.71^{b}	NA	BDL	BDL	BDL	BDL	BDL	BDL	BDL	1.18^{b}
S&BM	1.41^{ab}	0.92^{a}	BDL	BDL	BDL	BDL	BDL	0.54	0.98	BDL
S&BC300	0.93^{a}	1.08^{b}	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.60^{a}
S&BC550	BDL***	0.85^{a}	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.90^{ab}

* Duncan's multiple range tests (SPSS, 22.0) were used to determine the significance levels ($p < 0.05$) within the defined E_H windows for various treatments.

** NA = Not Applicable

*** BDL = Below the Detection Limit

6.4 Phytoavailability of Pb under Various E_H Conditions

The pattern of Pb phytoavailability under different E_H conditions increased slightly after the 200 mV E_H window for CS, S&BM, and S&BC300 (Fig. 6-7), which is similar to the tendency of phytoavailability of As. Based on the results of sequential extraction, the potential labile Pb (soluble + exchangeable and sorbed + carbonate fraction) in this study only reached ~3% of the total Pb (Fig. 6-1), which suggested the phytoavailable Pb in the CS is limited. The highest phytoavailability of Pb was found between 200 to 200' mV E_H windows (almost the highest E_H condition) for CS, S&BM, and S&BC300. Under oxic conditions ($E_H > 0$ mV) and pH ranged from 4.5-5.0, sulfide is oxidizing to sulfate, which lead to the release of Pb bond to sulfide fraction (Takeno, 2005). According to our sequential extraction result, part of Pb is bonding to the sulfide fraction, which could lead to the increment of the phytoavailable Pb. The phytoavailable Pb decreased with the E_H pattern from 200, 250 to 200' and 100' mV window in the BC550 treatment, which is different from the other treatments. This phenomenon is most probably due to the shift of slurry pH from 5.0 to 6.5 in the above E_H windows (Fig. 6-2). It is believed that enhancement of the soil pH by amendments is one of the major ways to immobilize Pb (Ok et al., 2011b; Ahmad et al., 2012a). An increasing soil pH facilitated the sorption of Pb onto kaolinite, which probably due to the enhanced negative charge on the mineral surface (Ahmad et al., 2014a). An application of oak wood biochar successfully reduced the exchangeable Pb in soil, which is found significantly related to the soil pH, as reported by Ahmad et al. (Ahmad et al., 2014a). Although the extractant pH of phytoavailability test is around 1.6, the slurry pH was buffered more strongly by the addition of BC550 in comparison with the other treatments. Secondly, increasing phosphorus released in the aqueous phase when the pH become higher, as we mentioned in the previous section (Hartley et al., 2009). This could lead to more Pb precipitation with phosphorous, thus less phytoavailable Pb release. Cao et al. found that leachability of Pb (evaluated by the Toxicity Characteristic Leaching Procedure, USEPA method 1311) reduced by the application of a dairy manure biochar because of the forming of hydroxypyromorphite ($Pb_5(PO_4)_3OH$, $k_{sp} = 10^{-78}$) precipitation (Cao et al., 2011).

Phytoavailable Pb was significantly decreased by BC550 and BM for most of the E_H windows, while slightly by BC300 (Table 6-6). BM, BC300 and BC550 generally exhibit slightly alkaline pH conditions indicating their good potential to decreased phytoavailable Pb by increasing the net negative charge of soil constituents as mentioned above (Almaroai et al., 2013b; Ahmad et al., 2014b). Application of biochar increases soil pH and may lead to forming of Pb-hydroxide as well as Pb-phosphorus precipitations, therefore, reduce the phytoavailable or easily-mobilized Pb, which have been well documented in previous studies (Ahmad et al., 2012a; Ahmad et al., 2012c; Ahmad et al., 2016c). Biochar effects on mobility and phytoavailable metals in soil varied independent of feedstock type, pyrolysis temperature and the application rate (Almaroai et al., 2013b). In particular, a large amount of oxygen-containing functional groups, carboxyl groups (-COOH), on the surface of BM and BC300 could facilitate the immobilization of Pb by complexation (Rajapaksha et al., 2015). Also, the negatively charged surface of biochars might enhance the electrostatic attraction of cations like Pb to develop a π-cation electron donor-acceptor interaction (Ahmad et al., 2016b). Though BC550 has a higher surface area than BC300 and BM, sorption on the biochar surface is not considered as the chief reason for the higher reduction of phytoavailable Pb. That is because lower suppression of Pb leachability was found by activated carbon which has a much higher surface area than biochar were found in a previous study (Cao et al., 2011). Data of Pb mobility are limited because values often fall below detection limits of our ICP-OES; thus those data are presented in Fig. 6-8.

6.5 Summary

Overall, this study indicated that both the type of amendments and E_H variation significantly affected the mobility and phytoavailability of As and Pb. In general, low E_H conditions favored the mobility of As. The different behaviors of mobility and phytoavailability of As might be due to the low pH of the later extractant, which suggested that under oxic condition (E_H > 100 mV) rhizosphere exudates could still lead to higher available As. Unexpectedly, pine sawdust biomass has the best performance on controlling the mobility and phytoavailability of both As and Pb even under dynamic E_H conditions, which probably due to the abundant oxygen-containing functional groups on its surface and the slight acidic properties. The effectiveness of BC300 was considered between BM and BC550 for its sufficient organic functional groups. BC550 increased the mobility and phytoavailability of As, while reduced the phytoavailable Pb, which probably ascribe to the increment in the soil pH and containing less oxygen-containing functional groups. Thus, the selection of amendments for metal(loid) contaminated soils should be made carefully, especially for the application under a varied E_H condition, such as on a contaminated paddy soil with As and Pb.

CHAPTER 7. Integrating EDDS-enhanced washing with low-cost stabilization of metal-contaminated soil from an e-waste recycling site

7.1 Post-Remediation Leachability and Mobility

A field soil was employed in this study which is highly contaminated by Cu, Zn, and Pb from an e-waste recycling site (Table 3-1). Two-hour EDDS washing removed around 34% of Cu, 23% of Zn, and 31% of Pb from the soil, respectively. The selected short washing time, for the reasons of economical operation, was only able to extract a portion of the target metals that were weakly bound to the soil, which however should be the most labile and susceptible to leaching. Compared with the untreated soil, 2-h EDDS washing reduced the TCLP leachability of the three metals by >57% (Fig. 7-1a), but it dramatically increased the SPLP mobility of Cu (Fig. 7-1b). This was consistent with our previous findings that EDDS complexation with Cu was preferred over Zn and Pb (Tsang et al., 2009b; Lo et al., 2011a), such that the remaining Cu species in the washed soil were shifted to the exchangeable fraction as indicated by sequential extraction (Tsang et al., 2013a; Tsang and Hartley, 2014). Such labile fraction was prone to leaching out and the effect was more discernible in terms of SPLP mobility than TCLP leachability, because the former test employed a less aggressive condition (simulating metal leaching under acid rainfall) where the strongly bound metals leached out by a much smaller extent. These results illustrated the need for considering multiple endpoints of leaching tests and suggested the possible improvement by integrating stabilization after EDDS washing.

Figures 7-1a&b show that 2-month stabilization by biochars or CFA significantly reduced the TCLP leachability and SPLP mobility of Cu, Zn and Pb by >98% compared to that of untreated soil. The Pb and Zn concentrations in the leachate after TCLP and SPLP tests were below the detection limits of ICP-OES analysis (0.2 and 0.1 mg L^{-1}, respectively). After integrating 2-h EDDS washing with 2-month stabilization, the leachability and mobility of residual metals were notably reduced in comparison with 2-h EDDS washing alone, especially for Cu (Fig. 7-1c&d). It has been shown that Cu, Pb and Zn could be immobilized on the surface of the biochar via formation of surface complexes and precipitates, as well as ion exchange with oxygen-containing functional groups, carboxyl groups (-COOH) in particular (Uchimiya et al., 2011c; Rajapaksha et al., 2016). In addition, electrostatic attraction and cation-π electron donor-acceptor interactions could occur on the graphene-like surface of biochar (Qiu et al., 2009; Zhang et al., 2015; Ahmad et al., 2016b). Moreover, precipitation of newly formed Pb-containing minerals (such as ($Pb_5(PO_4)_3(OH)$)) was also identified as an immobilization pathway because of available phosphorus released from the biochar (Cao et al., 2011; Moon et al., 2013a). Similarly, for the amendment with CFA, the large quantities of Fe-, Al- and Ca-containing components might contribute to metal stabilization by surface complexation and electrostatic attraction onto the surface of CFA as well as carbonate/hydroxide precipitation (Ksp ($Cu(OH)_2$) = 2.2×10^{-20}, Ksp ($PbCO_3$) = 7.4×10^{-14}, Ksp ($Pb(OH)_2$) = 1.2×10^{-15}, Ksp ($Zn(OH)_2$) = 1.2×10^{-17}) (Lide, 2003). However, mineral precipitates could not be identified due to relatively low concentrations of Cu, Zn and Pb in the contaminated soil.

