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Speciation and leaching of trace metal contaminants from e-waste contaminated soils

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ABSTRACT

Primitive electrical and electronic waste (e-waste) recycling activities have caused serious environmental problems. However, little is known about the speciation and leaching behaviors of metal contaminants at e-waste contaminated sites. This study investigated trace metal speciation/mobilization from e-waste polluted soil through column leaching experiments involving irrigation with rainwater for almost 2.5 years. Over the experimental period, Cu and Zn levels in the porewater were 0.14 ± 0.08 mg/L, and 0.16 ± 0.08 mg/L, respectively, increasing to 0.33 ± 0.16 mg/L, and 0.69 ± 0.28 mg/L with plant growth. The amounts of Cu, Zn, and Pb released in surface soil (0–2 cm) contributed 43.8%, 22.5%, and 13.8%, respectively, to the original levels. The released Cu and Zn were primarily caused by the mobilization of the carbonate species of metals, including $Cu(OH)_2$, $CuCO_3$, and $Zn_5(CO_3)_2(OH)_6$, and amorphous Fe/Mn oxides associated fractions characterized by sequential extraction coupling with X-ray absorption spectroscopy. During the experiments, trace metals were not detected in the effluent, and the re-sequestration of trace metals was mainly attributed to the adsorption on the abundant Fe/Mn oxides in the sub-layer soil. This study quantitatively elucidated the molecular speciation of Cu and Zn in e-waste contaminated soil during the column leaching process.

INTRODUCTION

Electrical and electronic waste (e-waste) contamination in soil during rudimentary recycling activities for noble metals has become a globally environmental problem [1–4]. The presence of large amounts of multiple trace metals, including Cu, Zn, Pb, and Cd has been reported in surface soils used for the dismantling, burning, and acid washing of e-waste [1,2,5]. Trace metals in surface soil can contribute to the contamination of surface water and groundwater through runoff and vertical transportation [6–8], and also facilitate metal accumulation in vegetation through plant uptake [9,10].

Once deposited in soil, the mobility of trace metals strongly depends on their chemical speciation including chemical fraction, surface complex, and surface precipitation, etc., which are further affected by various environmental conditions [11–14]. In e-waste contaminated soil, batch experiments revealed that the exchange- able fraction of trace metals made up a very low percentage of the total levels [8,10], suggesting that they have a limited ability to leach from surface to deep soil. However, previous studies reported higher levels of trace metals in the middle layer of soil than in the surface at e-waste sites [5,15]. Of greater concern is the finding that the shallow groundwater (0.5–2.5 m) in an e-waste recycling site exhibited 9.0–31.1 μg/L of Cd − a level significantly higher than in the control site [6]. Therefore, the availability of metals and soil properties should have a profound influence on the leaching of trace metals from contaminated soils. Previous studies on landfill columns suggested that no significant leaching of trace metals from electronic devices occurs after 440 days [16] or 2 years [17]. In another study, 5.5–25.6 μg/L of Cu, Zn, and Pb were leached from e-waste loaded column test, with broken e-waste items (9.3–25.6 μg/L of Cu, Zn, and Pb) slightly but significantly higher than intact items (5.5–18.8 μg/L) [18]. Disagreements over the fate of trace metals from e-waste contaminated soils should primarily be associated with the speciation and leaching mechanism. However, to date, there is little information on this process. The traditional sequential extraction procedure (SEP) coupled with the recently developed molecular X-ray absorption near edge structures (XANES) [13,19] could provide valuable information on how metals mobilize from surface soil to deep soil and even into ground- water.

Besides physicochemical conditions, plant coverage also affect the speciation of trace metals in soil and consequently the environ- mental behaviors [14,20,21]. Plants directly absorb trace metals and introduce organic carbon and other compounds in the rhizosphere soil. The organic acids introduced in the rhizosphere can chelate with trace metals from Fe/Mn adsorbed or carbonate fractions, and contribute to the release of trace metals [20,22]. Furthermore, in our previous survey high levels of Cu and Zn were observed in the vegetables and wild plants in e-waste polluted soil [10], which may affect the environmental processes of metal contaminants. How- ever, there have been few studies on the effect of plants on trace metals speciation and transportation in e-waste contaminated soil.

Electronics dismantling activities in China primarily took place in the provinces of Guangdong and Zhejiang [10,23], where the local soils have become seriously polluted by e-waste, and have been exposed to rainfall and plant growth. The subtropical Pearl River Delta (PRD) region has humid subtropical weather with an annual average temperature of 22 ◦C and a yearly precipitation of 1690 mm, with occasional thunderstorms and typhoons [24]. Investigating the effects of rainwater and plant growth on trace metal leaching may provide practical insights for soil remediation efforts and environmental risk assessments for this region and other similarly polluted e-waste sites in the world.

The objectives of the present study were: (1) to evaluate the potential leaching of trace metals along the contaminated soil profile under plant growth; and (2) to study the underlying mechanisms controlling metal speciation and mobility in e-waste contaminated soils.

MATERIALS AND METHODS

Soil collection

The polluted soil with e-waste ash was collected from an open e-waste incineration site in Guangdong province, China [10]. The unpolluted soil was collected from an agricultural field in Hong Kong. The soil samples were collected using a stainless steel spade and stored in polythene zip-bags while being transported. They were air-dried in the lab and passed through a 2-mm sieve before use.

