Influence of EDTA washing on the species and mobility of heavy metals residual in soils

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ABSTRACT

Aiming to estimate the potential risk of ethylenediaminetetraacetic acid (EDTA)-enhanced soil washing, the heavy metal species and their mobility in the washed soil under different combinations were investigated by batch leaching tests and the sequential extraction procedure. Results demonstrate that the metal removal efficiency was rather low (less than 12%), partially due to the significant Ca dissolution and strong bonding between metals and the soil as well as the insufficient EDTA dosage. The washing combination of 0.0005 M EDTA and half-an-hour washing can enhance the instant mobility of Ni, Zn and Pb possibly owing to the slow detachment of EDTA-destabilized metals. Metal fractionation also exhibits the corresponding increase in their labile exchangeable fractions. Therefore, a more concentrated EDTA solution for a longer duration often decreased their mobility. The increase in some fractions of a curtain metal implies the redistribution of this metal during the EDTA soil washing. The pathway of such a redistribution may vary for different metals, but the redistribution to organic matter is often a slow process, while that to carbonates or Fe/Mn oxides is a faster one and even may occur in a half hour washing with 0.0005 M EDTA solution. These redistribution processes may also increase the metal chemical availability. Therefore, we should prudently control the chelating reagent concentration and washing duration to finally minimize the mobility and availability of the remaining heavy metals when designing the soil washing for the remediation of metal-contaminated soils.

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1. Introduction

Soil washing is an ex-situ remediation technology for separating contaminants from the bulk soil in either or both of the following ways: dissolving contaminants in solution by chelating agents or acid solution, as well as concentrating contaminants into a small volume of soil through particle size separation [1,2]. The concept of the latter is based on the findings that most contaminants tend to bind, either chemically or physically, to clay, silt, or organic soil particles [3,4]. The most extensively studied chelating agents for soil washing were ethylenediaminetetraacetic acid (EDTA) and their salts. They have been reported to appreciably increase the dissolution and mobilization of cationic heavy metals [5–10], and have low aquatic toxicity and no bioaccumulation in living organisms through the food chain [11]; therefore, they can function as one of promising washing agents for metal-contaminated sites. However, a significant part of heavy metals usually remains at the aged sites after EDTA-enhanced soil washing, especially if the soils are rich in organic matter or clays, inasmuch as these soil solid phases

often have a strong affinity with the target heavy metals [12–16]. If these residual heavy metals are present in chemically stable mineral forms or bound to non-labile soil fractions, they are less mobile and bioavailable, and hence less toxic. In fact, heavy metal mobility and bioavailability are increasingly used to symphonize the success of soil remediation instead of the total metal content [17]. However, the mobility and bioavailability of these heavy metals in the washed soils have been often neglected in most research on soil washing, although EDTA has also been proven to effectively increase the availability of heavy metals in the soil phrase, when being used to enhance the phyto-extraction efficiency of potential metal-accumulators [18–20]. In fact, the enhanced mobility of heavy metals, and the resulting eutrophication and nutrient deficiency have been suggested as the main concern about EDTA application by the technical meetings of European Union Member State Representatives [11].

As reported in the previous studies [21–23], EDTA can enhance the metal mobilization by two mechanisms: a fast thermodynamically favorable complexation between some cationic metals and EDTA, as well as a slow EDTA-promoted dissolution. The former can directly break down some weak bonds between metals and soils, while the latter can indirectly mobilize metals that are bound to oxides and organic matter through partially disrupting the soil

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Table 1
Characteristics of the studied soil.

Soil properties	Value	Characterization method	Equipment for characterization
pH	5.50	Method 9045 in USEPA SW-846	320 pH meter (Mettler Toledo, Switzerland)
Density (g cm^{-3})	1.06	–	–
Organic matter content (mass%)	5.98	Heating the dried samples at 350 °C for 5 h	–
Particle size distribution (vol%)			
Sand ($\geq$50 µm)	34.11	Directly scanning on	OMEC LS-POP(III) Laser
Silt (<50 µm, $\geq$2 µm)	59.16	the soil solution (1:10)	particle size analyzer
Clay (<2 µm)	6.73		(OMEC, China)
Metal contents (mg kg^{-1})			
Cu	798 ± 77	HCl–HF–HClO$_4$–HNO$_3$	Optima 3000XL
Ni	1933 ± 130	acid digestion, followed	Inductively coupled
Zn	13565 ± 975	by Method 6010C of	plasma-atomic
Cr	3912 ± 170	USEPA SW-846	emission spectrometer
Pb	976 ± 68		(PerkinElmer, USA)

structure. In aged contaminated sites, the majority of the metal species are bound to oxides or organic matter, EDTA-promoted dissolution can play a substantial role in the overall metal removal under the chelator adequacy [24]. EDTA-promoted dissolution itself also includes two steps: a fast adsorption of free or complexed EDTA onto specific surface sites via surface complexation, which can destabilize the metal–oxygen bonds in mineral structure, followed by a rate-limiting metal detachment from the oxide structure. Therefore, the kinetic metal detachment may potentially increase the mobility of EDTA-destabilized metals in the washed soil. In fact, a few studies addressed this issue, and found that the metals in the washed soils became more weakly adsorbed or labile [25,26]. Some research found that the mobility of some residual heavy metals, i.e., Pb, increased after seven days' abiotic aging [27]. Therefore, the magnitude of metal mobility could cause new problems for water resources, as metal contaminants could migrate from the soil to groundwater.

In addition, a high concentration of EDTA solution was found to dissolve indigenous oxides, carbonates and organic matter, and to appreciably alter both the physical structure and chemical properties of soils; nevertheless, the diluted EDTA solution has a priority to release the labile metal fractions with a minimal damage on the soil structure [23]. Therefore, the washing with a diluted EDTA solution may effectively reduce the risk of metal movement since the contribution of EDTA-promoted dissolution is very limited, although a substantial part of the metals may remain in the washed soils, especially at the heavily contaminated sites. However, a too diluted EDTA solution is always unable to release the majority of the labile fractions of metals, which is the source of the metal mobility in the washed soil. So, there is no doubt that further research, such as metal mobility and species influenced by washing duration and EDTA concentration, is required to avoid chelator-induced metal movement into groundwater.