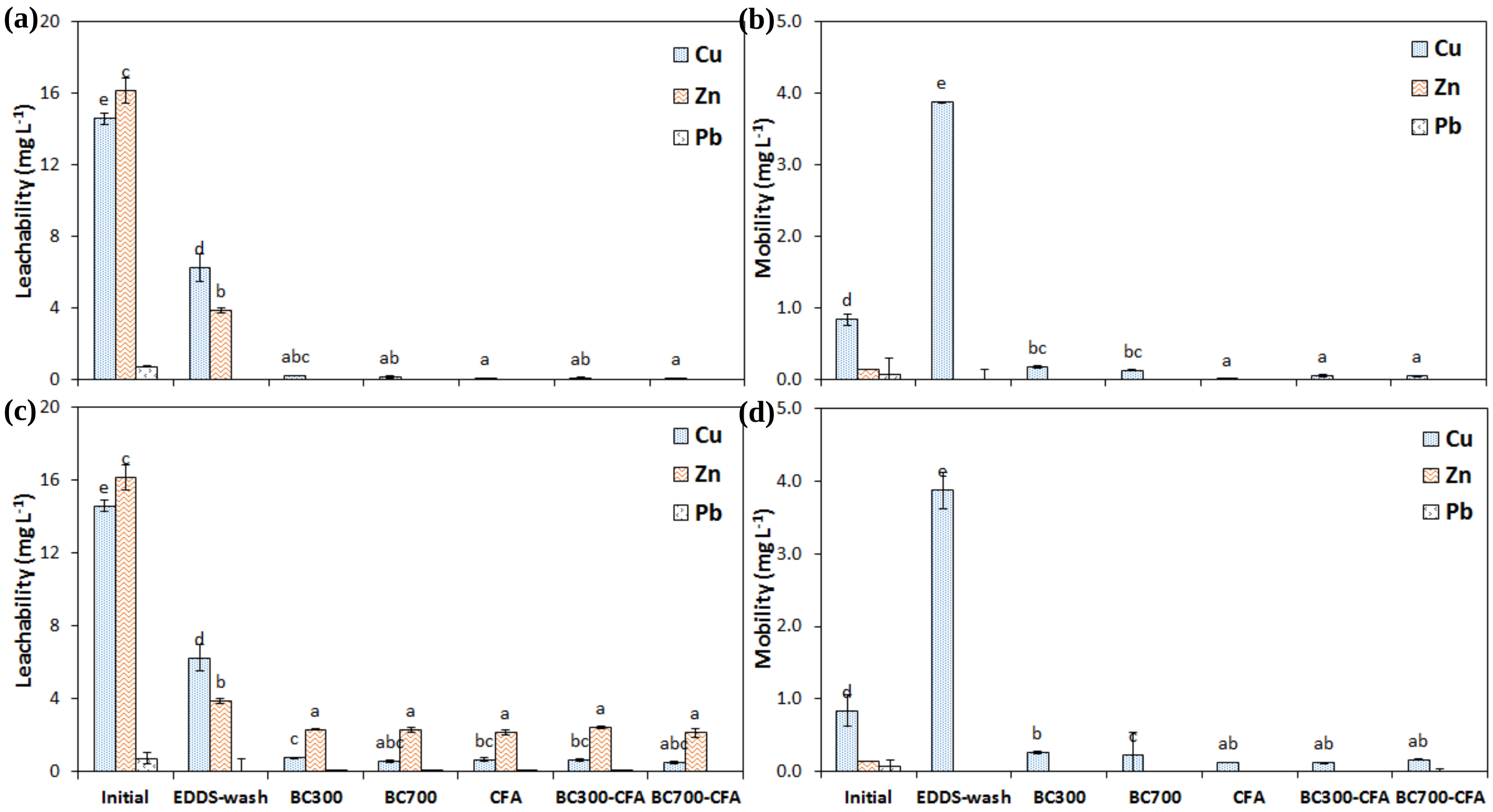


FIGURE 7-1 TCLP leachability (a&c) and SPLP mobility (b&d) of Cu, Zn and Pb in the e-waste contaminated soil after: (a&b) 2-month stabilization only; and (c&d) 2-h EDDS washing followed by 2-month stabilization. Different letters indicate a significant difference ($p < 0.05$) between different treatments for the same element.

However, it should be noted that the leachability was markedly higher and the mobility was slightly elevated following 2-month stabilization with 2-h EDDS washing (Figs 7-1c&d) than 2-month stabilization alone (Figs 7-1a&b). The effect was particularly notable for Zn, probably because metal exchange reactions of residual metal-EDDS complexes on the soil surfaces led to metal re-mobilization as observed in phytoremediation pot experiment (Komárek et al., 2010). The influence should be greater for Zn and Pb due to their weaker complex stability (Tsang et al., 2009b; Lo et al., 2011a), but the leachability and mobility of Pb were marginal in the untreated soil and became negligible after treatment in this study. Similarly, Yang et al. (2015) revealed that the $CaCl_2$-extracted Cu increased in an EDDS leaching test of biochar-amended contaminated soil. Therefore, if evaluated only in terms of leachability and mobility of residual metals, the effectiveness of 2-month stabilization was not improved by preceding 2-h EDDS washing.

7.2 Post-Remediation Phytoavailability and Bioaccessibility

Bioaccessibility of metal(loid)s is of more interest than their total concentrations in soil nowadays, which is defined as the chemical fraction that can be used for metabolism (Bolan et al., 2014). The phytoavailability of residual metals in the treated soil was first evaluated by means of DTPA extraction. It should be remarked that this was an operationally defined extraction method and its correlation with the actual plant uptake might vary with soil-plant ecosystems. Thus, the results were primarily used for illustrating the difference in post-remediation impacts. After 2-month stabilization alone, the reduction in DTPA-extractable Cu was about 12-18% but DTPA-extractable Zn and Pb levels were not decreased (Fig. 7-2a). These reductions of DTPA-extractable metals were possibly lower than the plant-extracted target metals in shoot tissues reported by previous studies, e.g., reduction of plant Cu uptake (from 11.6 to 6.2 mg kg^{-1}) and Pb (from 61 to 18 mg kg^{-1}) in the shoots of *S. plumbizincicola* using rice straw biochar was reported (Lu et al., 2014). This was possibly because DTPA extraction was a more aggressive method than direct measurement of plant uptake, where metal immobilization by biochar and/or CFA alone might not be stable enough, and thus there was a marginal reduction in the DTPA-extractable concentrations. Similarly, the metal bioaccessibility of the treated soil in the gastrointestinal tract of human, as indicated by SBET results, was only reduced by approximately 15-20% after 2-month stabilization by biochar and/or CFA (Fig. 7-2b), due to the strongly acidic digestive condition. These results revealed that although 2-month stabilization alone substantially minimized the leachability and mobility of target metals (Fig. 7-1a&b), its stability might be insufficient under stringent environmental conditions employed in the phytoavailability and bioaccessibility tests (Fig. 7-2a&b).

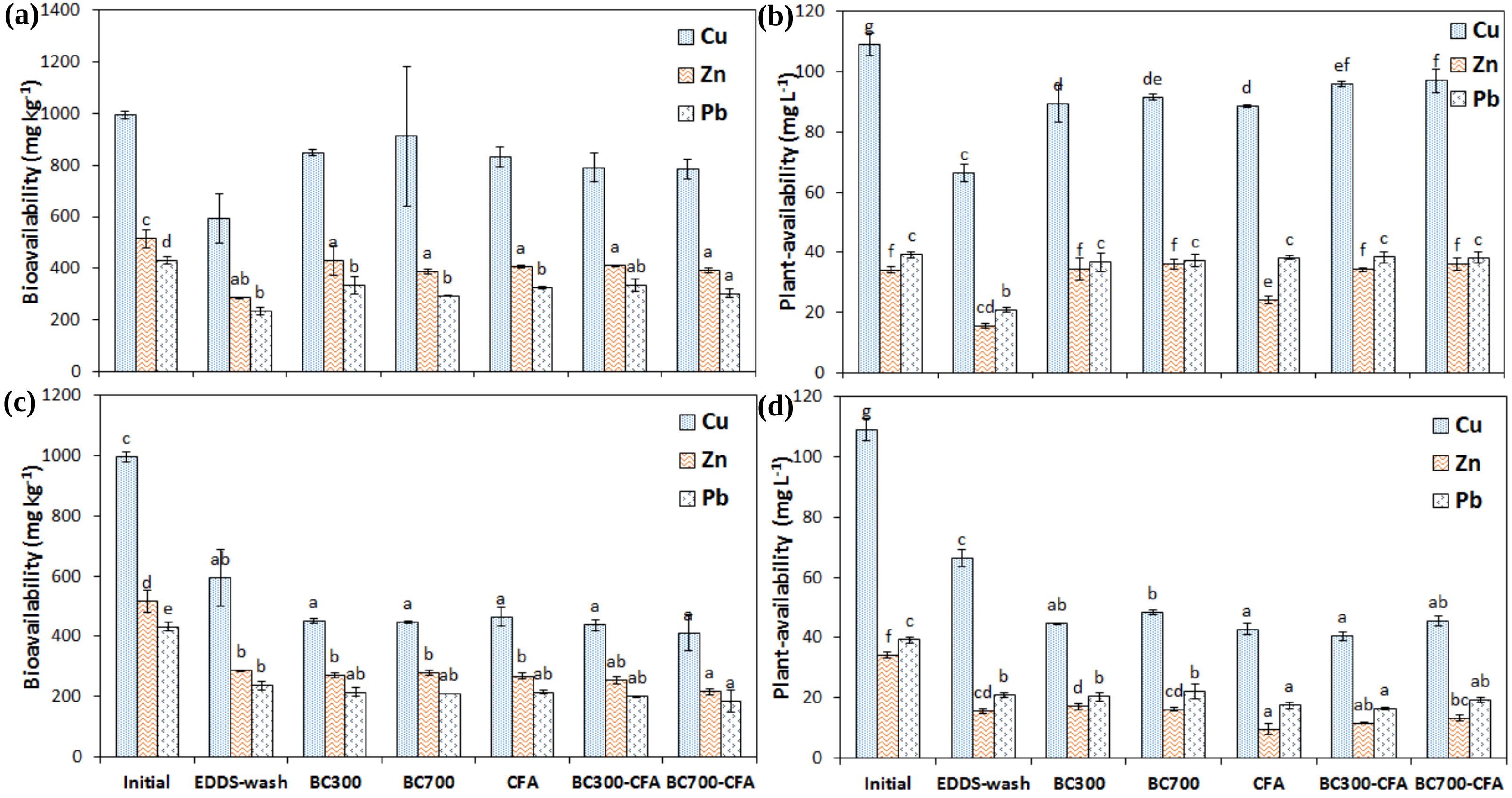


FIGURE 7-2 DTPA phytoavailability (a&c) and SBET bioaccessibility (b&d) of Cu, Zn and Pb in the e-waste contaminated soil after: (a&b) 2-month stabilization only; and (c&d) 2-h EDDS washing followed by 2-month stabilization. Different letters indicate a significant difference ($p < 0.05$) between different treatments for the same element.