Column set-up, plant growing, and sampling

The soil columns, designed to be 25 cm in diameter and 52 cm in height, were operated at 25 ◦C with a 16 h photoperiod per day (Fig. 1 and Fig. S1, Supplementary information). The columns were preassembled with Rhizon samplers with a microfiltration membrane of 0.12–0.18 µm (Rhizosphere Research Products, the Netherlands) for collecting porewater. The columns were divided into two layers using a polyamide mesh (60 µm in mesh): the upper-layer (0–20 cm) contained soil polluted with e-waste ash (11.55 kg), and the sub-layer (20–52 cm) contained unpolluted soil (19.14 kg). The top and bottom of the column were filled with two cm of quartz sand (grain size <0.5 mm) to guarantee that there would be no loss of soil during the leaching test.

To confirm the suitability of plant growth, the soil columns were irrigated using a 50 mL/day nutrient solution (2.1 g/L urea and 3.5 g/L KH_2PO_4) continuously for 8 days. Subsequently, the columns were saturated for 20 days using synthetic rainwater (in µmol/L: 3.20 P, 4.30 Na, 7.70 K, 5.00 Ca, 1.20 Mg, 28.00 Cl^-, 3.20 SO_4^{2-}, and 142.8

NH_4NO_3, pH 5.50) [21]. After three months of soil aging, *Elsholtzia splendens* seeds were sterilized using 30% H_2O_2 for 5 min, rinsed with sterile distilled water, germinated on filter paper, and grown in two duplicate columns to study the effect of vegetation on the transport of trace metals. Eight months later, the shoots of the *Elsholtzia splendens* were collected. Because of the poor growth and low concentrations of trace metals in the *Elsholtzia splendens*, another plant, a species of ryegrass, was selected and grown after the *Elsholtzia splendens*. Another two columns were operated with- out plants as the normal leaching group.

The columns were irrigated discontinuously using synthetic rainwater at alternate flow rates of 0.86, 1.87, and 3.31 L/day over 882 days (~2.5 years, Fig. 2), which resulted in 680 L of rainwater. This corresponded to 2.1 years of rainfall, taking into consideration the annual precipitation in the subtropical PRD region [24]. Because acid rain sometimes occurs in the study area [25], the columns were irrigated with synthetic acid rainwater (of the same composition as the rainwater but with a pH of 4.5) for the last 60 days.

Porewater samples (30 mL with the initial 2 mL being discarded) were collected 17 times over the leaching test, filtered using 0.22 μm membranes, and stored at 4 °C before analysis. In all, one harvest of *Elsholtzia splendens* and six harvests of ryegrass were obtained during the leaching period. At the end of the leaching test, the soil columns were carefully dissected into layers of one cm for further chemical analysis.

Analyses of soil, plant, and porewater samples

The pH of the soil samples was determined by mixing 10 g of soil and 25 mL of DI water. The organic content was measured using the loss of weight after ignition at 450 ◦C. The cation exchange capacity (CEC) was determined using a sodium acetate method [26].

The plant shoot samples, polluted soil, unpolluted soil, and the spent soil after the column leaching test were air-dried, ground using an agate mortar, and digested with 4:1 (V/V) concentrated HNO3 and HClO4 [24]. Five operationally defined chemical fractions of trace metals were analyzed using a modified Tessier SEP [10,24]; details are given in the supplementary information.

Using inductively coupled plasma atomic emission spec- troscopy (ICP-AES, Perkin Elmer Optima 3300DV) an analysis was conducted for all of the metals contained in the digested solution, extracted solution, and porewater samples [27]. Porewater samples were examined for pH, total organic carbon (TOC) (TOC analyzer, Shimadzu, model: ASI-5000A), and major anions using a DX-500 ion chromatography system (Dionex, US).

The water and soil chemistry of the normal leaching and plant- grown columns were examined for statistical significance by means of a paired T test (statistical significance at $p < 0.05$) using PASW Statistics 18 software.

Characterization of soil samples

The surface morphology of the soil was examined using a JELO Model JSM-6490 scanning electron microscope (SEM) with an energy dispersive X-ray (EDX) detector. X-ray powder diffraction (XRD) was recorded on a Rigaku SmartLab X-Ray Diffractometer at 40 kV, 100 mA using a Cu target tube and a graphite monochroma- tor. The analysis of the XRD data was performed using the PDF-2 reference database from the International Center for Diffraction Data [28].

The Cu K-edge (8979 eV) and the Zn K-edge (9659 eV) XANES spectra of the soil samples were collected at beamline 01C1 at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The XANES sample preparation, standard references, data collection procedure, and analysis have been described in our previous reports [29,30] and more details can be found in the supplementary information.

QA/QC

QCIn the analysis of metals, standard reference material (SRM2709, the National Institute of Standards and Technology, USA)was used for every batch of digestion and analysis. Reagent blank and analytical duplicates, which made up 10% of the entire set of samples, were also used to test the accuracy and precision of the analysis. The digestion recovery rates were around 76.6-106% for all metals in NIST SRM 2709, with the exception of Al(45.0 ± 5.2%), Fe (72.4 ± 4.1%), Mn (71.6 ± 3.3%), Ca (67.1 ± 3.4%), Mg(67.3 ± 3.3%), and Pb (57.6 ± 5.1%). The relative standard deviations for all of the elements determined in the duplicate digested samples ranged from 0.08-14.5%. The recovery rates of the sum of the five fractions from SEP compared with the independent total concertation ranged from 75.6–120%. The averaged data for the duplicate columns are reported in the table and figures.