Therefore, the objective of this study is to investigate the influences of contact period and EDTA concentration on the metal mobility and species in the soil remedied by EDTA-enhanced soil washing.

2. Materials and methods

The studied soil was collected from the upper soil layer 0.5–1.0 m below the ground surface in a demolished electroplating plant site located in the North of Guangzhou City, China. The collected soil was ground, uniformed and air-dried at 20 °C, and sieved by a 60-mesh laboratory test sieve. In fact, in our running pilot EDTA-enhanced soil washing, the sand fraction of the soil (more than 60 meshes, about 86 mass%) could be separated by the sharking sieve and grit chamber, and thus directly disposed to the site even after being washed by the diluted 0.0005 M EDTA solu-

tion, since the concentrations of the metals residual in the sand fraction can satisfy the regulatory authorities [28]. However, most metals are still bound to the fine silt and clay fractions, which only account for only 14 mass%, so their species and mobility need specific attention, since they often decide whether the further disposal technology is required, as well as the selection and performance of the further disposal technology. Therefore, the fine fraction was employed for this study. This fraction was characterized, and its main properties, as well as the characterization methods and equipment are summarized in Table 1. It was slightly acidic with a high level of organic matter, and the major heavy metals of concern in this soil were copper (Cu), nickel (Ni), chromium (Cr) and lead (Pb), especially zinc (Zn) whose concentration was very high.

To probe the influence of contact time and/or EDTA concentration on metal mobility in the EDTA-washed soil, every 1.0 g of the soil was mixed with 20 mL EDTA solution of different concentrations (0.005 M, 0.001 M, or 0.0005 M) in 100-mL glass bottle by a rotary shaker of 200 ± 5 rpm for different washing durations (0.5 h, 1.0 h, or 2.0 h). The detailed operating parameters are listed in Table 2. Then the washing solution and the soil were separated by centrifuging at 5000 rpm for 10 min, and heavy metals of concern (Cu, Ni, Zn, Cr and Pb) and soil component elements (Ca, Fe, Mg, Al and Mn) in the supernatant were measured by Optima 3000XL inductively coupled plasma-atomic emission spectrometer (PerkinElmer, USA), based on Method 6010C of USEPA SW-846 [29]. The residue was flushed with deionized water to completely remove the dissociated metals and EDTA. The metal mobility in this residue was then determined by batch leaching tests, where this residual soil was mixed with 10-mL sulfuric acid-nitric acid solution (2:1 ratio, pH 3.20 ± 0.05) at 20 ± 2 °C for 18 ± 2 h on a rotary shaker at about 200 ± 5 rpm, then the extract was separated from the soil by filtration with 0.6–0.8 micrometer filter membrane, and then acidified with 10% HNO$_3$ to pH less than 2 to avoid precipitation and stored in refrigerant (less than 4 °C) for heavy metal determination. In order to further investigate the heavy metal species affected by washing combinations during the

Table 2
Washing combinations of EDTA-enhanced soil washing.

Index	Washing time (h)	EDTA concentration (M)
Exp. 1	0.5	0.0005
Exp. 2	0.5	0.001
Exp. 3	0.5	0.005
Exp. 4	1.0	0.0005
Exp. 5	1.0	0.001
Exp. 6	1.0	0.005
Exp. 7	2.0	0.0005
Exp. 8	2.0	0.001
Exp. 9	2.0	0.005

Table 3
Sequential extraction for metal fractionation [30].

Index	Metal fractionation	Extraction agents	Extraction conditions
S1	Exchangeable	1 M $MgCl_2$, pH 7	1 h, room temperature
S2	Weakly complexed and bound to carbonates	1 M CH_3COONa, pH 5	5 h, room temperature
S3	Bound to Fe/Mn oxides of low crystallinity	0.04 M $NH_2OH–HCl$ in 25% (v/v) CH_2COOH	6 h, 96 °C
S4	Bound to organic matter and sulfides	30% H_2O_2 + HNO_3 (pH 2), 3.2 M $CH_3CO_2NH_4$ in 20% (v/v) HNO_3	5 h, 85 °C
S4	Residual	Concentrated HCl, HF, $HClO_4$, HNO_3	6 h, 190 °C

EDTA-enhanced soil washing, the metal species in the soil washed by Exp. 1, Exp. 3, Exp. 7 and Exp. 9 were fractionated by the traditional sequential extraction scheme [30] (the detailed extraction reagents and operating conditions are listed in Table 3). All these experiments were performed in at least triplicate.

3. Results and discussion

3.1. Heavy metal removal by EDTA washing

Fig. 1 shows the removal efficiencies of Cu, Ni, Zn, Cr and Pb under the different combinations. As a whole, the removal efficiencies of these metals, especially Pb and Ni, all seemed very low, even when washing with the highest 0.005 M EDTA. In fact, Pb and Ni were often considered as less extractable metals in soils in the previous studies [31]. One potential reason was that the added EDTA was much less than the stoichiometric requirement for 1:1 metal–EDTA complex, which was about 0.02 M EDTA at this ratio of washing solution to soil (20:1). Moreover, the strong bonding between these metals and soil particles, which are rich in clay minerals and organic matter in this aged site, also can result in such a low metal removal. The issue on metal fractions in the soil will be subsequently discussed in detail.

As shown in Fig. 1, a longer contact time and/or a more concentrated EDTA solution often induced higher metal (i.e., Cu, Ni, Zn and Pb) removal efficiencies, while the Cr removal seemed less dependent on these washing combinations. As widely known, EDTA can enhance the metal mobilization through the formation of stable and soluble metal–EDTA complexes and/or the EDTA-promoted metal dissolution [23]. In general, EDTA complexation is the dominant mechanism for most cationic metal removal, and this process often depends on EDTA concentrations, especially when the concentrations are less than the stoichiometric requirement [7]. However, EDTA-promoted dissolution also often makes a substantial contribution to the metal release from the aged contaminated soil, where most metals are bound to oxides and organic matter. The EDTA-promoted dissolution is a kinetic process, and the contact time thus often plays an important role herein. However, the results in Fig. 1 show that the increase of contact time from half-an-hour to an hour, even 2 h, caused a very subtle increment in the metal removal efficiencies, much less than those with the EDTA concentration increase. It infers that the contribution of EDTA-promoted dissolution to the cationic metal release was very limited among the studied combinations. Many previous studies also confirmed it, and found that at the low ratio of chelator to metals, just like herein, the mineral dissolution was insignificant [24,32].