In contrast, 2-h EDDS washing was able to remove 40-50% of the DTPA-extractable metals and 50-60% of the SBET-extractable metals, which considerably enhanced the effectiveness of subsequent 2-month stabilization (Fig. 7-2c&d). Because amendments with biochar and CFA primarily served to stabilize the weakly bound metals in soil via adsorption, complexation and precipitation due to increase of soil pH and additional sorption capacity (Ahmad et al., 2012c; Shaheen et al., 2014), this study showed that preceding 2-h EDDS washing enabled removal of bioavailable metals and thus significantly reduced the resultant DTPA- and SBET-extractable metals. However, there was little difference between the stabilization effectiveness of the three amendments (i.e., individual or combined applications of biochar produced at different temperatures and CFA), as indicated by the same letters and overlapping error bars of the same metals in Figures 7-1 and 7-2. It has been shown that biochar produced at low temperatures (e.g., 300 °C) contained more functional groups, because at higher temperatures (e.g., above 400 °C) dehydration and deoxygenation decreased the H/C and O/C ratios and reduced the biochar polarity and functional group density (Uchimiya et al., 2011c; Ahmad et al., 2014b; Usman et al., 2015). Metals would be more strongly stabilized by biochar with a higher density of oxygen-containing functional groups. Despite the large discrepancy in biochar and CFA properties (e.g., surface area, pH, and surface acidity), the difference in performance was not obvious in this study, probably because the high level of amendments (10 wt%) provided considerable metal immobilization capacity and offset the importance of material characteristics. Nevertheless, as this study was conducted in laboratory conditions, future studies would be needed to ascertain the resilience of metal stabilization under variable redox conditions as well as different cropping and irrigation practices in field conditions.

7.3 Mitigation of Risks to Human Health

The non-cancer risk to children due to contaminated water (Fig. 7-3a, mainly because of high Pb mobility) was noticeably reduced by 2-h EDDS washing but the increased Cu mobility still resulted in an unacceptable risk, because excess Cu can lead to adverse effects such as nausea, vomiting, stomach cramps, and diarrhea (ATSDR, 2015). In comparison, 2-month stabilization with or without EDDS washing minimized the hazard index values below 0.8 (indicative of safe consumption). The cancer risk of contaminated water was negligible. Thus, subsequent addition of biochar and/or CFA decreased the non-cancer risk of EDDS-washed soil. On the other hand, via accidental soil ingestion, children might be exposed to significant non-cancer risk (Fig. 7-3b) and moderate cancer risk (Fig. 7-3c), which predominantly derived from Pb that can cause severe damage to human nervous system, brain and kidneys (ATSDR, 2015). These risks were reduced to some extent by biochar and/or CFA amendments by means of reducing the bioaccessible concentrations of metals in the soil. However, apparently, prior EDDS washing helped to mitigate the residual risks after stabilization because weakly bound metals were extracted by EDDS beforehand. Similar changes were observed for adults (Fig. 7-4), who were less susceptible to exposure to contamination. Hence, EDDS washing followed by soil stabilization successfully minimized the residual risks from moderate to acceptable levels (hazard index ~ 1 and cancer risk ~ 10^{-6}). It should be noted that there are limitations in the interpretation of SBET results as it is an *in vitro* chemical extraction method (Ahmad et al., 2012c; Luo et al., 2012a). An estimate of uncertainty is required for extrapolating the *in vitro* results to *in vivo* bioavailability values for a more accurate, site-specific risk assessment (Scheckel et al., 2009).

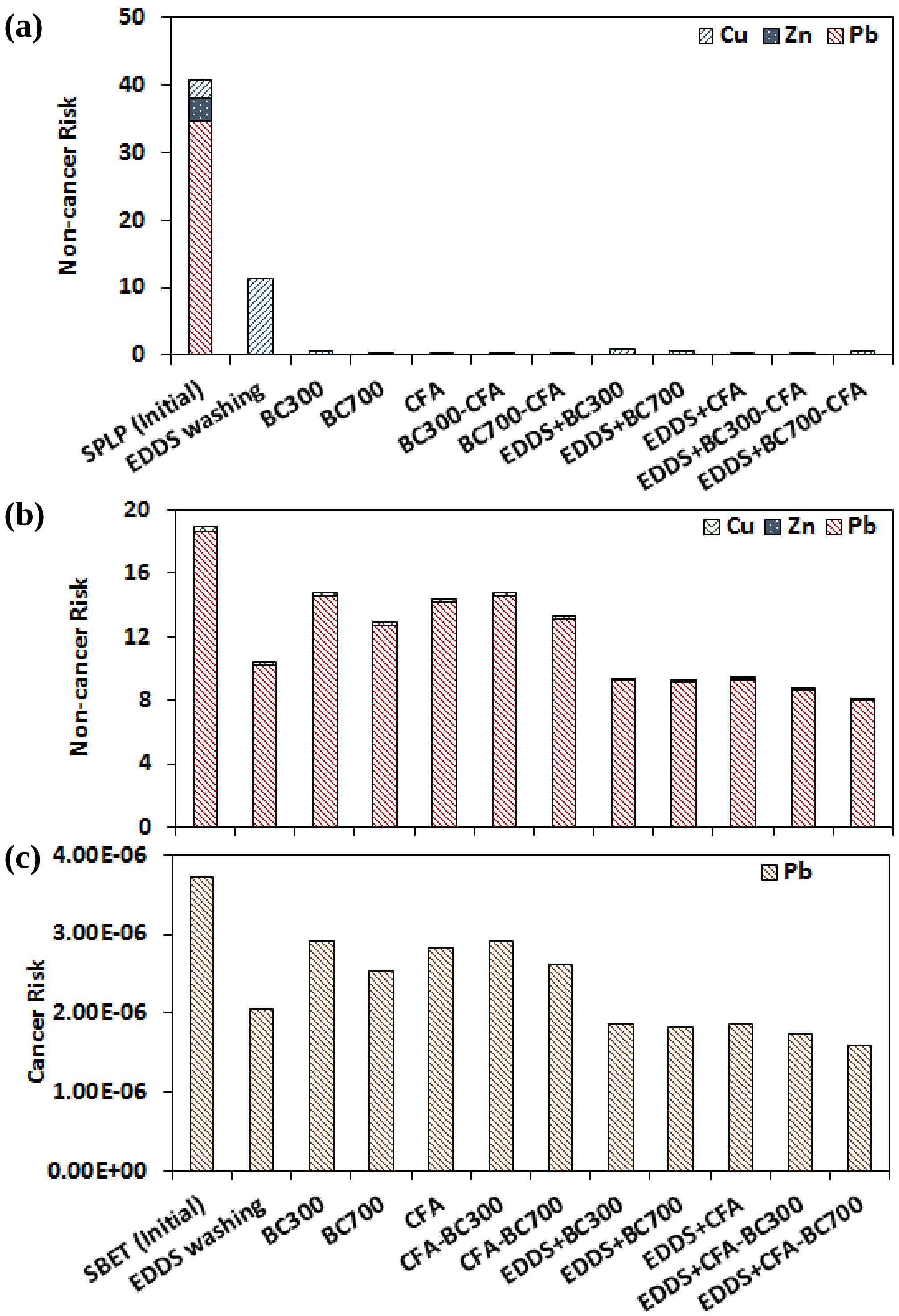


FIGURE 7-3 Estimated health risks for children after 2-h EDDS washing, 2-month stabilization, and both treatments, of the e-waste contaminated soil: (a) non-cancer risk of water consumption based on the SPLP results; (b) non-cancer risk of accidental soil ingestion based on the SBET results; and (c) cancer risk of accidental soil ingestion based on the SBET results.