RESULTS

Characterization of the soils

The polluted and unpolluted soil exhibited pH of 7.0 and 7.6, organic carbon of 3.6% and 2.6%, and CEC (meq/100 g) of 5.4 and 3.6, respectively (Table 1). The polluted soil was seriously contaminated with trace metals from the e-waste burning activities, with 590 mg/kg Cu, 298 mg/kg Zn, 320 mg/kg Pb, 7.1 mg/kg Ni,

19.7 mg/kg Cr, and 0.22 mg/kg Cd. Of these, the concentrations of Cu, Zn, and Pb were 10–40 times higher than the background concentrations in the PRD agricultural soil (Table 1), and were focused in this study. The unpolluted soil contained similar levels of trace metals as the background values in the PRD.

In the XRD analysis, the soil exhibited strong peaks of quartz and weak peaks of clay minerals (Fig. S2, Supplementary information), with no significant change in crystalline phase between the original and the spent soil after the leaching tests. The SEM showed long sticks (tens of μm in length) with aggregated particles in the original e-waste contaminated soil, while such particles were not observed in the unpolluted soil (Fig. S3 a-c, Supplementary information). Those long sticks may be attributed to the burning residues of the printed circuit boards, which were coated with noble metals [31]. The EDX results demonstrated that trace metals were heterogeneously distributed within the original contaminated soil, with Cu (10.8%), Zn (2.9%), and Pb (3.5%) on some scattered particles (Fig. S3-d, Supplementary information), levels that were much higher than in the bulk soil samples (Cu of 0.06%, Zn of 0.04%, and Pb of 0.04% in Table 1). The percentages of trace metals observed in our study were comparable to the percentages of Cu (10.00-22.03%), Zn (1.3 ± 0.6%), and Pb (1.0-5.0%) in the original waste of the printed circuit boards [32,33]. Furthermore, an EDX analysis showed that after the column leaching tests the subsoil contained higher levels of Cu (1.2%) and Pb (1.2%) (Fig. S3-f, Supplementary information) than that in the original unpolluted soil (Table 1).

Trace metals in porewater

During the 2.5 years of the leaching test (Fig. 2), an analysis of the porewater showed no detectable concentrations of trace metals in the effluent from the columns (Fig. 3). However, elevated levels of 0.52 mg/L of Cu and 1.18 mg/L of Zn were observed in the pore-water at a depth of 0–24 cm. From Periods I to III, the Cu and Zn levels in porewater gradually increased, indicating that trace met-als were being leached from the e-waste contaminated soil over an extended period of time. The long-term effect of plant growth on metal mobility was also observed with the concentrations of Cu (0.33 ± 0.16 mg/L) and Zn (0.69 ± 0.28 mg/L) in porewater at Period III in the plant columns (Fig. 3). The concentrations were slightly but significantly higher ($p = 0.012$ for Cu and $p = 0.001$ for Zn in Table S1, Supplementary information) than those of the nor-mal leaching columns without plants (0.14 ± 0.08 mg/L for Cu and0.16 ± 0.08 mg/L for Zn). A decrease in the pH of the irrigation water from 5.5 (rainwater) to 4.5 (acid rainwater) led to a significant decrease of pH in the porewater (Fig. S4, Supplementary information), and further facilitated the release of Cu and Zn from soil to porewater between Period II and Period III (Fig. 3).The concentration of Pb in porewater was usually at a level of several g/L or below, due to the lower solubility of Pb com-pounds and their stronger affinity to soil minerals in comparison with Cu and Zn [12,34]. During the leaching test, very little Al(ND-0.09 mg/L), Mn (ND-0.26 mg/L), and no Fe were found in the porewater (Fig. S5, Supplementary information). A relatively low concentration of organic carbon was observed in the porewater (1.3–16.7 mg/L TOC in Fig. S6, Supplementary information).

Trace metals in soil

After 2.5 years of conducting the column leaching tests, 43.8% of the Cu, 22.5% of the Zn, and 13.8% of the Pb were mobilized from the surface 0–4 cm layer (Fig. 4), and accumulated in the 6–10 cm layer. With regard to the unpolluted subsoil, the layer of 20–21 cm was enriched with Cu (45.6 mg/kg in the plant-grown column and 25.6 mg/kg in the normal leaching column) and Zn (107.1 mg/kg in the plant-grown column and 55.3 mg/kg in the normal leaching column). A significant difference was observed in concentrations of Zn ($p = 0.001$) and Pb ($p = 0.000$) in soil along the depth profile between the plant-grown columns and the columns without plants, while no difference was seen in the concentration of Cu ($p = 0.288$, Table S1, Supplementary information).

Aluminum, Fe, and Mn were also leached from the upper-layer of soil (Fig. S8, Supplementary information) and probably formed (hydr)oxides in the deeper soil layer at the circumneural pH [35,36]. Over the duration of the leaching test, Ca and Mg were continuously lost from the soil to the porewater (Fig. S8, Supplementary information), and their levels were generally higher in the presence of plants [21].

Effect of plants on trace metal mobility

After the Elsholtzia splendens was harvested, Cu (12.8 mg/kg), Zn (116 mg/kg), and Pb (1.5 mg/kg) were found in the shoots of the plants. Afterwards, ryegrass was grown in columns. After analyzing a total of six harvests of shoots, much higher levels of trace metals were found in the ryegrass (43.8–411 mg/kg for Cu, 127–933 mg/kg for Zn, and 6.3-49.1 mg/kg for Pb in Fig. S9, Supplementary information) than in the Elsholtzia splendens. A calculation of mass indicates that the two kinds of plants had absorbed a total of 8.6 mg of Cu, 19.7 mg of Zn, and

1.0 mg of Pb from the soil. The sequence of absorption of the three metals was consistent with our previous finding that vegetables and plants from the e-waste contaminated sites contained higher levels of Zn than of Cu and Pb [10].