As shown in Fig. 1, the Cr removal was independent of the EDTA concentrations and washing durations. As introduced above, an electroplating plant was previously located in this site, and anionic Cr(VI) as the form of chromate used to be massively applied there. The Cr(VI) is of high mobility and toxicity, but is readily reduced to cationic species of Cr(III) by organic matter and divalent irons. Therefore, Cr exists in soils as the species of either hexavalent chromium [Cr(VI)] or trivalent chromium [Cr(III)] [33]. The Cr(VI) in soils exists as the insoluble precipitates such as $ZnCrO_4$ in the presence of other cationic heavy metals, or adsorbed as inner-sphere complex on the surface of hydrous oxides, or is generally slightly adsorbed to amorphous ferric hydroxides or clay minerals [34]. The former two forms of Cr species will be mobilized if the cationic metal (i.e., Zn herein) or the adsorbed hydrous oxides is released or dissolved by EDTA solution, so their mobilization often depends on EDTA concentrations. The latter is weakly bound, and it inasmuch can be easily released even through the quick electrostatic exchange with some anions [33]. The Cr(III) species exist as co-precipitates with ferric hydrous oxides (i.e., $Cr_xFe_{1-x}(OH)_3$) or phosphates or trivalent oxide that both have low mobility and bioavailability in soils [35]. Like the above-mentioned cationic metals, Cr(III) can be removed by EDTA solution mainly through the formation of Cr(III)–EDTA complex or the dissolution of ferric hydroxides, both of which generally relies on EDTA concentrations. Therefore, the independence of Cr removal on the washing combinations, as shown in Fig. 1, hints that the removed Cr may be mainly from the hexavalent species slightly adsorbed by amorphous ferric hydroxides or clay minerals.

3.2. Soil dissolution during EDTA washing

However, as reported in many previous studies, EDTA is a nonspecific chelating agent and the major componental cations in soils such as iron (Fe), cadmium (Ca), magnesium (Mg), aluminum (Al), and manganese (Mn) are also often extracted during EDTA-enhanced soil washing, facilitating soil structures destroyed or changed [23,36]. Table 4 lists the concentrations of these elements in the solution after washing. These results show that the most significant soil componental element released during EDTA-enhanced soil washing was Ca, while other componental elements (i.e., Fe, Mg, Al, and Mn) were less substantial. The similar phenomenon was observed by other researchers [37–39], who also observed the tremendous amount of Ca dissolution in calcareous soils. Whereas, the conditional stability constant of Ca–EDTA ($K_{ca–EDTA} = 10^{4.1}$ at pH 5) is much less than that of the target metal–EDTA complexes (i.e., $K_{Cu–EDTA} = 10^{12.2}$, $K_{Ni–EDTA} = 10^{12.0}$, $K_{Zn–EDTA} = 10^{9.9}$, $K_{Pb–EDTA} = 10^{11.4}$ at pH 5) as well as Fe–EDTA ($K_{Fe–EDTA} = 10^{14.79}$ at pH 5.0) and Al–EDTA ($K_{Al–EDTA} = 10^{9.55}$ at pH 5) [40], so the great Ca dissolution cannot result from the ther-
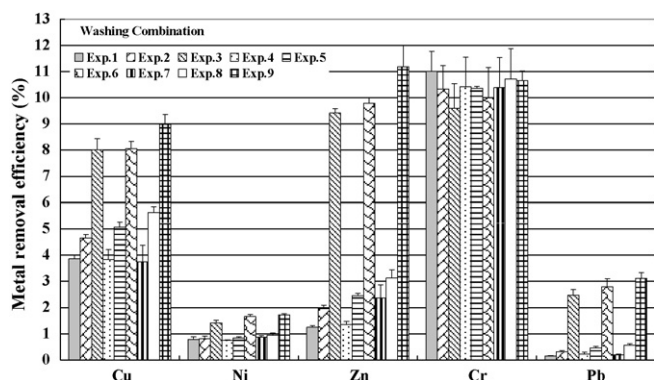

Fig. 1. Metal removal among different washing combinations (the operating conditions of Exps. 1–9 are listed in Table 2).

Table 4
Soil dissolution during EDTA washing.

Index	Concentration of soil componental elements in washing solution (mmol kg^{-1})				
	Fe	Ca	Mg	Al	Mn
Exp. 1	0.072 ± 0.004	83.8 ± 1.6	0.946 ± 0.216	0.176 ± 0.065	0.009 ± 0.005
Exp. 2	0.054 ± 0.013	101.8 ± 7.2	0.987 ± 0.031	0.102 ± 0.028	0.023 ± 0.005
Exp. 3	0.354 ± 0.022	181.5 ± 8.0	2.355 ± 0.257	1.130 ± 0.102	0.146 ± 0.018
Exp. 4	0.076 ± 0.013	80.7 ± 0.6	0.967 ± 0.093	0.111 ± 0.000	0.009 ± 0.000
Exp. 5	0.094 ± 0.009	90.9 ± 6.2	1.121 ± 0.123	0.250 ± 0.028	0.023 ± 0.005
Exp. 6	0.358 ± 0.067	182.5 ± 17.2	2.293 ± 0.062	0.574 ± 0.158	0.141 ± 0.000
Exp. 7	0.076 ± 0.036	78.2 ± 1.7	1.100 ± 0.216	0.130 ± 0.019	0.014 ± 0.005
Exp. 8	0.076 ± 0.040	83.7 ± 18.2	1.265 ± 0.226	0.111 ± 0.009	0.027 ± 0.005
Exp. 9	0.372 ± 0.076	164.3 ± 5.3	2.602 ± 0.535	1.038 ± 0.510	0.168 ± 0.027