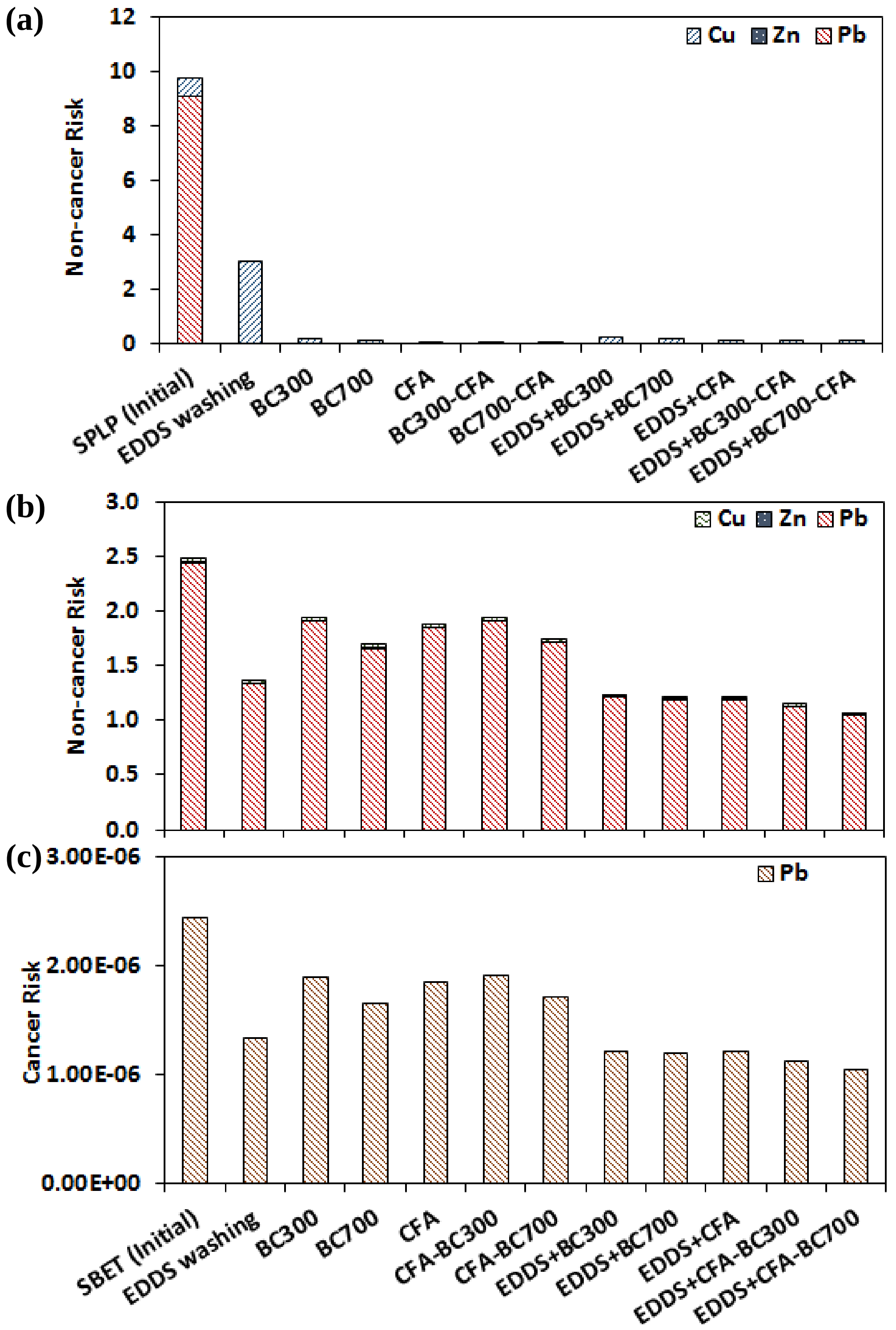


FIGURE 7-4 Estimated health risks for adults after 2-h EDDS washing, 2-month stabilization, and both treatments, of the e-waste contaminated soil: (a) non-cancer risk of water consumption based on the SPLP results; (b) non-cancer risk of accidental soil ingestion based on the SBET results; and (c) cancer risk of accidental soil ingestion based on the SBET results.

7.4 Summary

This study integrated 2-h EDDS washing with subsequent 2-month soil stabilization using biochar and/or CFA for mitigating the impact of residual metals. Both individual and combined applications of biochar and CFA significantly reduced the leachability and mobility of Cu, Zn and Pb in the EDDS-washed soil. On the other hand, while the phytoavailability and bioaccessibility were reduced by stabilization to some extent, they were more effectively mitigated by prior EDDS washing that removed the weakly bound metals. As a result, Pb that poses the greatest risk to human health via water consumption was minimized to acceptable level and the risk associated with soil ingestion was reduced by half. Therefore, the integration of EDDS washing with subsequent soil stabilization can offer a cost-effective measure to alleviate concerns about post-remediation fate of residual metals in the treated soil.

CHAPTER 8. Risk Mitigation by Waste-Based Permeable Reactive Barriers for Groundwater Pollution Control at E-Waste Recycling Sites

8.1 SPLP Tests of E-Waste Soil

The SPLP tests of the composite sample of e-waste soil in this study showed 0.841 mg L^{-1} of Cu, 0.144 mg L^{-1} of Zn, and 0.080 mg L^{-1} of Pb in the leaching solution, while the concentration for Cd, Cr, and As were extreme low and under the detection limit. Compared to the initial metal concentrations in the soil (1280 mg Cu kg^{-1}, 706 mg Zn kg^{-1}, and 520 mg Pb kg^{-1}), mass balance calculations using the dissolved concentrations and liquid-to-solid ratio (20 L kg^{-1}) suggested that only 1.32% of Cu, 0.41% of Zn, and 0.31% of Pb were labile and leachable from this composite soil sample during acidic rainfall events. Thus in this study, the authors want to only focus on Cu, Zn and Pb. Although a large proportion of metals were bound to the soil and less mobile, the concentration of Pb in SPLP solution notably exceeded the National Drinking Water Standard of China (0.01 mg L^{-1}, GB5749-2006) and the Maximum Contaminant Level of the United States (0.015 mg L^{-1}, USEPA 2009). On the other hand, Cu and Zn concentrations were still acceptable (Cu: 1.0 mg L^{-1}, Zn: 1.0 mg L^{-1} (GB5749-2006); and Cu: 1.3 mg L^{-1}, Zn (non-enforceable secondary standards): 5 mg L^{-1} (USEPA2009)). Thus, when acidic rainfall infiltrates through contaminated soil at e-waste recycling sites, dissolved Pb in water is considered as the major risk driver that probably presents significant human health risks (e.g., delays in physical and mental development of children, kidney problems and high blood pressure of adults).

TABLE 8-1 Characteristics of the low-cost adsorbents

Type	**Major Components**
Limestone	$CaCO_3$
Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$
AMDS	Al_2O_3 (33.7)/Fe_2O_3 (16.4)/SiO_2 (6.3)/CaO (1.9)/MgO (0.3)/MnO (0.1)/LOI (34.0)/Zn (0.005)/Cu (0.004) (wt%)
CFA	Ca (13.6)/Si (9.1)/Fe (6.2)/Al (2.2)/Zn (0.533)/Cu (0.04)/Cr (0.006) (wt%)
Biochar*	Ca (2.174)/Mg (0.146)/Fe (0.041)/Al (0.017)/Mn (0.002)/Zn (0.007)/ Cu (0.002)/ As (0.001)/Pb (0.001) (wt%)
FWC*	Ca (2.424)/Mg (0.183)/Fe (0.165)/Al (0.043)/Mn (0.011)/Zn (0.027)/Cu (0.003)/As (0.001) (wt%)

***Analyzed by ICP-OES (Perkin Elmer Optima 3300DV)**

8.2 Adsorption Isotherms of Low-Cost Adsorbents

In the adsorption isotherms of all low-cost adsorbents, preferential metal ion adsorption was observed in the order of Pb > Cu > Zn (Fig. 8-1), which was in line with reported competitive adsorption of metals (Park et al., 2016). Among them, AMDS, FWC, and CFA demonstrated superior adsorption performance. The parameter values of fitting experimental data to Langmuir and Freundlich isotherm models were summarized in Table 8-2. For example, the adsorption of Pb on limestone, AMDS, and FWC was both fitted to Langmuir and Freundlich isotherm. For apatite, it is best fitted with Freundlich isotherm inferring heterogeneous adsorption affinity and/or involvement of precipitation, whereas the data better matched to the Langmuir isotherm for CFA and biochar, hinting relatively homogeneous surface sites and monolayer coverage. However, it should be cautious that such interpretation on sorption mechanisms and adsorbent nature is unavoidably speculative and inconclusive (e.g., necessary but insufficient conditions), which should not be over-stressed until additional tests and direct evidence are available and supportive. Thus, the adsorption isotherms were considered to serve only for comparison purpose in this study.

For Pb adsorption, based on the Langmuir isotherm, CFA and FWC exhibited the highest adsorption capacities (b) of 50.5 mg g^{-1} and 49.3 mg g^{-1}, compared to those of AMDS (20.7 mg g^{-1}), biochar (10.2 mg g^{-1}), apatite (5.53 mg g^{-1}), and limestone (3.68 mg g^{-1}). The adsorption coefficients (K_F) of the Freundlich isotherm also suggested that CFA and FWC had the strongest adsorption abilities followed by AMDS and biochar. Similarly, for Cu adsorption, CFA exhibited the highest adsorption capacity (38.0 mg g^{-1}), followed by FWC (15.6 mg g^{-1}), AMDS (13.0 mg g^{-1}), biochar (7.51 mg g^{-1}), apatite (2.23 mg g^{-1}) and limestone (b = 1.69 mg g^{-1}). In contrast, for Zn adsorption, AMDS and biochar exhibited the highest adsorption capacities (2.44-2.56 mg g^{-1}) followed by limestone (0.76 mg g^{-1}), but all were significantly lower than those of Pb and Cu adsorption. In summary, CFA and FWC showed a strong ability to adsorb Pb and Cu while AMDS was the best adsorbent for Zn. The difference in immobilization efficacy of these adsorbents was further investigated in PRB column leaching tests and discussed in the following sections.