Sequential extraction analysis

To reveal the underlying leaching mechanism of trace met- als during the column test, the chemical fractions of Cu, Zn, and Pb through the soil depth profiles were investigated using SEP (Fig. 5 and Table S2-4, Supplementary information). The origi- nal e-waste polluted soil had very limited exchangeable fractions (0.2–1.0 mg/kg, 0.0–0.2%) of Cu, Zn, and Pb, showing their low availability to plants [10]. The contribution of carbonate/adsorbed fractions in the original e-waste contaminated soil was 85% for Cu, 68% for Zn, and 75% for Pb (Table S2-4, Supplemen- tary information), which could be released when environmental conditions change [21,22]. After the column leaching process, at the surface soil layer (0–1 cm) the adsorptive/carbonate pro- portion of trace metals largely decreased from 147.0 mg/kg to 16.3–23.9 mg/kg for Cu, from 72.6 mg/kg to 1.5–2.3 mg/kg for Zn, and from 72.6 mg/kg to 17.1–20.1 mg/kg for Pb. Accordingly, at the upper-layer soil (0–20 cm), the exchangeable fraction increased to 0.2–8.0% (0.5–28.0 mg/kg) for Cu, 1.0–10.6% (0.7–33.9 mg/kg) for Zn, and 0.0–8.3% (0.2–23.2 mg/kg) for Pb, with significantly high percentage of 7–8% for Cu, 5–8% for Zn, and 7.8–8.3% for Pb at 0–1 cm layer.

X-ray absorption near edge structure analysis

Although information on the change in the chemical fractions of trace metal as a result of leaching may be provided by SEP, only a limited amount of information on the exact molecular transformation can be obtained using this operationally defined method to elucidate the mobilization of metals. Due to the sensitive characteristics of elucidating the element oxidation state and bonding information [11], the XANES technique was employed in the current study. The linear combination fitting analysis of XANES indicated that in the original e-waste contaminated soil, the species of Cu was mostly associated with Fe/Mn oxides (65%), carbonate (13%), and $Cu(OH)_2$ (15%) (Fig. 6, Tables 2–3, and Fig. S10, Tables S5-S8 Supplementary information), while Zn was mostly associated with Fe/Mn oxides (43%), $Zn_2(OH)_2CO_3$ (38%), and ZnS (18%) species. No sulfate-associated species for Cu and Zn were observed in the original e-waste contaminated soil using the XANES analysis, suggesting little presence of exchangeable fractions, consistent with the SEP results (Fig. 5 and Table S2-4, Supplementary information). No metallic Cu or Zn, or CuCl was observed in the soil samples. Two previous studies [37,38] reported that in the original e-waste ash, Cu was primarily associated with $CuCO_3$ (28–49%), HA (50%), cuprospinel ($CuFe_2O_4$, 42–44%), or 38–45% CuCl, while Zn was in $ZnCl_2$ (44–51%), $ZnCO_3$ (38%), and ZnS (33%). Variations in the metal species could be a result of the types of e-waste involved [37], the temperature and ambience of the incineration [39], and the surrounding environmental and soil conditions [22,40].

After the leaching test, we found a general increase in the Fe/Mn oxides bonded Cu species from 65% in the original sample to 79–89% in the plant-treated columns and to 57–76% in the columns without plants (Table 2), while the trend of an increase in the Zn adsorbed species was not significant from 43% in the original sample to 39–47% after column leaching test (Table 3). Relatively higher per- centages of sulfate-bound species of 7–10% for Cu and ND-7% for Zn were found in the 0–2 cm top layer in both kinds of columns, in com- parison with those observed (ND) in the original soil. The increase in sulfate species suggests that there was more available Cu and Zn after the leaching tests because the sulfate species represent the weakly associated outer-sphere surface complexes [19,41]. The $Cu(OH)_2$ (13%) that was observed in the original e-waste contaminated soil significantly decreased to 0–1% in the plant-grown columns, and to 3–5% in the columns without plants. $CuCO_3$ showed a decrease from the initial 11% to 2–7% in the plant-grown soil samples, but varied from 4 to 17% in the non-plant soil samples. $Zn_5(CO_3)_2(OH)_6$ showed a slight decrease from the initial 38% to 29–34% in the plant-grown columns, and to 26–36% in the columns without plants. For the organic bonded species, only 4–7% of Zn was associated with HA at the 1–2 cm layer, while no observation was found for Cu and Zn with HA in the other samples. A small amount of phosphate bonded Cu/Zn was sometimes observed in the soils, especially for Zn, of which $Zn_3(PO_4)_2$ increased slightly from zero in the original sample to 0–7% in plant-grown columns, and to 6–11% in the non-plant columns.

DISCUSSION

During the 2.5 years of the column leaching test, trace metals were not detected in the leachate at the bottom of the columns, but level of ~ 1 mg/L was observed in the porewater in the top-layer soil profile. Previous reports also suggested a negligible concentration of trace metals [17] or a low level of 0.06 mg/L Cu, 0.13 mg/L Zn, and 0.05 mg/L Pb in the effluent from columns loaded with electronic devices after about

14–21 months [16,18]. In addition, the loss of Cu, Zn, and Pb at the 0–4 cm layer and their accumulation at the 4–10 cm layer in the soil column [42] demonstrated the downward mobilization of the leached trace metals.

The mobility and bioavailability of trace metals in contaminated soil are affected by their solubility and geochemical interactions with the soil interface [12,14,43]. Using SEP, the mobilization of Cu and Zn at the 0–2 cm soil layer was caused by the loss of carbon- ate and adsorptive fractions over the period of the column leaching tests (Fig. 5). The carbonate and adsorbed species in the soil samples analyzed from the SEP results were consistent with the XANES analysis ($p = 0.75$, Fig. S11, Supplementary information). The mobilized Cu and Zn at the 0–2 cm soil layer were re-sequestrated in the subsoil, which was also indicated by the increased concentrations of metals from the SEM-EDX analysis (Fig. S3, Supplementary information).