modynamically favorable complexation between Ca and EDTA. It is likely ascribed to the proton-promoted dissolution of Ca (pH 4.7–5.2 for 0.005–0.0005 M EDTA solution) as well as the cation exchange between Ca^{2+} and Na$^+$ in the solution [41]. The great amount of dissolved Ca then can quickly complex with the free EDTA to form Ca–EDTA, and significantly diminish the EDTA extraction effectiveness of target metals as shown in Fig. 1, likely due to the kinetic metal exchange reaction between the Ca–EDTA and the sorbed target metals on the soils [21,23,38,39]. The low levels of Al, and Mn and Fe in the solution also revealed the limited contribution of EDTA-promoted dissolution to the overall metal removal, since EDTA-promoted dissolution often considerably increases the Al, Mn and Fe release from the soil [23]. During the soil washing, the pH of the mixture solution, initially ranged between 4.9 and 5.3, marginally increased to 5.4–5.6 after a 2-h washing. Although the increase in pH during soil washing has often been reported in the previous studies [15,23], such a subtle increase in pH also indicates the limited kinetic reaction between EDTA solution and some soil componental metals, such as Al and Fe, since the dissolution of these oxides always consumes a bulk of H$^+$ in the solution. Moreover, as shown in Table 1, a higher concentration of EDTA solution (Exps. 1–3, or 4–6, or 7–9) always was accompanied with more soil componental elements released in the solution, suggesting that the extent of soil dissolution is dependent on EDTA concentration. This also supports that the soil dissolution is a result of EDTA-promoted dissolution. Nevertheless, their increment with a longer washing duration was not substantial, and a longer time of washing even slightly decreased the Ca concentration in washing solution. It has been reported that the Ca–EDTA complexes itself can mediate Fe and Al dissolution and this reaction has slower kinetics [21,23]. Consequently, Ca was re-adsorbed on the soil particles at a longer contact time [41],

while Fe and Al concentrations in the washing solution slightly increased.

3.3. Heavy metal mobility in the washed soil

In order to investigate the heavy metal mobility affected by EDTA washing, the batch leaching test with H$_2$SO$_4$–HNO$_3$ (pH 3.2) solution was conducted on the washed soils and the unwashed soil. Moreover, inasmuch as the toxicity of different metals always varies, we normalize the individual metal contents in the extracts by comprehensively considering their individual toxicity. We defined a mobility index (MI) with Eq. (1), similar to the widely used Hakanson ecological risk index [42], aiming to estimate the overall metal mobility as well as the resulting potential harmful effect on the washed soils.

$$MI = \sum_{n=1,}^{5} \frac{M_i}{R_i}, \tag{1}$$

where M_i is the metal concentrations in the extracts from the soil, R_i is the threshold of this metal in the soil to be identified as a hazardous solid waste, prescribed by Chinese Ministry of Environmental Protection (CMEP) [43].

According to the above definition, a greater MI value implies a greater potential harmful effect associated with the metal mobility in the washed soil, and a MI value less than 1 hints that the soils was not identified as a hazardous metals any longer after washing. The metal concentrations in the H$_2$SO$_4$–HNO$_3$ extracts as well as their relative MI are summarized in Table 5. The highest MI value for the unwashed soil revealed that the EDTA-enhanced sol washing indeed reduces the metal mobility to different extents. Washing with a more concentrated EDTA solution for a longer washing dura-

Table 5
Metal mobility from the washed soil and unwashed soil.

Index	Metal concentrations in the H$_2$SO$_4$–HNO$_3$ extracts (M, mg L^{-1})					Mobility index (MI)[b]
	Cu	Ni	Zn	Cr	Pb	
Unwashed soil	3.30 ± 0.15	1.11 ± 0.03	0.47 ± 0.04	55.15 ± 0.31	0.028 ± 0.001	3.94
Soil washed in Exp. 1	2.53 ± 0.04	2.86 ± 0.04	206.07 ± 0.54	9.56 ± 0.26	0.431 ± 0.035	3.38
Soil washed in Exp. 2	1.12 ± 0.03	0.26 ± 0.04	1.95 ± 0.16	10.75 ± 0.24	0.036 ± 0.013	0.81
Soil washed in Exp. 3	0.74 ± 0.07	0.18 ± 0.03	5.90 ± 0.31	10.16 ± 0.51	0.058 ± 0.004	0.79
Soil washed in Exp. 4	1.20 ± 0.07	0.31 ± 0.04	2.19 ± 0.20	9.58 ± 0.15	0.053 ± 0.024	0.75
Soil washed in Exp. 5	1.05 ± 0.13	0.25 ± 0.02	2.41 ± 0.48	9.37 ± 0.12	0.046 ± 0.011	0.72
Soil washed in Exp. 6	0.46 ± 0.08	0.16 ± 0.02	4.38 ± 0.41	9.06 ± 0.12	0.043 ± 0.010	0.69
Soil washed in Exp. 7	0.98 ± 0.08	0.25 ± 0.02	1.98 ± 0.14	7.71 ± 0.12	0.046 ± 0.010	0.60
Soil washed in Exp. 8	0.85 ± 0.05	0.23 ± 0.03	2.21 ± 0.20	8.02 ± 0.14	0.043 ± 0.017	0.62
Soil washed in Exp. 9	0.54 ± 0.01	0.18 ± 0.01	2.69 ± 0.41	5.38 ± 0.6	0.035 ± 0.002	0.43
Reference (R)[a]	100	5	100	15	5	–

[a] The metal threshold in the soil to be identified as a hazardous waste, prescribed by CMEP.

[b] Calculated based on $MI = \sum_{n=1,} \frac{M_i}{R_i}$.

tion often decreased the overall metal mobility in the washed soil, especially when EDTA concentration increased from 0.0005 M to 0.001 M for a half-an-hour washing. The residual concentrations were above the limits set by regulatory authorities [28]; the leachable metals, however, were efficiently removed and treated soils were all acceptable in terms of leaching toxicity, since all the MI values in the washed soils were less than 1, except in Exp. 1.

