

Application of EDTA decontamination on soils affected by mining activities and impact of treatment on the geochemical partition of metal contaminants

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ABSTRACT

Two soil samples were collected at mining areas located in southern Hunan Province, China. EDTA extraction of Pb, Zn, Cu and Cd from these two tailing soils was studied using column leaching experiments. The redistributions of heavy metals (HMs) were determined using the modified BCR (Community Bureau of Reference) sequential extraction procedure, before and after EDTA extraction. The results indicated that EDTA was an effective extractant because of its strong chelating ability for various HMs. The proportions of Pb, Zn, Cu and Cd in the four fractions varied largely after EDTA extraction. The extraction efficiency of EDTA of the acid-extractable fraction (AEX) was significant in shallow soil column, while in deeper soil column, decrease of the extraction efficiency of reduced (RED), oxidizable (OX) and residual fractions (RES) was obtained, which was mainly due to the decrease of EDTA concentration.

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1. Introduction

In China, as a principal raw materials supplier, the mining industry has to expand continuously to meet the demands of the ever-increasing economic growth. More than 95% of non-renewable energy sources, 80% of industrial raw materials and over 75% of agricultural means of production come from the mining and minerals industries [1]. However, contamination of soil by HMs, especially those in mine-tailing areas, poses a serious threat to the environment [2]. These heavy metals may adversely affect the soil ecology, agricultural productivity, food chain and water quality [3]. Thus, soil remediation of the mining area is very important and exigent nowadays.

In general, the feasible techniques that aim to remove HMs from contaminated soils include phytoremediation, microbial remediation and physical-chemical remediation [4]. In the physical-chemical remediation methods, chelating agents are always used to enhance heavy metal removals. These chelating agents remove HMs with less impact on soil properties than other decontamination systems, thus show a significant potential to extract HMs from the contaminated soils [5]. In comparison with other chelating agents, EDTA presents the following advantages: a low degree of biodegradability in soil [6] and moreover a high level of complexing capacity with respect to HMs [7]. The chelat-

ing agent EDTA not only can form soluble complexes with metals, but may also influence the distribution of metals in the fractions by moving metals from less water soluble fractions to more soluble fractions.

During recent years, approaches for removing HMs from contaminated soils using EDTA have been reported [8,9]. Many studies have shown that EDTA is effective in removing Pb, Zn and Cu from contaminated soils, although extraction efficiency depends on many factors such as the liability of HMs in soil, the strength of EDTA, electrolytes, pH and the soil matrix [10,11]. Several papers deal with the extraction of heavy metals by soil washing but the aim of most of them was to compare the effectiveness of different chelating agents (EDTA, citric acid) towards selected metal extraction or to optimize the solid/liquid ratio to achieve a stated metal extraction yield [12]. Only few papers focus their attention to assess the transfer characteristics and redistribution of HMs in the column extraction procedure [13].

Different extraction techniques are useful for different types of soils, or for different soil conditions. For soils in the mining areas, which are usually acidic and with low organic matter content, new technique has been employed in research studies [14,15], and was found to be an effective way to study redistribution among fractions caused by changes in soil properties. With this technique, it is possible to study metal solubilization by EDTA, not only by how much it dissolves metals from the solid phase, but also how it affects the redistribution between soil fractions.

The aims of this study were to investigate the extraction efficiency of heavy metals with EDTA in the contaminated tailing soils

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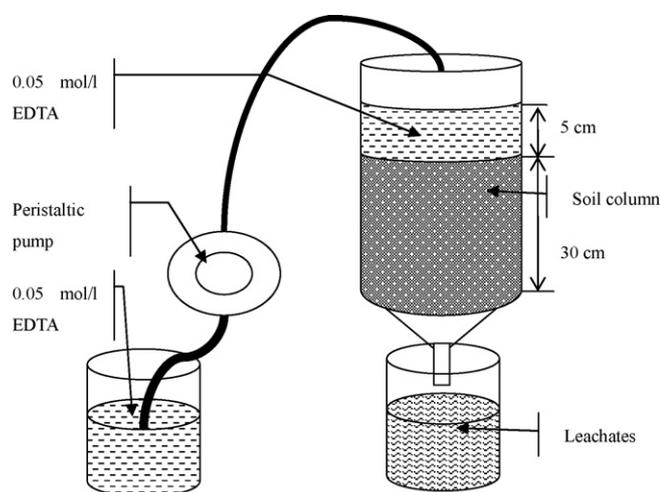


Fig. 1. Schematic illustration of experiment apparatus.

located in Southern Hunan, China and to study the HMs redistribution in soils of different depth, resulted from washing with the chelating extractant-EDTA. The sequential extraction procedure was also used to determine the redistribution between fractions.

2. Materials and methods

2.1. Soil sampling, description and analytical measurements

Surface soil samples (0–20 cm) were collected from two tailing areas in Hunan Province: Yongzhou Pb/Zn Mine (Soil Y) and Chejiang Cu Mine (Soil C), where soils were contaminated with Pb, Zn, Cu and Cd in varying degrees due to mining activities. The soil samples were air-dried, sieved to >2 mm, homogenized, and stored for laboratory analysis.