During the re-sequestration process, an increase of the adsorbed species of Cu seen in the XANES results occurred as the percent- age of $Cu(OH)_2$ and $CuCO_3$ decreased (Table 2). The increasing percentages of the adsorbed species indicated the re-adsorption of those dissociated Cu on the Fe/Mn oxide, as high concentrations of Fe (12.0–14.7 g/kg, Table 1) and Mn (356–435 mg/kg) were present in the soil. Different from Cu, $Zn_5(CO_3)_2(OH)_6$ showed a slight decrease in the column leaching test (Table 3), while the phosphate bonded species of $Zn_3(PO_4)_2$ increased slightly in the surface soil layer (1–6 cm), which should be due to the association with the added P in the rainwater. The difference in the results for Zn from those for Cu probably contributed to the thermodynamically most stable characteristic of Zn (hydr)oxides and Zn (hydroxy)carbonates at typical soil pCO_2 levels [28], and related complex environmental matrix [43,44]. The immobilization of Cu and Zn was attributed to their ready sequestration by the abun- dant reactive sites and/or to their precipitation properties under a circumneural pH condition in the porewater (6.50–8.33, Fig. S4, Supplementary information).

The mobilization of trace metals, including Cu, Zn, and Pb, is usually affected by plant-induced organic matter in soil. Generally, plant-facilitated Cu and Zn are released from soil into porewater, as suggested by their higher aqueous concentrations in the plant-grown columns than in the non-plant columns (Fig. 3) with a significant difference in Period III ($p < 0.05$ for Cu and Zn in Table S1, Supplementary information). As seen by the slightly higher TOC after the plants begin to grow (Fig. S6, Supplementary information), plant exudates such as oxalic acid and amino acids [20,21,45] can readily chelate with trace metals in soils, and consequently facilitate their release from soil into porewater [20,40]. These geo- chemical reactions can trigger the release of trace metals into porewater. As a result, more Zn and Pb (but not Cu) were lost in the 0–4 cm layer of soil from the plant-grown columns than from the non-plant columns (Fig. 4), possibly due to leaching promoted by plant roots. The distinct result for Cu from Zn and Pb was prob- ably caused by differences in their colloidal mobilization behavior in the two kinds of columns, which will be discussed later.

Although *Elsholtzia splendens* is a Cu-tolerant plant found in Cu mining areas [46], it showed a much lower uptake of Cu than ryegrass, possibly due to serious synergistic contamination with multiple trace metals, and persistent organic pollutants [37,47]. The results also highlighted the limitations of some hyperaccumulator plants under different soil conditions.

To examine the leaching mechanism of trace metals in the soil depth profile, a mass balance of Cu and Zn from porewater and plant uptake for each soil layer was estimated and compared with the chemical analysis of the spent soil after the leaching tests. The results of the calculation suggest that the released (accumulated) Cu and Zn along the soil depth were generally consistent with the sum of the porewater and plant absorption (Fig. S12, Supplementary information). In addition, Cu showed a slightly higher release of 24.6 mg for the plant-grown columns and 51.1 mg for the non-plant columns at the 0–2 cm layer (dashed box in Fig. S12-I, Supplementary information). The "extra" release of Zn of 20.1 mg for the plant-grown columns and 5 mg for the non-plant columns (Fig. S12- II, Supplementary information) was not as great as that of Cu. The amount of the lost Cu suggests that another release pathway may exist during the leaching process. In addition to mobilizing as soluble species in porewater, trace metals can also be transported as soil colloidal phases, including Cu-bearing aggregated particles [48], which probably could contribute to the excess in the release of Cu. The higher extra release of Cu in comparison to Zn can be attributed to the much higher percentage of Cu (22.03%, wt.) than Zn (1.26%, wt.) in the incinerated ash of the printed circuit boards [33]. More colloidal mobilization for Cu was observed in the normal columns than in the plant-grown columns (Fig. S12-I, Supplementary information), possibly because the roots of the plants controlled the soil erosion rates [49]. The inhibition of the colloidal mobilization of Cu by plant roots likely explains the insignificant plant-facilitated effect on Cu (different from that on Zn and Pb) in the soil pro-file between the plant-grown columns and the non-plant columns [21,50]. Overall, over the long term in a natural process, the trace metals released from topsoil can penetrate the adsorptive sites in the subsoil and be transported downwards. Thus, they should be remediated to avoid further contamination to groundwater because the shallow aquifers in the area have a depth of only 0.5–2.5 m [6,15,44]. This pattern probably further explains why in recent studies groundwater samples in Longtang, China were found to contain 0.11 mg/L of Cu and 0.03 mg/L of Zn after about 5 years of illegal e-waste recycling activity there [15], while samples from the study area contained 9.0–31.1 μg/L of Cd [6].

CONCLUSION

The current study evaluated the contamination of trace metals in e-waste polluted soil and their leaching mechanism in soil columns for ~2.5 years. Our results showed no trace metals in the leachate at the bottom of the columns, but a one mg/L level of Cu and Zn was found in the porewater in the topsoil layers. The release of trace metals could contaminate the subsurface soil and was greater with plant growth. Sequential extraction results and a XANES analysis indicated that Cu and Zn in the carbonate/amorphous Fe/Mn oxide phases can be bioavailable and mobilized during the long-term rainwater irrigation and plant-growing process. The Cu and Zn that were released can be sequestrated on the abundant Fe/Mn oxides in the sub-layer of soil. Our study characterized the molecular speciation and mobilization behavior of trace metals from e-waste contaminated soil and provided solid evidence of their potential impact on subsurface soil and even shallow groundwater.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2016.12.060.