However, the different properties of metals as well as their various release mechanisms result in the diversity of their mobility from the washed soils. As shown in Table 5, the Zn extracted from the unwashed soil was very low (0.47 mg L^{-1} in the extract solution), but that from the soil washed by Exp. 1 was unexpectedly high (206 mg L^{-1}). The similar trend was also observed on Pb and Ni extracted. As reported in the previous studies, EDTA-induced metal dissolution includes two steps: a fast adsorption of free or complexed EDTA onto specific surface sites via surface complexation, which can destabilize the metal–oxygen bonds in mineral structure, followed by a rate-limiting metal detachment from the oxide structure [21–23]. The metal mobility in the washed soil is decided on the difference between the destabilized metals and the detached ones during the EDTA washing. If the destabilized metals are more than the detached ones, the metal mobility will increase, because the 18-h hydrogen-promoted dissolution (pH 3.2) always prefers to extract these destabilized but undetached metals in the batch leaching test. The metal destabilization only depends on the EDTA concentration, while the metal detachment is often relevant with washing durations, as well as the strength of metal–oxygen bonds and metal–EDTA complexes. High mobility of Zn, Pb and Ni in the soil washing in Exp. 1 is likely because a portion of these EDTA-destabilized metals via surface complexation are not yet detached owing to too short washing time and too diluted EDTA solution.

In addition, more Zn was extracted in the batch leaching test from the soil that was washed in advance with a more concentrated EDTA solution for 1 h or 2 h; nevertheless, similarly higher EDTA concentrations contrarily decreased the level of Cr, Cu and Ni exacted. Comprehensively comparing the mobility of these metals among different combinations, we can infer that a 2-h washing may be not adequate to completely detach all the destabilized Zn, and the Zn detachment process may be slower than Cu, Cr and Ni. This inference is consistent with the previous finding [44], which found that Cu was released earlier than Zn in the column flushing. In addition, the kinetic metal exchange between Ca–EDTA and adsorbed Zn (reaction rate constant is about 1100 M^{-1} s^{-1} [21]) as well as the redistribution of Zn [24,32] in the washed soils may also be the reasons for such an increase in the Zn mobility.

3.4. Metal species changed by EDTA washing combinations

The metals in the soils washed by Exp. 1, Exp. 3, Exp. 7 and Exp. 9 as well as the unwashed soil were fractionated by sequential extraction procedure to further investigate the metal fractions affected by EDTA concentrations and washing duration during EDTA-enhanced soil washing. The results are presented in Fig. 2, and the percentages herein were calculated based on the individual metal contents in the unwashed soil. As shown in Fig. 2, the exchangeable fractions (S1) of all heavy metals of interest, especially Pb, Zn and Ni, were of little significance in the unwashed soil. Since this soil was collected from a 10-year industrial waste site, most weakly bound exchangeable metals had been leached or immigrated, or transformed by weathering. More important, the sand fraction had been separated from the bulk soil, and the remaining fraction was rich in clay minerals and organic matter, which always prefers to form relatively strong bonds with metals after 10-year aging. The low level of metals in S1 also was an important reason for the lower metal removal efficiencies by EDTA-enhanced soil washing.
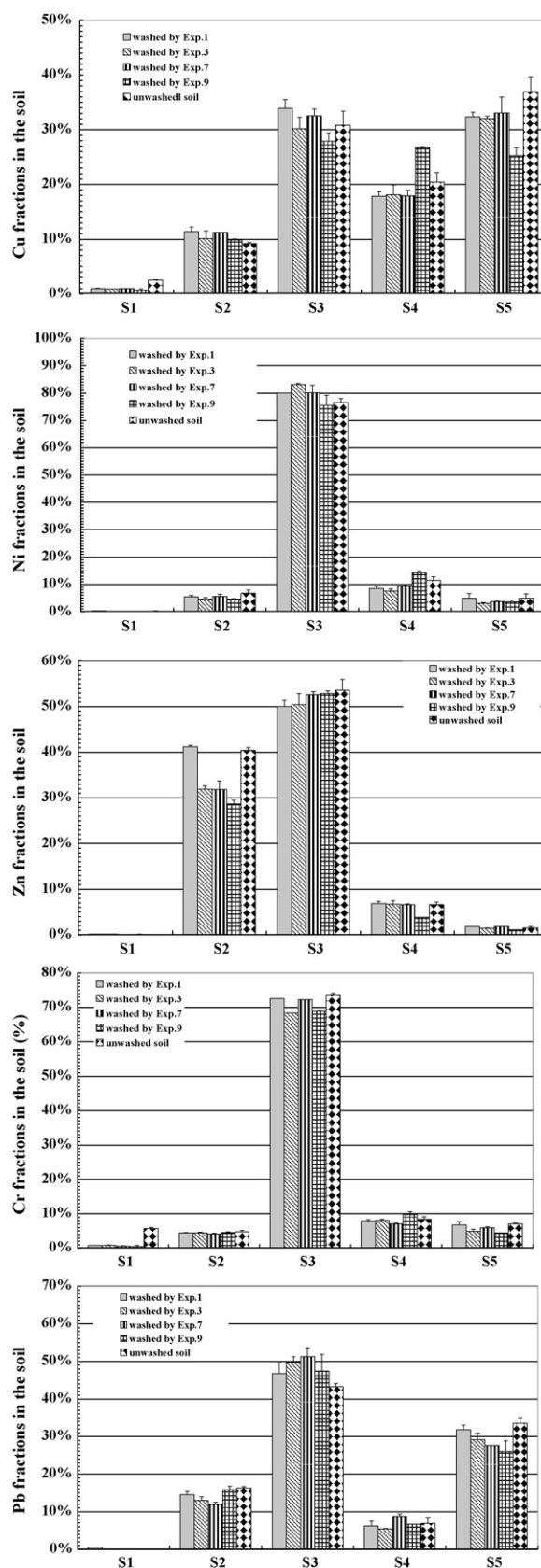