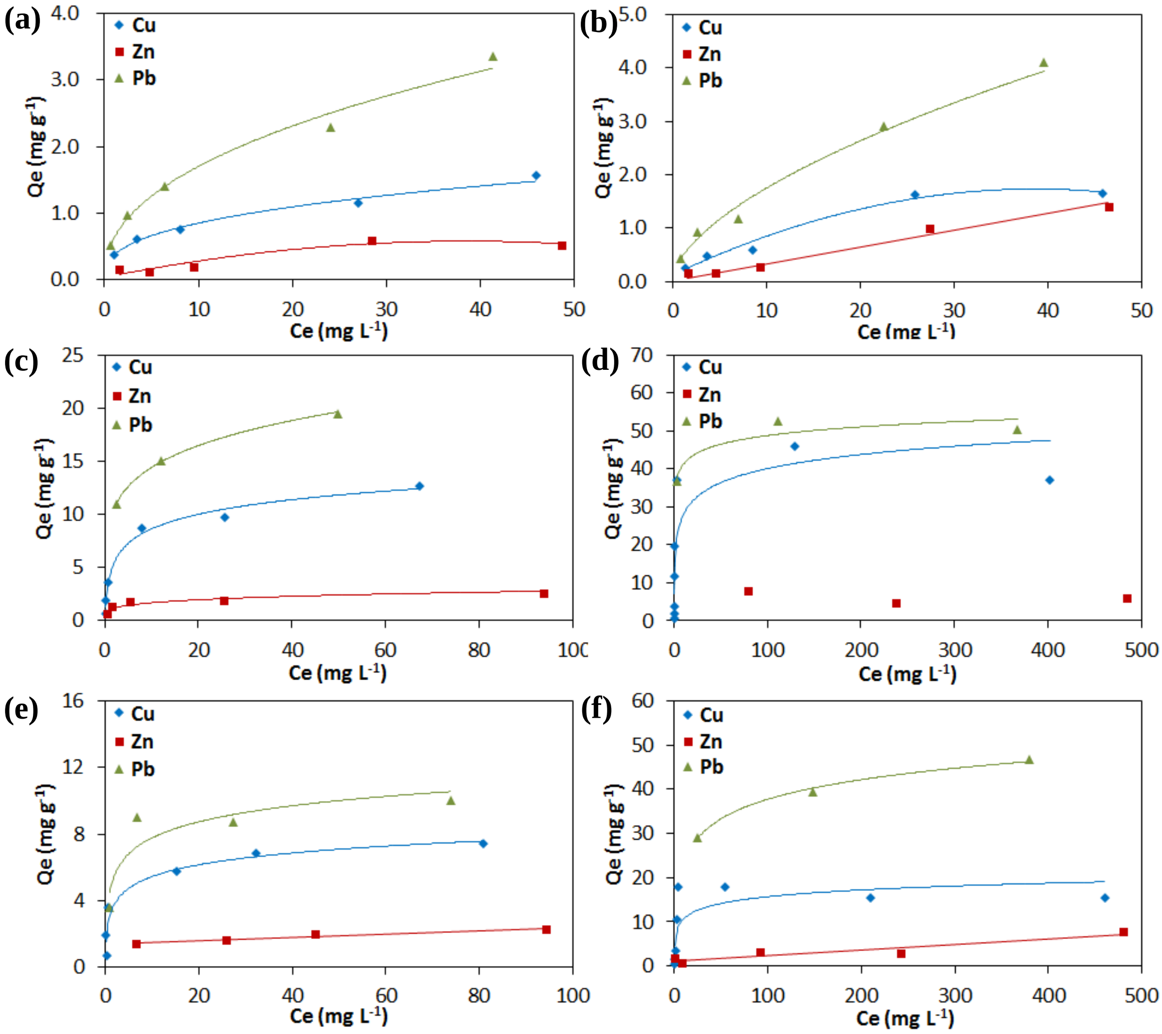


FIGURE 8-1 Adsorption isotherms of Cu, Zn, and Pb on low-cost adsorbents: (a) limestone, (b) apatite, (c) AMDS, (d) CFA, (e) biochar, and (f) FWC.

TABLE 8-2 Parameter values for Cu, Zn and Pb adsorption isotherms

			Limestone	**Apatite**	**AMDS**	**CFA**	**Biochar**	**FWC**
Cu	*Langmuir*	K_L (L mg^{-1})	0.14	0.07	0.27	1.57	0.44	0.26
		b (mg g^{-1})	1.69	2.23	13.0	38.0	7.51	15.6
		r^2	0.96	0.92	0.99	0.99	0.99	0.99
	Freundlich	K_F (mg g^{-1}(L mg^{-1})^n)	0.37	0.22	2.59	N.A.	2.26	N.A.
		n	0.36	0.55	0.43	N.A.	0.31	N.A.
		r^2	0.99	0.97	0.85	N.A.	0.75	N.A.
Zn	*Langmuir*	K_L (L mg^{-1})	0.06	N.A.	0.31	N.A.	0.11	N.A.
		b (mg g^{-1})	0.76	N.A.	2.56	N.A.	2.44	N.A.
		r^2	0.78	N.A.	0.99	N.A.	0.99	N.A.
	Freundlich	K_F (mg g^{-1}(L mg^{-1})^n)	0.09	0.07	0.98	N.A.	0.94	N.A.
		n	0.46	0.74	0.23	N.A.	0.19	N.A.
		r^2	0.74	0.90	0.85	N.A.	0.95	N.A.
Pb	*Langmuir*	K_L (L mg^{-1})	0.12	0.06	0.31	0.88	0.47	0.04
		b (mg g^{-1})	3.68	5.53	20.7	50.5	10.2	49.3
		r^2	0.96	0.87	0.99	0.99	0.99	0.99
	Freundlich	K_F (mg g^{-1}(L mg^{-1})^n)	0.62	0.45	9.24	34.1	4.26	16.7
		n	0.44	0.59	0.19	0.076	0.23	0.17
		r^2	0.99	0.98	0.99	0.88	0.79	0.99

Remarks: initial concentration = 2-500 mg L^{-1}; adsorbent dosage = 2.5 g L^{-1}; temperature = 25 °C; time = 24 h; N.A. = Not Applicable.

8.3 Continuous Leaching of PRB Columns with Synthetic SPLP Solution

The application of PRBs was evaluated by continuous leaching of synthetic SPLP solution at pH 4.2 through sand columns containing 10wt% of low-cost adsorbents. The worst-case scenario was simulated by metal spiking at 50-fold of SPLP results of composite soil sample, i.e., Cu (42.1 mg L^{-1}), Zn (7.21 mg L^{-1}) and Pb (4.01 mg L^{-1}), in view of recognized heterogeneity in contamination age and leaching characteristics across e-waste recycling sites (Leung et al., 2008; Luo et al., 2011; Liu et al., 2013). As shown in Figure 8-2, breakthrough of Cu occurred in approximately 30 PVs and a stable plateau was shown after 120-140 PVs in the limestone and apatite columns (Fig. 8-2a), whereas Zn started to breakthrough in 20 PVs and approached influent concentration in a rather short period of 40 PVs (Fig. 8-2b). The breakthrough of Cu and Zn was aligned with the observed pH decrease from 9.9 to 9.1 (limestone) and 6.3 to 5.4 (apatite) within 40 PVs, respectively, due to continuous leaching of unbuffered acidic SPLP solution. It was noted in the limestone column that effluent Cu only reached approximately 80% of its influent concentration after 150 PVs, possibly due to precipitation with dissolved carbonate ions and/or strong adsorption on calcite (a crystalline form of $CaCO_3$) (Rangel-Porras et al., 2010).

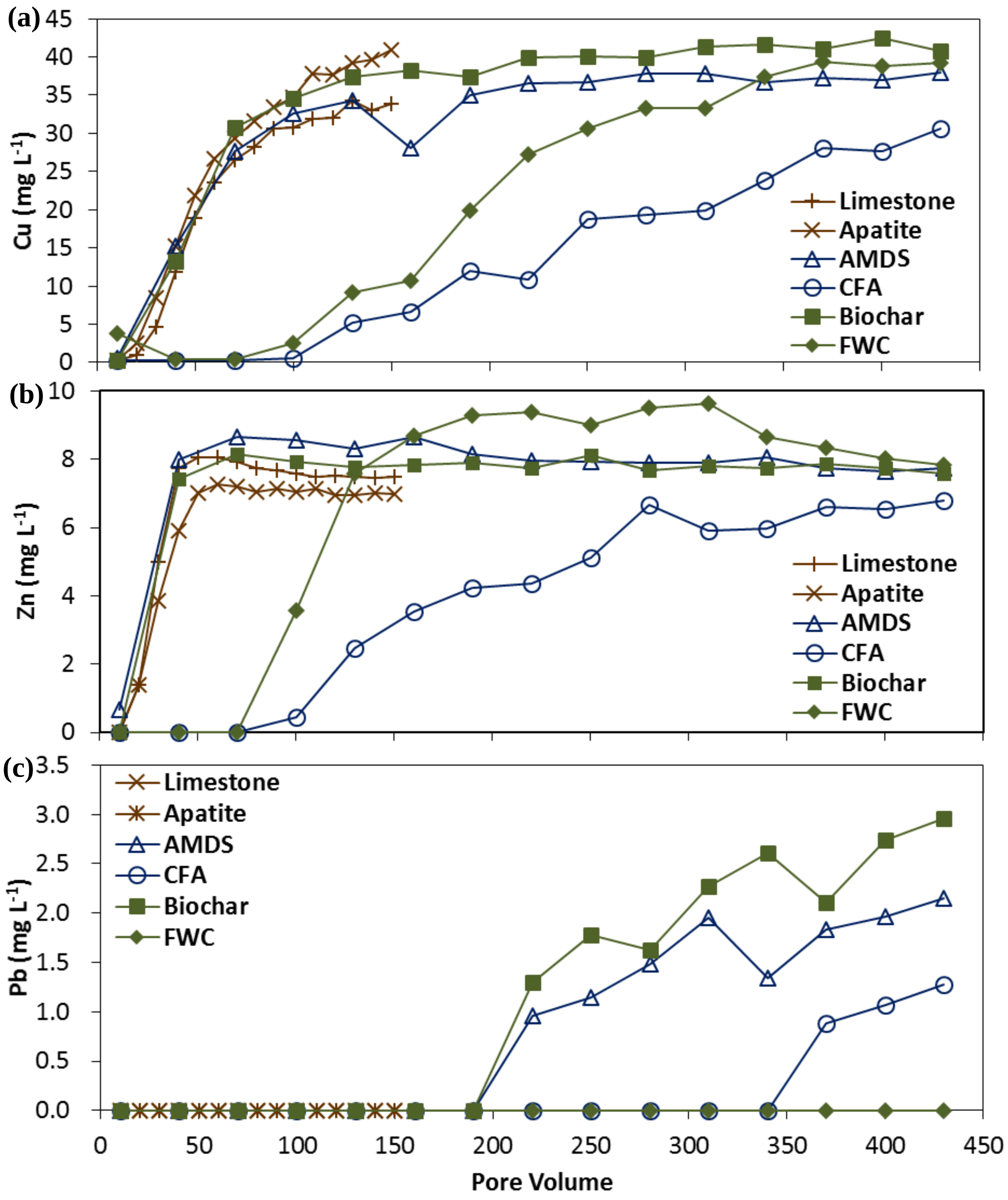


FIGURE 8-2 Breakthrough curves of metal-containing SPLP solution leaching through sand columns filled with 10% low-cost adsorbents: (a) Cu, (b) Zn, and (c) Pb (initial concentrations were 42.1 mg L^{-1} of Cu, 7.21 mg L^{-1} of Zn, and 4.01 mg L^{-1} of Pb at pH 4.2).