LIST OF TABLES AND FIGURES

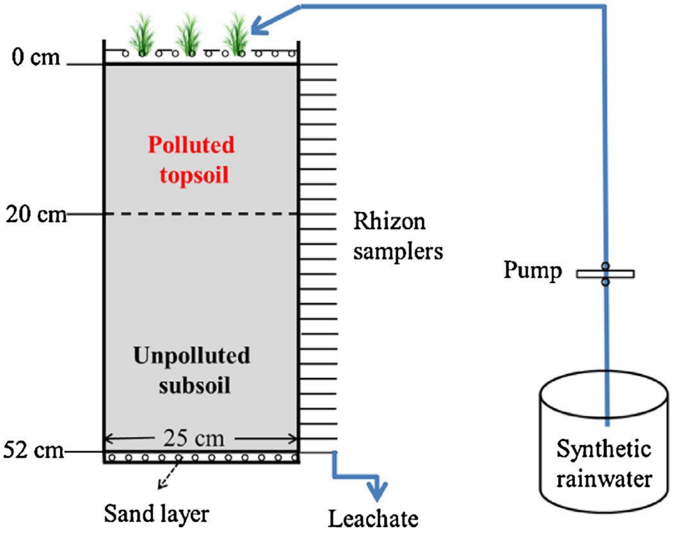

Fig. 1. Scheme of the columns. Plants (Elsholtzia splendens or ryegrass) were grown on a sandy layer of soil in some columns, while no plants were grown in other columns.

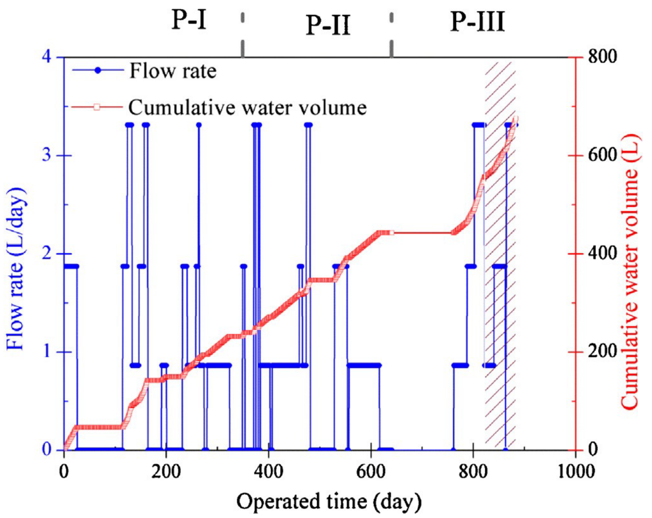

Fig. 2. Column leaching tests, including flow rate and accumulative water volume. Synthetic rainwater was used, except for the last 60 days, when synthetic acid rain- water was used (the diagonal line area). Three representative periods (Period I, P-I, 0-353 days; Period II, P-II, 354-641 days; and Period III, P-III, 642-882 days) were selected for comparison.

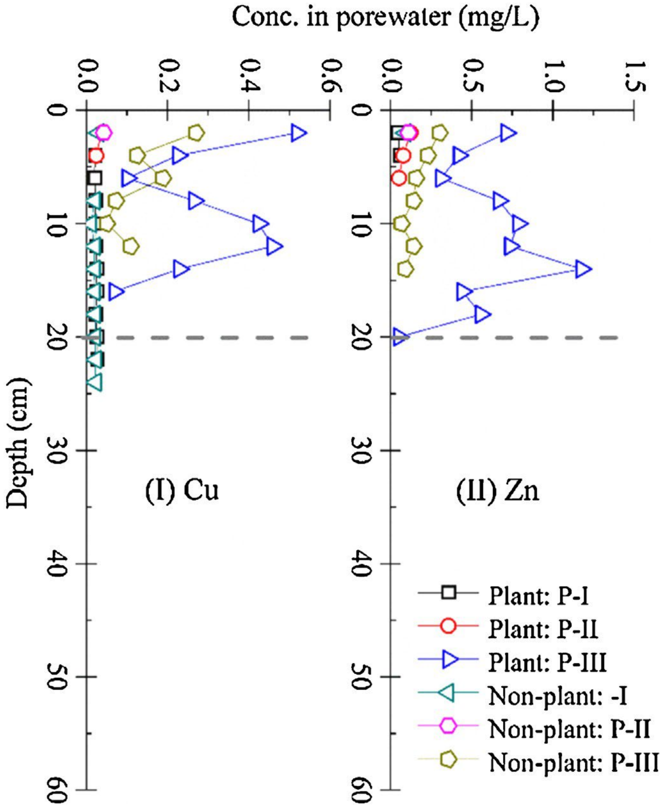

Fig. 3. Cu and Zn concentrations in porewater at Periods I, II, and III for plant-grown and normal (non-plant) columns (Fig. 2). The concentrations of Pb in porewater were too low to be detected.