Fig. 2. Metal fractions affected by EDTA-enhanced soil washing (the metal percentages are calculated based on their individual contents in the unwashed soil. The operating conditions for Exp. 1: 0.0005 M EDTA, 0.5 h; for Exp. 3: 0.005 M EDTA, 0.5 h; for Exp. 7: 0.0005 M EDTA, 2.0 h and for Exp. 9: 0.005 M EDTA, 2.0 h.).
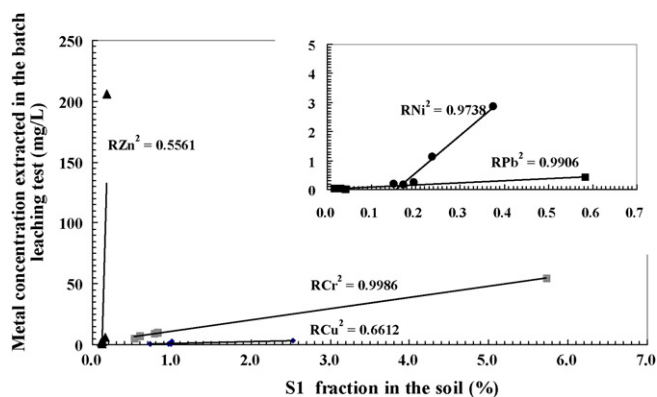
Fig. 3. Linear relationship between the exchangeable metal fraction (S1) and that extracted in the batch leaching tests.

However, the main metal fractions were found to vary in different metals, implying the different mechanisms for metal retention in soils and metal removal by EDTA. The Cu in the unwashed soil was dominantly in the most stable fraction-residual fraction (S5), followed by the fractions bound to Fe/Mn oxides of low crystallinity (S3), the fractions bound to organic matter and sulfides (S4), and fractions bound to carbonates (S2), and S1 was negligible. Ni in the unwashed soil was primarily bound to S3, and Pb was bound to S3 and S5.

Most Zn in the unwashed soil was in the S2 and S3 fractions. Because this soil had a high Zn loading, the contribution of strong bonds (S4 and S5) was diluted by the weak bonds (S2 and S3), and thus weakened the average bonding between Zn and soil particles. The higher Zn removal efficiencies than Pb and Ni also was likely attributable to it, although Pb–EDTA and Ni–EDTA complexes are more stable than Zn–EDTA. Fig. 2 also shows that Zn in the S2 fraction was substantially reduced by EDTA washing, especially at a high EDTA concentration. This decrement in S2 approached or exceeded over the overall Zn removal, implying that the Zn removed primarily originated from S2.

Among these metals in the unwashed soil, Cr showed the greatest percentage of S1 (5.7%) in the unwashed soil, so Cr demonstrated the highest mobility in the leaching test from the unwashed soil. The major Cr fraction in the unwashed soil was S3, because Cr(VI) can be easily reduced with Fe(II) and soil organic matter [45,46], the resulting Cr(III) as the most mimetic of Fe often form the stable mixed α(Fe, Cr)OOH (goethite structure) due to their similar ionic radii [47]. Fig. 2 also shows that this fraction could be removed by washing with 0.005 M EDTA, and some Fe was accordingly released into solution (Table 4), as previously reported [34]. Since Fig. 2 demonstrates that the removal of Cr in S3 relies on the EDTA concentrations, the independence of the overall Cr removal on the EDTA concentrations suggests that the contribution of the removal of S3 is not crucial during the EDTA washing. It can also be corroborated by the low Fe/Mn level in the washing solution, as listed in Table 4.

Fig. 2 also showed that the change of the metal fractions differed for various combinations of EDTA concentrations and washing durations. The S1 fractions of Zn, Pb and Ni in the soil washed by Exp. 1 increased on the basis of those in the unwashed soil, hinting a substantial redistribution to S1 via the metal–EDTA-destabilization. A higher EDTA concentration increased the S1 of Zn after a one or 2-h washing, but decreased the S1 of other metals. This phenomenon is consistent with the trend of the metals extracted in the batch leaching tests (linear correlation coefficient $R_{Zn}^2 = 0.56$, $R_{Cu}^2 = 0.66$, $R_{Cr}^2 = 1.00$, $R_{Pb}^2 = 0.99$, $R_{Ni}^2 = 0.97$, as illustrated in Fig. 3), disclosing that the extracted metals in the leaching tests mainly originate from the S1 fraction. Therefore, the levels

of the metal extracted in the batch leaching test just indicate the instant metal mobility.

Similarly, a more concentrated EDTA solution (i.e., 0.005 M) often caused a greater decrement in the S2 of Cu, Ni, Pb and Zn during EDTA washing, while a longer contact time did not substantially decrease them except for Zn. Therefore, a half hour seems adequate to remove Cu, Ni or Pb in S2 by EDTA, and the removal of Zn in S2 may be not as fast as these metals.

The metal fractions of S2, S3 or S4 were found to increase for some washing combinations for all heavy metals of interest, indicating that the portions of these metals were redistributed during the washing procedure: some fractions were destabilized and readsorbed on the carbonates, Fe/Mn oxides, or soil organic matter and sulfides. The redistribution of Cu to S2, as well as Cu and Pb to S3, was even observed in the combination of a diluted 0.0005 M EDTA solution and a half hour of washing. But the redistribution to S4 only occurred in a long contact time (i.e., 2-h washing for Pb, Zn and Ni), and in some cases, a high EDTA concentration (i.e., 0.005 M) was also required (such as Cu). Therefore, the metal redistribution to S4 during soil washing is inferred as a kinetic process, and the metal redistribution to S2 or S3 is much faster.

The residual fraction of metals (S5) was expected to be very stable and cannot generally be removed or changed. However, in this study S5 of all the metals decreased in the soil washed in Exp. 9, where a high EDTA concentration (0.005 M) and a long time of washing (2 h) were employed. The similar finding was reported by Lei et al., who also observed that the metal in S5 decreased during EDTA washing [26].

As illustrated in Fig. 2, the concurrence of the decrease in S5 and the increase in S4 was observed for Cu and Ni and Cr, hinting that these S5 probably was redistributed to S4, if they were not completely detached from the soil particles. Similarly, S5 of Zn was probably redistributed to S3, while that of Pb was probably redistributed to S2. However, these redistributions are likely an apparent redistribution process: EDTA-enhanced soil washing destabilizes the S5 of metals in the unwashed soil, and makes them detachable by the attacks of the extraction agents for S2, S3 or S4 during the sequential extraction procedure; the level of S2, S3, and S4 were therefore observed to increase. As reported by many previous studies, the determination of heavy metal fractions by the sequential extraction procedures is only operationally defined, and is generally considered to be more qualitative than quantitative to provide good insight into the metal distribution and mobility [48]. Therefore, the apparent metal redistribution obtained by the sequential extraction procedure only reflects the increase in the chemical availability of these metals after EDTA washing. Extensive investigations are thus required in the future to reveal its mechanism.