In contrast, no Pb breakthrough was detected throughout 150 PVs leaching of the limestone and apatite columns (Fig. 8-2c). Although solution pH was decreased by acidic leaching within the first 40 PVs and remained stable thereafter, there was still sufficient alkalinity (pH 9.1) for lead carbonate precipitates to form in the limestone column, whereas dissolved phosphate effectively precipitate with Pb to form pyromorphite-like mineral even under a slightly acidic condition (pH 5.4) in the apatite column (Conca and Wright, 2006; Ahmad et al., 2014b). Therefore, natural inorganic minerals of limestone and apatite in the PRBs could minimize Pb leaching for at least 150 PVs but they were unsuccessful for immobilizing Cu and Zn only after a short period of acidic rainfall leaching.

As for the inorganic industrial by-products, the performance of AMDS columns was comparable to those of natural minerals, whereas CFA illustrated significantly better immobilization abilities. Since AMDS accommodated a high BET surface area (196.7 m^2 g^{-1}) and significant amounts of amorphous oxides/hydroxides (45% of total Fe and 33% of total Al), it showed promising metal stabilization as a soil amendment of contaminated soils (Tsang et al., 2013b; Tsang and Yip, 2014). However, when applied as PRB column in study, its adsorption capacity for Cu and Zn was rather quickly exhausted by continuous leaching of acidic rainfall (Fig. 8-2a and 2b). Nearly all Zn and 80% of Cu were leached out in the effluent after approximately 40 and 100 PVs, respectively, which was associated with the gradual decrease of pH from 5.8 to 4.9 within 100 PVs. In comparison, the breakthrough of Pb appeared only after 220 PVs and then effluent concentration slowly increased to about 2 mg L^{-1} until 450 PVs (Fig. 8-2c). The presence of poorly crystalline Fe/Al oxides/hydroxides would present plentiful surface hydroxyl sites for metal adsorption (Cui et al., 2011; Zhang et al., 2015), yet AMDS was found to be less suitable as PRBs because Cu and Zn immobilization was susceptible to pH change associated with acidic rainfall leaching within the first 30-100 PVs, although Pb could be immobilized for a prolonged duration of 220 PVs.

By contrast, CFA exhibited higher capacity and resilience of metal immobilization against continuous leaching, where the initial pH was gradually decreased from 6.5 to 5.6 in 100 PVs and then remained stable. In addition to high BET surface area (211.6 m^2 g^{-1}), the CFA possessed an acid neutralizing capacity of 54.3% $CaCO_3$, because it contained 12% merwinite ($Ca_3Mg(SiO_4)_2$), 4% calcite ($CaCO_3$), 2% portlandite ($Ca(OH)_2$), as well as 5700 mg kg^{-1} and 6760 mg kg^{-1} of amorphous Fe and Al oxides/hydroxides (Wang et al., 2013; Tsang et al., 2014). Abundant quantities of inorganic minerals and black carbon residues in CFA proved to enable stable metal immobilization by carbonate/hydroxide precipitation and adsorption onto surface hydroxyl sites (Wang and Wu, 2006; Moon et al., 2013b). As a result, metal breakthrough was observed after 130 PVs (Cu), 100 PVs (Zn), and 370 PVs (Pb), respectively, and then their effluent concentrations gradually increased and reached approximately 75% (Cu), 90% (Zn), and 30% (Pb) of corresponding influent concentrations when approaching 450 PVs (Fig. 8-2a-c).

Comparing the carbonaceous recycled products, the biochar column illustrated breakthrough curves comparable to those of AMDS column, while the FWC column was notably more effective for retarding the metal breakthrough (Fig. 8-2a-c). In the biochar column, Cu and Zn started to breakthrough within 40 PVs and then approached influent concentration within approximately 70 PVs (Zn) and 220 PVs (Cu), respectively. The breakthrough of Pb occurred at 220 PVs and its effluent concentration reached about 3 mg L^{-1} after 450 PVs. The initial solution pH of 6.5 was gradually decreased to 5.6 within the first 100 PVs. In contrast, no Pb was detected in the effluent of FWC column throughout 450 PVs, whereas the breakthrough of Cu and Zn was observed at about 100 PVs and they reached plateau after 190 PVs (Zn) and 370 PVs (Cu), respectively. The solution pH was slowly decreased from 7.0 to 5.0 in about 200 PVs, illustrating a relatively low buffering capacity of FWC such that metal immobilization was probably a result of surface complexation rather than precipitation.

It is interesting to note that the BET surface areas of biochar and FWC were 178.5 m^2 g^{-1} and 0.47 m^2 g^{-1}, suggesting that high surface area of biochar did not offer better performance than FWC. This was probably because the biochar was derived from woody yard waste that comprised ample lignocellulosic structure for developing high porosity but lacked reactive surface sites. Based on Boehm's titration results, the acidic functional group densities of biochar were 0.174 mmol g^{-1} carboxylic, 0.032 mmol g^{-1} phenolic, and negligible lactonic, whereas those of FWC were 0.031 mmol g^{-1} carboxylic, 0.487 mmol g^{-1} phenolic, and 0.069 mmol g^{-1} lactonic, respectively. Thus, the total surface acidity on biochar and FWC were 0.206 mmol g^{-1} and 0.587 mmol g^{-1}, whereas the total surface basicity of biochar and FWC were 1.22 mmol g^{-1} and 0.79 mmol g^{-1}. This clearly indicated that the biochar surface accommodated only a small amount of acidic groups compared to basic groups, while FWC surface contained higher density of acidic functionalities and less basicity. These results suggested that surface chemistry of carbonaceous adsorbents (e.g., biochar and FWC) was more influential for pH-resilient metal immobilization in the PRB columns than their physical properties of surface area and pore volume, which was in line with earlier findings for activated carbon (Tsang et al., 2007a; Liu et al., 2008). Therefore, attention should be paid to tailoring the composition of blended precursor materials and pyrolysis condition, which would be significant factors determining the surface characteristics including oxygen-containing groups and surface area (Ahmad et al., 2014b; Park et al., 2015; Zhang et al., 2015).

The results of the column tests were largely consistent with the batch tests. For Cu and Zn, CFA exhibited the best immobilization performance among the six materials considered, while FWC was the best for Pb. In general, the applicability of CFA and FWC was followed by AMDS, biochar, apatite, and limestone. Many factors might contribute to the removal ability among various adsorbents. pH is an important factor for metal sorption via affecting the both the metal chemistry, the degree of ionization and the surface charge of sorbent. It is generally considered that a higher pH condition favors the adsorption of the metal ions, because the release of photons from functional groups on the surface makes the surface negative (Reddad et al., 2002; Rahman and Islam, 2009). In this study, the adsorption ability is higher for those potential PRB materials has a higher buffer pH ability, which is in line with the pervious study. Although the pH indeed affect the metal behaviors in the liquid but it is not the key factor in this study. Other factors like the surface area also affect the adsorption ability. AMDS, CFA, and biochar have high surface area of around 170-210 m^2 g^{-1}, while FWC has a low surface area of only 0.47 m^2 g^{-1}. In fact the FWC has better removal ability in both batch and column test, which was due to the rich acidic functional groups of carboxylic and phenolic that have the affinity of metal complexation (Sud et al., 2008). Therefore the major mechanism of AMDS and CFA for removing the metal ions in effluent might lie in the large amount of amorphous oxides/hydroxides and carbonates groups.

However, it was noted that while there was negligible metal(loid)s leaching (< 0.001 mg L^{-1}) from CFA in preliminary SPLP test, FWC and AMDS contained certain amount of indigenous Zn content that would gradually leach out under continuous leaching and result in effluent concentration exceeding influent concentration (i.e., overshoots observed in breakthrough curves). On the other hand, dissolved organic carbon leaching from biochar and FWC could form soluble metal complexes that facilitate their transport (Farrell and Jones, 2010; Tsang et al., 2013b; Tsang and Hartley, 2014). Therefore, these issues should be monitored and a mixture of low-cost adsorbents together with commercially available zero-valent iron and activated carbon may warrant consideration.