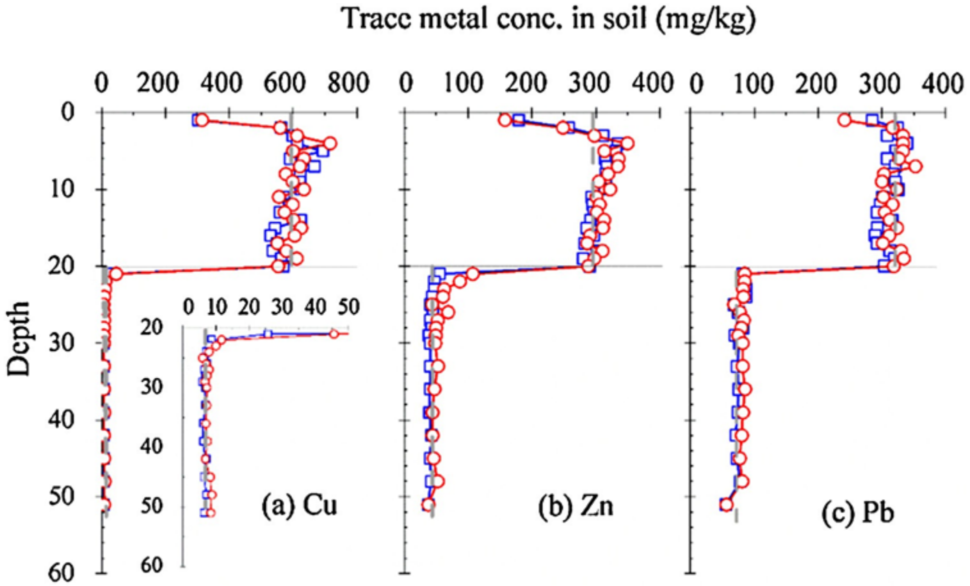

Fig. 4. Cu, Zn, and Pb concentrations in soils after the column leaching tests. The vertical lines represent the concentrations of metal in the original contaminated soil. The horizontal lines represent the boundary between the topsoil and the subsoil

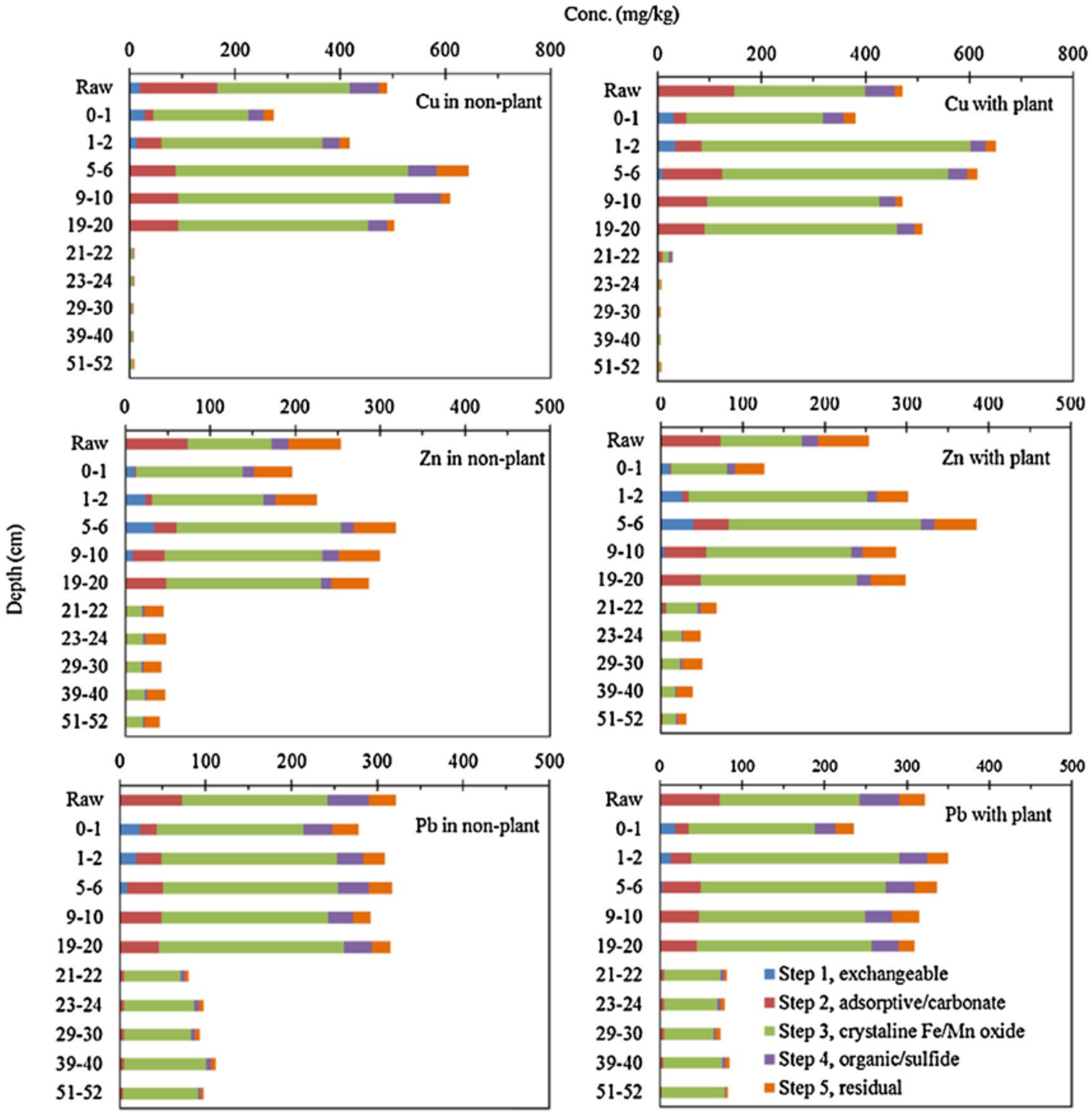

Fig. 5. Operationally defined chemical fractions of Cu, Zn, and Pb in soils after the column leaching tests using a sequential extraction method. Original soil Raw represents the initial e-waste contaminated soil.