4. Conclusion

Currently, most studies on EDTA-enhanced soil washing focus on the metal removal effectiveness, but in fact the mobility of metals still remaining in the washed soil does dominate the ecological risk of the washed soil, as well as finally decide the success or failure of soil washing technology. Therefore, we herein pay specific attention on the metal mobility and species in the soil already remedied by EDTA-enhanced soil washing.

Results demonstrate that the washing combination of a diluted 0.0005 M EDTA and a half hour of washing duration increased the amounts of Cu, Ni, Zn and Pb extracted, likely because portion of these metals were destabilized by EDTA surface complex, but had yet not been detached from the soil structure herein. A linear correlation between the metals extracted and the exchangeable fractions indirectly corroborated this reason. However, a more concentrated

EDTA solution after a one or 2-h washing often lessens the Cu, Pb, Ni and Cr extracted, but increase the Zn mobility from the washed soil, hinting a much slower Zn detachment during EDTA-enhanced soil washing. The increase of the metal fraction bound to carbonates, or Fe/Mn oxides or organic matter during EDTA-enhanced soil washing implies the metal redistribution: the redistribution to organic matter is often a slow process, while that to carbonates or Fe/Mn oxides is a faster one and even occur in a half hour washing with 0.0005 M EDTA solution. This fast redistribution also may increase the metal chemical availability. Accordingly, the concentration of chelating agent and the washing duration are the two key factors, and a diluted EDTA concentration with a short washing duration often facilitates the redistribution of the remaining metals to the exchangeable fraction as well as those bound to carbonates and Fe/Mn oxides, and enhances the mobility and availability of these metals in the washed soil.

Consequently, engineers should be prudent to control the EDTA concentrations and washing duration to minimize the soil dissolution during washing and avoid the metal mobility problem in the residual after soil washing remediation, when designing the soil washing technology. Especially when the metal mobility and availability are used to evaluate the soil washing performance, we should comprehensively balance whether the washing combination is capable to release the majority of the labile fractions of target metals, but still unable to lead to significant metal redistribution from the refractory fractions to the labile ones. In addition, the mechanism of metal redistribution is still not very clear, so further investigation is required to deepen the understanding of the metal mobility and species affected by EDTA-enhanced soil washing as well as to guide the soil washing design.

Acknowledgements

References

[1] Federal Remediation Technologies Roundtable, Compiled from Remediation Technology Screening Matrix and Reference Guide, fourth ed., available at http://www.frtr.gov/matrix2/section1/toc.html.

[2] K. Maturi, K.R. Reddy, Extraction of mixed contaminants from different soil types, Soil Sediment Contam. 17 (2008) 586–608.

[3] R.L. Zimdahl, R.K. Skogerboe, Behavior of lead in soils, Environ. Sci. Technol. 11 (1977) 1202–1207.

[4] R. Raghavan, Cleaning excavation solid using extraction agents: a state-of-the-art review, EPA/600/2-89/034, Risk reduction engineering laboratory, Office of research and development, Cincinnati, OH, USA, 1989.

[5] A.P. Davis, I. Singh, Washing of zinc (II) from contaminated soil column, J. Environ. Eng. 121 (1995) 174–185.

[6] R.J. Abumaizar, E.H. Smith, Heavy metal contaminants removal by soil washing, J. Hazard. Mater. 70 (1999) 71–86.

[7] R.W. Peters, Chelating extraction of heavy metals from contaminated soils, J. Hazard. Mater. 66 (1999) 151–210.

[8] R. Bassi, S.O. Prasher, B.K. Simpson, Extraction of metals from contaminated sandy soil using citric acid, Environ. Prog. 19 (2000) 275–282.

[9] S. Tandy, K. Bossart, R. Mueller, J. Ritschel, L. Hauser, R. Schulin, B. Nowack, Extraction of heavy metals from soils using biodegradable chelating agents, Environ. Sci. Technol. 38 (2004) 937–944.

[10] W.H. Zhang, I.M.C. Lo, EDTA-enhanced washing for remediation of Pb-and/or Zn-contaminated soils, J. Environ. Eng. 132 (2006) 1282–1288.

[11] European Chemical Bureau, European Union Risk Assessment Report on Na₄EDTA, Office for Official Publications of the European Communities, Italy, 2004.

[12] J. Pichtel, B. Vine, P. Kuula-Vaisanen, P. Niskanen, Lead extraction from soils as affected by lead chemical and mineral forms, Environ. Eng. Sci. 18 (2001) 91–98.

[13] N. Finzgar, D. Lestan, Multi-step leaching of Pb and Zn contaminated soils with EDTA, Chemosphere 66 (2007) 824–832.

[14] W.H. Zhang, D.C.H. Tsang, I.M.C. Lo, Removal of Pb by EDTA-washing in the presence of hydrophobic organic contaminants or anionic surfactant, J. Hazard. Mater. 155 (2008) 433–439.

[15] Z.L. Zou, R.L. Qiu, W.H. Zhang, H.Y. Dong, Z.H. Zhao, T. Zhang, X.G. Wei, X.D. Cai, The study of operating variables in soil washing with EDTA, Environ. Pollut. 157 (2009) 229–236.

[16] K.R. Reddy, S. Chinthamreddy, Comparison of different extractants for removing heavy metals from contaminated clayey soils, Soil Sediment Contam. 9 (2000) 449–462.

[17] J. Kumpiene, A. Lagerkvist, C. Maurice, Stabilization of As, Cr, Cu, Pb and Zn in soil using immobilization, J. Waste Manage. 28 (2008) 215–225.

[18] E. Meers, A. Ruttens, M. Hopgood, E. Lesage, F.M.G. Tack, Potential of *Brassic rapa, Cannabis sativa, Helianthus annuus* and *Zea mays* for phytoextraction of heavy metals from calcareous dredged sediment derived soils, Chemosphere 61 (2005) 561–572.