8.4 Mitigation of Human Health Risks by Waste-Based PRBs

A generic risk assessment was conducted to provide screening information about the human health suffer by Cu, Zn and Pb-contaminated groundwater. The exposure of human receptors to Cu, Zn, and Pb in groundwater in the vicinity of e-waste recycling sites could occur via two major pathways: (a) direct oral ingestion of groundwater (CDI_i); and (b) dermal absorption via showering (CDI_d), (Ni et al., 2011; Luo et al., 2012c; USEPA, 2013b, a). The human health risks associated with Cu, Zn and Pb uptake are primarily non-carcinogenic effects, whereas Pb is considered class B2 (probable human carcinogen based on carcinogenicity in animals) but Cu and Zn are considered class D (not classifiable as to human carcinogenicity) according to IRIS of USEPA. The exposure dose of the above exposure routes can be calculated using Eqs. 1 and 2 (USEPA, 2004) along with representative parameter values in the literature (Table 8-3). The non-cancer risks of individual metals through different exposure pathways are expressed as hazard quotient (HQ, Eq. 9-3), which add up to total cumulative risks as hazard index (HI, Eq. 9-4) for evaluation. The lifetime cancer risk is calculated by multiplying the exposure dosage via oral ingestion by corresponding slope factor (Eq. 9-5).

$$CDI_i = \frac{C_W \times IR \times EF \times ED}{BW \times AT} \tag{9-1}$$

$$CDI_d = \frac{C_W \times SA \times K_P \times ET \times EF \times ED \times CF}{BW \times AT} \tag{9-2}$$

$$HQ_{i\ or\ d} = \frac{CDI_{i\ or\ d}}{RfD_{i\ or\ d}} \tag{9-3}$$

$$\text{Non-cancer risk: HI} = \Sigma\text{HQ} = HQ_i + HQ_d \tag{9-4}$$

$$\text{Lifetime cancer risk} = CDI_i \times SF_i \tag{9-5}$$

The limestone, apatite, AMDS and biochar columns were only effective for risk mitigation for 20-40 PVs (Fig. 8-3), after which the HI well exceeded 1 that was indicative of non-cancer health risk due to the high influent concentration of Cu (42.1 mg L^{-1}). Howeever, Cu is essential for good health, high levels of Cu may cause nausea, vomiting, stomach cramps, or diarrhea (ATSDR 2015). It was noted that early breakthrough of Zn did not cause risk concern throughout the leaching process. Although influent concentration of Zn (7.21 mg L^{-1}) was moderately high, it was insufficient to trigger adverse health effects that are observed with large doses of zinc (10-15 times higher than the recommended dietary allowances) (ATSDR 2015).

TABLE 8-3 Parameters used for human health risk assessment

	Definition	Unit	Value	References
CDI_i	Chronic daily intake by oral ingestion	mg kg^{-1} d^{-1}	(Eq. 9-1)	USEPA 2011
CDI_d	Chronic daily intake by dermal absorption	mg kg^{-1} d^{-1}	(Eq. 9-2)	USEPA 2011
IR	Ingestion rate	L d^{-1}	2	USEPA 2011
EF	Exposure frequency	d yr^{-1}	350	USEPA 2004
ED	Exposure duration	yr	30	USEPA 2011
BW	Average body weight	kg	70	USEPA 2011
AT	Average time	d	10,950 (non-carcinogens) 25,550 (carcinogens)	USEPA 2004 USEPA 2011
SA	Exposed skin area	cm^2	18,000	USEPA 2004
K_p	Dermal permeability coefficient	cm h^{-1}	Cu: 0.001 Zn: 0.0006 Pb: 0.0001	USEPA 2004 USEPA 2004 USEPA 2004
ET	Exposure time during bathing/shower	h d^{-1}	0.25	USEPA 2004
CF	Unit conversion factor	L cm^{-3}	0.001	USEPA 2004
SF	Slope factor (carcinogens)	(mg kg^{-1} $d^{-1})^{-1}$	Pb: 8.5×10^{-3} (oral)	USEPA 2004
RfD_i	Chronic oral reference dose	mg kg^{-1} d^{-1}	Cu: 0.04 Zn: 0.3 Pb: 2.74×10^{-4}	US EPA 2013b US EPA 2013b WHO 2011
ABS_{GI}	Gastrointestinal absorption factor	(unitless)	Cu: 1.0 Zn: 1.0 Pb: 1.0	US EPA 2013a
RfD_d	Chronic dermal reference dose = $RfD_i \times ABS_{GI}$	mg kg^{-1} d^{-1}	Cu: 0.04 Zn: 0.3 Pb: 2.74×10^{-4}	USEPA 2004

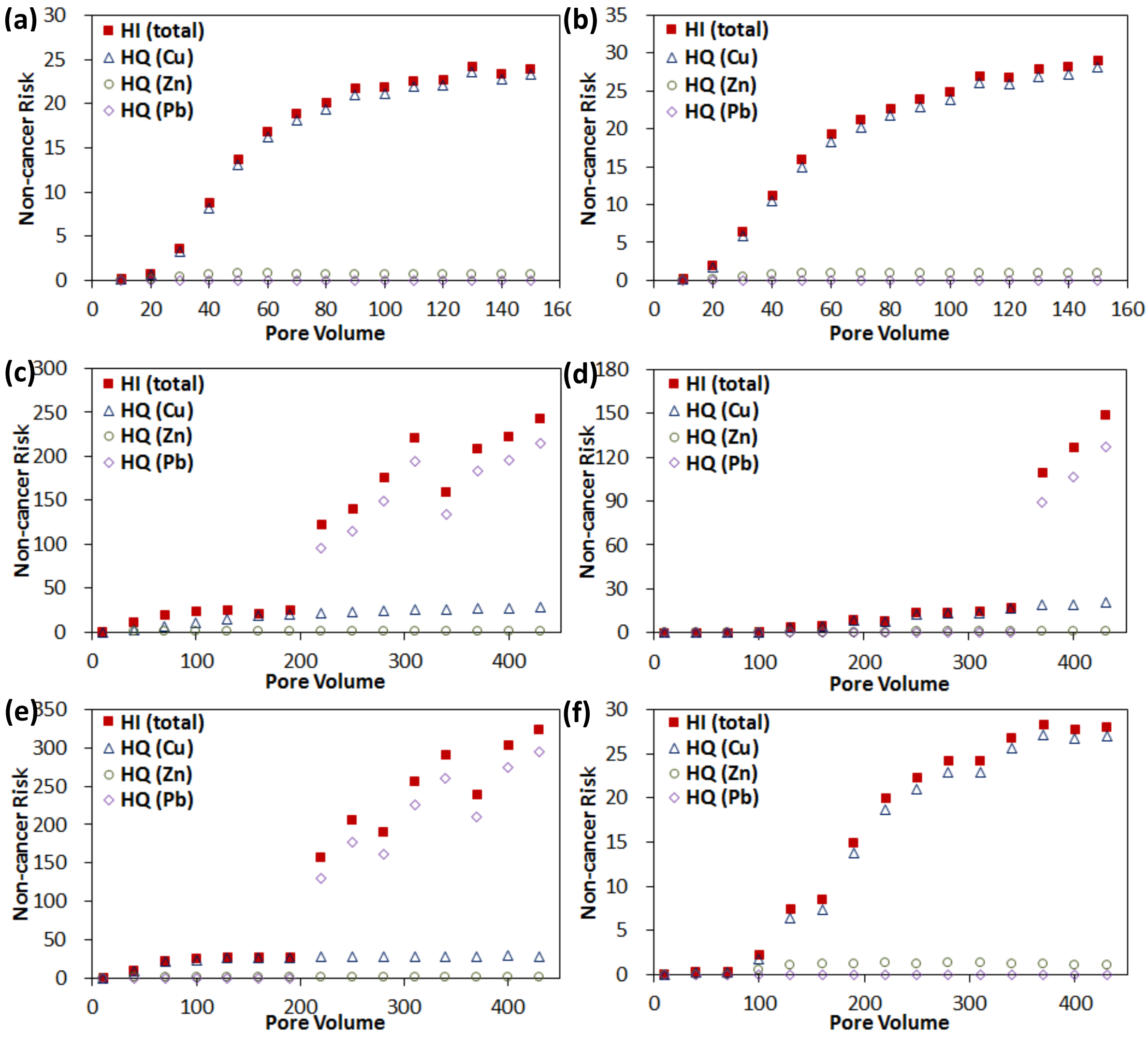


FIGURE 8-3 Non-cancer risk Variation of HI of groundwater downstream of waste-based permeable reactive barriers: (a) limestone, (b) apatite, (c) AMDS, (d) CFA, (e) biochar, and (f) FWC (hazard index (HI) is the sum of individual hazard quotients (HQ) of Cu, Zn, and Pb, i.e., health effects are assumed to be additive).

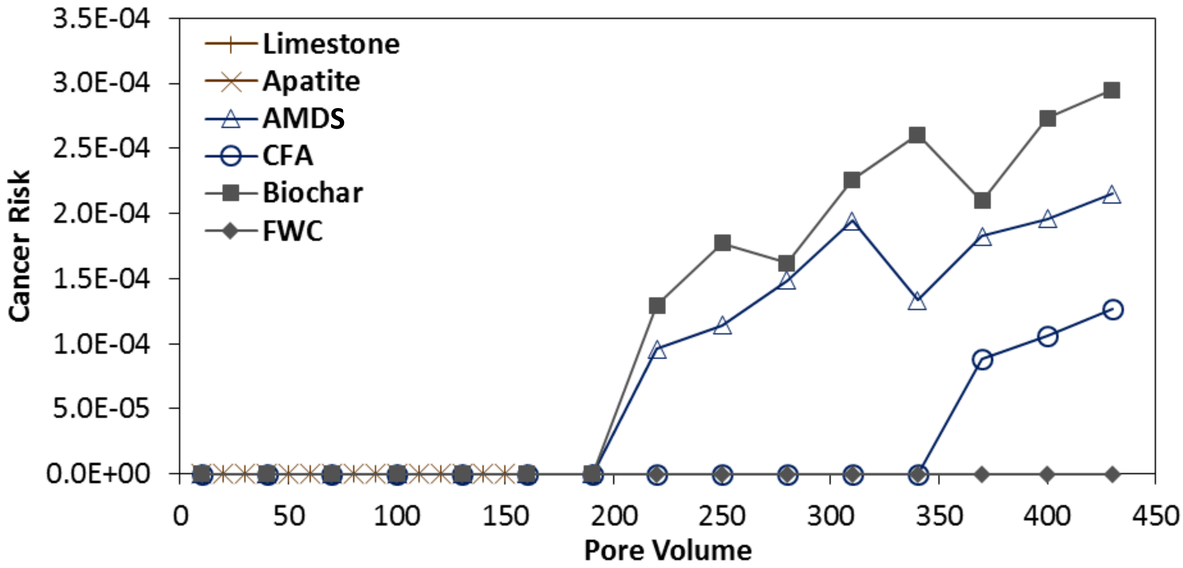


FIGURE 8-4 Lifetime cancer risk (due to Pb) of groundwater downstream of waste-based permeable reactive barriers: (a) limestone, (b) apatite, (c) AMDS, (d) CFA, (e) biochar, and (f) FWC.