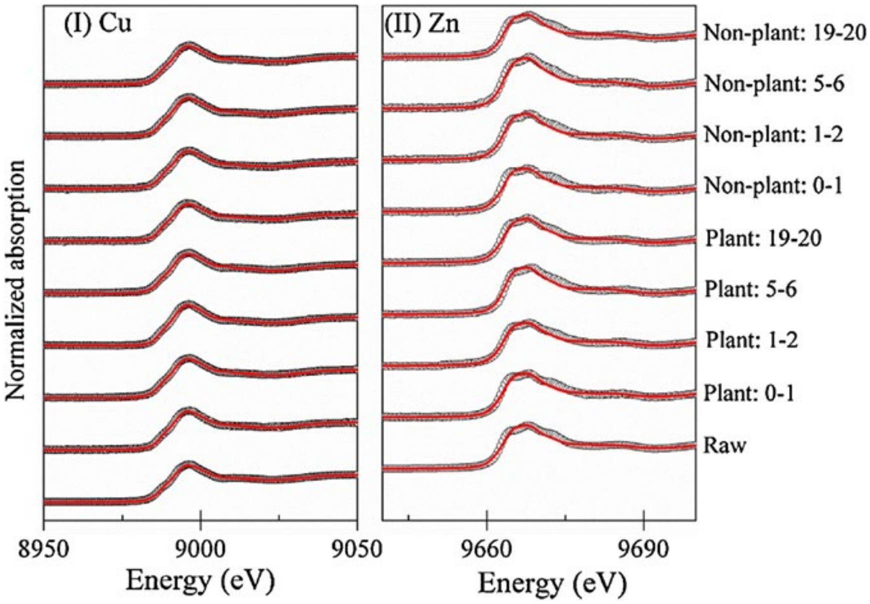

Fig. 6. The linear combination fitting (LCF) results of Cu (I) K-edge and Zn (II) K-edge XANES spectra in the original e-waste contaminated soil (original) and the spent soil (plant-grown columns and columns without plants) after the leaching test. Symbols represent the XANES spectra with red lines indicating as the linear combination fitting (LCF). The results of the fitting are reported in Tables 2–3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1. The physiochemical properties and elemental concentration (mg/kg, dry weight) of the topsoil and subsoil in the leaching columns, and the background (Bkg) values of trace metals in the soil of Guangdong province [10].

Element	Polluted soil (topsoil)	Unpolluted soil (subsoil)	Bkg value
pH	7.0	7.6	
Organic carbon%	3.6	2.6	
CEC (meq/100 g)	5.4	3.6	
Porosity	43%	44%	
Al	47,500	32,000	
Fe	14,700	12,000	
Mn	435	356	
Ca	3730	2260	
Mg	751	660	
Cu	590	6.4	17.0
Zn	298	41.6	47.3
Pb	320	67.0	36.0
Ni	7.1	3.4	14.4
Cr	19.7	15.2	50.5
Cd	0.22	0.06	0.06

Table 2 Copper species (%) in the original e-waste contaminated soil and the spent soil along the depth of the soil (cm) after the column leaching test using XANES analysis by linear combination fit.

Sample	$CuSO_4$	$Cu(OH)_2$	$CuCO_3$	$Cu_3(PO_3)_2$	CuO	Cu-Fh	Cu-HA	CuS	Summing $CuCO_3$and Cu-Fh	R-factor	Reduced chi-square
Original soil	0	15	13	0	2	65	0	5	78	0.0011	0.0003
Plant: Depth 1	8	1	6	0	0	79	0	6	85	0.0015	0.0004
Plant: Depth 2	7	0	4	0	2	79	0	8	83	0.0013	0.0003
Plant: Depth 6	8	1	2	0	0	89	0	0	91	0.0013	0.0003
Plant: Depth 20	4	0	3	0	5	81	0	7	84	0.0020	0.0005
Non-plant: Depth 1	10	5	10	11	0	64	0	0	74	0.0038	0.0009
Non-plant: Depth 2	7	4	7	5	0	71	0	6	78	0.0013	0.0003
Non-plant: Depth 6	5	3	12	0	0	76	0	4	88	0.0018	0.0004
Non-plant: Depth 20	0	1	11	0	6	76	0	6	87	0.0009	0.0002

Table 3 Zinc species (%) in the original e-waste contaminated soil and the spent soil along the depth of the soil (cm) after the column leaching test using XANES analysis by linear combination fit.

Sample	$ZnSO_4$	$Zn(OH)_2$	$Zn_2(OH)_2CO_3$	$Zn_3(PO_4)_2$	Zn-Fh	Zn-HA	ZnS	ZnO	Summing Carbonate andZn-Fh	R factor	Reduced chi-square
Original soil	0	1	38	0	43	0	18	0	80	0.0064	0.0017
Plant: Depth 1	0	0	29	7	45	0	19	0	74	0.0084	0.0023
Plant: Depth 2	5	0	31	7	39	7	11	0	70	0.0054	0.0015
Plant: Depth 6	4	0	31	14	41	0	10	0	72	0.0078	0.0024
Plant: Depth 20	4	0	34	0	47	0	15	0	81	0.0058	0.0016
Non-plant: Depth 1	3	0	26	10	43	0	18	0	69	0.0146	0.0033
Non-plant: Depth 2	7	0	28	9	43	4	9	0	71	0.0072	0.0022
Non-plant: Depth 6	0	0	36	6	47	0	8	3	83	0.0108	0.0038
Non-plant: Depth 20	5	0	27	11	46	0	11	0	73	0.0067	0.0017

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