[19] B. Nowack, R. Schulin, B. Robinson, Critical assessment of chelant-enhanced metal phytoextraction, Environ. Sci. Technol. 40 (2006) 5225–5232.

[20] Y.B. Sun, Q.X. Zhou, L. Wang, W.T. Liu, The influence of different growth stages and dosage of EDTA on Cd uptake and accumulation in Cd-hyperaccumulator (*Solanum nigrum* L.), Bullet. Environ. Contam. Toxicol. 82 (2008) 348–353.

[21] B. Nowack, L. Sigg, Dissolution of Fe (III) (hydr)oxides by metal–EDTA complexes, Geochim. Cosmochim. Acta 61 (1997) 951–963.

[22] G. Sposito, The Surface Chemistry of Natural Particles, Oxford University Press, Oxford, UK, 2004.

[23] D.C.W. Tsang, W.H. Zhang, I.M.C. Lo, Copper extraction effectiveness and soil dissolution issues of EDTA-flushing of contaminated soils, Chemosphere 68 (2007) 234–243.

[24] T.C.M. Yip, D.C.W. Tsang, K.T.W. Ng, I.M.C. Lo, Kinetic interactions of EDDS with soils. 1. Metal re-sorption and competition under EDDS deficiency, Environ. Sci. Technol. 43 (2009) 831–836.

[25] A. Barona, I. Aranguiz, A. Elias, Metal associations in soils before and after EDTA extractive decontamination: implications for the effectiveness of further clean-up procedures, Environ. Pollut. 113 (2001) 79–85.

[26] M. Lei, B.H. Liao, Q.R. Zeng, P.F. Qin, S. Khan, Fraction distributions of lead, cadmium, copper, and zinc in metal-contaminated soil before and after extraction with disodium ethylenediaminetetraacetic acid, Soil Sci. Plant Anal. 39 (2008) 1963–1978.

[27] M. Udovic, D. Lestan, Pb, Zn and Cd mobility, availability and fractionation in aged soil remediated by EDTA leaching, Chemosphere 74 (2009) 1367–1373.

[28] Chinese Ministry of Environmental Protection, Standard for Soil Quality Assessment for Exhibition Site HJ350-2007, China Environmental Science Press, Beijing, China, 2007.

[29] Environmental Protection Agency of the United States, Test Methods for Evaluation of Solid Waste, third ed., US Government Printing Office, Washington, DC, USA, 1995.

[30] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, Anal. Chem. 51 (1979) 844–851.

[31] J. Labanowski, F. Monna, A. Bermond, P. Cambier, C. Fernandez, I. Lamy, F. Oort, Kinetic extractions to assess mobilization of Zn, Pb, Cu, and Cd in a metal-contaminated soil: EDTA vs. citrate, Environ. Pollut. 152 (2008) 693–701.

[32] D.C.W. Tsang, T.C.M. Yip, I.M.C. Lo, Kinetic interactions of EDDS with soils. 2. Metal–EDDS complexes in uncontaminated and metal-contaminated soils, Environ. Sci. Technol. 43 (2009) 837–842.

[33] F.X. Han, Y. Su, B.B.M. Sridhar, D.L. Monts, Distribution, transformation and bioavailability of trivalent and hexavalent chromium in contaminated soil, Plant Soil 265 (2004) 243–252.

[34] K. Kuo, M.S. Lai, C.W. Lin, Influence of solution acidity and CaCl₂ concentration on the removal of heavy metals from metal-contaminated rice soils, Environ. Pollut. 144 (2006) 918–925.

[35] S.E. Fendorf, Surface reactions of chromium in soils and waters, Geoderma 67 (1995) 55–71.

[36] C. Kim, Y. Lee, S.K. Ong, Factors affecting EDTA extraction of lead from lead-contaminated soils, Chemosphere 51 (2003) 845–853.

[37] A. Polettini, R. Pomi, E. Rolle, The effect of operating variables on chelant-assisted remediation of contaminated dredged sediment, Chemosphere 33 (2007) 866–877.

[38] N. Papassiopi, S. Tambouris, A. Kontopoulos, Removal of heavy metals from calcareous contaminated soils by EDTA leaching, Water Air Soil Pollut. 109 (1999) 1–15.

[39] P. Theodoratos, N. Papassiopi, T. Georgoudis, A. Kontopoulos, Selective removal of lead from calcareous polluted soils using the Ca–EDTA salt, Water Air Soil Pollut. 122 (2000) 351–368.

[40] I. Kolthoff, P. Ewing, Treatise on Analytical Chemistry, second ed., Wiley, New York, USA, 1979.

[41] L.D. Palma, Influence of indigenous and added iron on copper extraction from soil, J. Hazard. Mater. 170 (2009) 96–102.

[42] L. Hakanson, An ecological risk index for aquatic pollution control-a sedimentological approach, Water Res. 14 (1980) 975–1001.

[43] Chinese Ministry of Environmental Protection, Solid Waste-Extraction Procedure for Leaching Toxicity – Sulfuric Acid and Nitric Acid Methods, China Environmental Science Press, Beijing, China, 2007.

[44] B. Sun, F.J. Zhao, E. Lombi, S.P. McGrath, Leaching of heavy metals from contaminated soils using EDTA, Environ. Pollut. 113 (2001) 111–120.

[45] D.L. Sedlak, P.G. Chan, Reduction of hexavalent chromium by ferrous iron, Geochim. Cosmochim. Acta 61 (1997) 2185–2192.

[46] K.R. Pagilla, L.W. Canter, Laboratory studies on remediation of chromium contaminated soils, J. Environ. Eng. 125 (1999) 243–248.

[47] A. Manceau, M.L. Schlegel, M. Musso, V.A. Sole, C. Gauthier, P.E. Pettt, F. Trolard, Crystal chemistry of trace elements in natural and synthetic goethite, Geochim. Cosmochim. Acta 64 (2000) 3643–3661.

[48] R.N. Yong, C.N. Mulligan, Natural Attenuation of Contaminants in Soils, Lewis Publishers, Boca Raton, Florida, USA, 2004.