Nevertheless, Pb is notably the major risk driver, even at a relatively lower influent concentration (4.01 mg L^{-1}). The HI sharply increased by 5-10 times along with the breakthrough of Pb at 220 PVs of AMDS and biochar columns and 370 PVs of CFA column, respectively (Fig. 8-3), which may cause severe damage to nervous system, brain and kidneys, particularly jeopardizing children's mental and physical growth (ATSDR 2015). In addition, as a probable human carcinogen, Pb leaching simultaneously raised lifetime cancer risk from less than 10^{-6} (acceptable) to 10^{-4} (moderate risk) (Fig. 8-4). Therefore, CFA and FWC were the best PRB materials. The non-cancer risk was minimized to acceptable level (HI < 1.0) for 100 PVs by FWC and 130 PVs by CFA, whereas lifetime cancer risk was mitigated to acceptable level (< 10^{-6}) for 430 PVs by FWC and 190 PVs by CFA. A combined use of CFA and FWC may provide best mitigation of overall risk, and their longevity is estimated to be 100-200 PVs (actual timespan depends on flow velocity and PRB thickness) in the worst-case scenario of this study after which the PRBs should be replaced by new materials.

8.5 Summary

This study evaluated the potential of low-cost adsorbents as PRBs media for pollution control of contaminated groundwater due to infiltration of acidic rainfall through e-waste recycling sites. Batch adsorption isotherms indicated that inorganic industrial by-products and carbonaceous recycled products were more effective than natural inorganic minerals for the removal of toxic metals. Continuous column leaching of unbuffered SPLP solution revealed that PRBs containing 10 wt% of limestone, apatite, acid mine drainage sludge and wood-derived biochar were effective for a shorter period of time, whereas those of coal fly ash and food waste compost successfully mitigated overall risks to an acceptable level for a prolonged period of leaching. The leaching of Cu caused non-cancer risk while later-stage leaching of Pb significantly elevated both non-cancer and lifetime cancer risk. Therefore, waste-based PRBs with selected adsorbents (e.g., coal fly ash, food waste compost, or both) present a promising way to treat contaminated groundwater and mitigate human health risk. Future efforts are suggested to tailor the surface characteristics of low-cost adsorbents with respect to engineering applications and environmental/agricultural needs.

CHAPTER 9. Conclusions and Recommendations

9.1 Conclusions

In this thesis, EDDS, a biodegradable chelating agent, was investigated with low-cost amendment stabilization to reduce the leachable and bioaccessible metal(loid)s in the treated soils. Meanwhile, EDDS extraction was evaluated through various washing schemes (multiple washing steps and gradient dosage of chelant) and a combination with selective dissolution techniques. Also, an investigation of As and Pb immobilization by pine sawdust biomass/biochar was studied under various E_H conditions that is a typical and significant factor under natural conditions, especially for paddy and flooding soils. Besides the total metal extraction efficiency, leachability, mobility, phytoavailability, and bioaccessibility of the residual metal(loid)s, the soil microbial activities, and available soil nutrients, were evaluated after the above various treatments. A study of groundwater remediation using low-cost adsorbents as the media of PRBs also conducted. A summarized table (Table 9-1) is presented to compare the metal extraction efficiencies, leachability, and drawbacks among the different remediation technologies used in this study. The main findings of this study are believed to be helpful for understanding and improving the real application of soil remediation of metal(loid)s, which are recapped as follows:

1. Due to the high toxicity of Pb and the calculated human health risk assessment results, removing the Pb should be the key target to remediate the contaminated soil (mainly by Cu, Zn, and Pb) from an e-waste recycling site. However, EDDS extraction used various washing schemes cannot fulfill this goal due to the low EDDS extraction efficiency of Pb. Thus, a combination of EDDS and EDTA is

recommended to be used in soil washing, which also reduces the use of the non-biodegradable EDTA. Multi-pulse washing scheme achieved comparable removal results in comparison with the continuous washing for 24 h. That is because the continuous washing may lead to a significant amount of dissolved mineral elements complete with target trace metals (Cu, Zn, and Pb). In addition, continuous EDDS washing enhanced the leachability of Cu, which might be due to the readsorption of Cu-EDDS complexes on the minerals which can be solved by subsequent water washing. Based on the modeling results, the mixed use of EDDS and EDTA can be examined with different ratios in the future study.

2. A pretreatment of various selective dissolution methods was used to dissolve the strongly bound metals and facilitate the subsequent EDDS extraction. The reductants and organic acids have shown strong capacity to extract the metals than the oxidants and alkaline solvents. It might relate to the soil properties that most of the target metals bound to the oxide fraction. However, increasing cytotoxicity, suppressed enzyme activities, and decreased available nutrients in the soil were found after the two-stage washing in comparison with EDDS extraction only. The LMWOAs, which bring less adverse ecological impacts on the treated soil and naturally exist in soils, were preferred in the pretreatment than the reductants. One thing should be noticed that empirical dosages were used for of different reagents (reductants/oxidant/alkaline solvents/organic acids) based on the literature review rather than a constant value, which makes it difficult to do comparison among the different treatments. This drawback can be further improved in the future study.

3. Both the types of the amendments and E_H variation affected the phytoavailability and mobility of As and Pb in the soil after the stabilization for 105 days. The mobility of As increased with decreasing E_H, which is consistent with previous studies. A contrasting behavior of the phytoavailability of As was observed, which may result from the strongly acidic extractant. In general, biochar produced at higher temperatures has higher alkalinity, which favorites the immobilization of Pb while has an opposite effect on As. Thus, due to the lability of metal(loid) stabilization, a simple EDDS extraction is proposed beforehand. However, the phytoavailability test of metal(loid)s should be replaced by real plant/earthworm bioavailability test, due to the strong extraction efficacy of the extractant. In addition, detailed studies should be focused on the mechanism for stabilization of Pb and As.

4. Both 2-h EDDS extraction and combined remediation with 2-month biochar and/or CFA-induced soil stabilization significantly alleviated the leachability and mobility of Cu, Zn, and Pb in the soil. However, the phytoavailability and bioaccessibility of the above metals decreased marginally after the 2-month stabilization. Soil washing by EDDS removed those weakly bound metals that are also believed to be bioaccessible and available for plant uptake. Therefore, the integration of EDDS extraction and stabilization is considered as a suitable technique for the e-waste contaminated soil. Still, additional studies on cytotoxicity, enzyme activity, and available nutrients before and after treatments should be evaluated in the future. Besides, the dosage of amendments should be reduced to 2% to see the difference among various amendments.

5. Low-cost adsorbents were evaluated as the media of PRBs for a synthesized contaminated groundwater based on the infiltration of acidic rainfall through the e-waste contaminated soil. Column leaching experiments showed that limestone, apatite, AMDS, and biochar showed efficient only for short-time adsorption, while CFA and FWC achieved acceptable human health risk results. The results of column leaching test were consistent with batch adsorption experiments. Thus, waste-based materials as CFA and FWC are able to serve as potential media in PRBs to remediate the groundwater which results from the e-waste contaminated soil. However, simple kinetic studies should be conducted for various adsorbents.

9.2 Recommendations for Future Work

To have a better understanding of the integrated study of EDDS extraction and low-cost amendments stabilization. The interaction between various metal-EDDS complexes (in this study, Cu, Zn, and Pb) and amendments (biochar or CFA) should be explored under single metal conditions or multi-metals condition using short-term batch adsorption experiment and long-term incubation experiment. Besides, it is worthy to investigate the leachability, mobility, phytoavailability, and bioaccessibility of metal(loid)s in the treated soil under various E_H conditions after treating by an integrated study of EDDS extraction and stabilization. Real phytoavailability tests using plants or crops should also be investigated based on the specific contaminants in the contaminated soil.

TABLE 9-1 Comparison on extraction efficiencies and leachability of Cu, Zn and Pb among selected techniques used in this study

Type of the methods	**Extraction Efficiency (%)**			**Leachability (mg L^{-1})**			**Drawbacks**
	Cu	Zn	Pb	Cu	Zn	Pb	
Multi-pulse A washing schemes (EDDS only)	51.1	32.9	47.0	3.34	1.92	0.09	High cost of operation
Multi-pulse A washing schemes (EDTA only)	65.6	52.0	72.5	1.26	1.06	NA	
Multi-pulse A washing schemes (EDDS+EDTA)	66.5	51.3	73.2	3.40	1.30	0.09	
Oxalate + EDDS extraction	78.0	78.3	76.1	10.5	2.81	0.08	Increased metal leachability and bioaccessibility
Citrate + EDDS extraction	58.8	36.5	69.4	9.67	2.71	0.11	
NH_2OH-HCl + EDDS extraction	81.5	64.9	5.42	3.07	0.85	0.16	High impact on the soil properties
EDDS extraction + stabilization (SBC300)	-	-	-	0.76	2.34	NA	High cost
EDDS extraction + stabilization (SBC700)	-	-	-	0.57	2.28	NA	
EDDS extraction + stabilization (CFA)	-	-	-	0.67	2.16	0.02	

*The cost of EDDS, EDTA, biochar, and CFA are 2000-5000, 1000-5000, 50-300, and 40 USD ton^{-1} respectively.

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