Soil pH was determined using a pH-meter (pHS-3C). Organic matter was measured with standard methods [16], while soil particle-size analysis was carried out using a JL-1155 laser particle analyzer. Before determining the total concentrations of Pb, Zn, Cu and Cd in the soil using a flame atomic absorption spectrometer (FAAS), the soil samples were digested with $\text{HNO}_3\text{--HF--HClO}_3\text{--H}_2\text{O}_2$. All the extractions and digestions were performed in triplicate.

2.2. Column study

The PVC column used in the present study was of inner diameter (ID) 5.5 cm and length 30 cm. A filter paper and a nylon mesh were inserted in the bottom of PVC columns, which were packed in small

incremental steps with the soil to obtain a uniform bulk density as the original soil samples (Fig. 1). The soil columns were then wetted with deionized water from the bottom. These were kept for one week to reach steady-state conditions before the leaching experiment.

Leaching experiments were performed with 0.05 mol/l EDTA at room temperature (22–24 °C). EDTA was added to the column by means of a four-way Watson–Marlow peristaltic pump, controlling the liquid height 5 cm higher of the soil surface (Fig. 1). When the extract liquid volumes collected from the bottom of the columns were two times more than the soil volumes, the process of extraction was ended, which maintained for about 24 h. Thereafter, the extraction efficiencies for Pb, Zn, Cu and Cd were evaluated (with 5 cm as unit). Leachates were transferred to polyethylene bottles, and stored at <4 °C before analysis.

2.3. Analysis

Before the extraction procedure, the distribution of four fractions: acid-extractable, reducible, oxidizable and residual fractions, for Pb, Zn, Cu and Cd in soils were determined with the optimized BCR procedure [17]. Then the sequential extraction procedure using the optimized BCR sequential extraction procedure was carried out to ascertain redistributions of Pb, Zn, Cu and Cd after extraction. The details of BCR procedure were listed in Table 1.

All reagents used in this study are analytical grade.

3. Results and discussion

3.1. Soil properties

The chemical and physical properties of the soils are set out in Table 2, which indicates that metal pollution in these two tailing areas is very serious. Total concentrations of Pb, Zn, Cu and Cd in these two areas exceeded the maximum level of National Standard enormously (Pb \leq 300 mg/kg, Zn \leq 250 mg/kg, Cu \leq 100 mg/kg, Cd \leq 0.6 mg/kg). The relatively low pH and low organic matter content of the test soils determine that phytoremediation is useless in the present study. According to the textural analysis, both of the two soil samples can be classified as silt sand.

3.2. Extraction efficiencies

The extraction efficiencies for different HMs with the depth of the soil column are presented in Fig. 2. As seen in Fig. 2, the high extractable efficiency of HMs in soil samples by EDTA suggested that EDTA have the potential to remediate tailing soils in our present study. This is likely to be related to the strong complexing capacity of EDTA with respect to HMs and the formation of

Table 1
Optimized BCR sequential extraction procedure

| Step | Operational definition ^a | Chemical reagents and conditions |
|------|-------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1 | Acid-extractable | 1.0 g soil added 40 ml of 0.11 M HOAc, shake for 16 h at 22 ± 5 °C; extractant was separated from the solid residue by centrifugation at 3000 rpm for 20 min |
| 2 | Reducible | To step 1 residue added 40 ml of 0.5 M NH ₄ OH·Cl from a 1-l solution containing 25 ml of 2 M HNO ₃ (pH 1.5), shake for 16 h at 22 ± 5 °C; centrifuged at 3000 rpm for 20 min |
| 3 | Oxidizable | To step 2 residue added 10 ml of H ₂ O ₂ (pH 2–3), 1 h at room temperature; heated to 85 ± 2 °C for 1 h; added a further 10 ml of H ₂ O ₂ and heated to 85 ± 2 °C for 1 h; added 50 ml of 1 M NH ₄ OAc (pH 2) and shake for 16 h at 22 ± 5 °C; centrifuged at 3000 rpm for 20 min |
| 4 | Residual | Added 40 ml of 0.5 M NH ₄ OH·Cl in residue obtained from step 1 from a 1-l solution containing 25 ml of 2 M HNO ₃ (pH 1.5), shaken for 16 h at 22 ± 5 °C; centrifuged at 3000 rpm for 20 min |

^a Acid-extractable: AEX; reducible: RED; oxidizable: OX; residual: RES.

Table 2
Physicochemical characteristics of the soils

| Tailing soil | pH | Organic matter (%) | Sand (%) | Silt (%) | Clay (%) | Total Pb (mg/kg) | Total Zn (mg/kg) | Total Cu (mg/kg) | Total Cd (mg/kg) | Total Fe (mg/kg) | Total Mn (mg/kg) |
|--------------|-----|--------------------|----------|----------|----------|------------------|------------------|------------------|------------------|------------------|------------------|
| Soil Y | 4.8 | 6.37 | 24.06 | 69.35 | 6.59 | 6871.8 | 2981.7 | 546.5 | 110.3 | 361.2 | 78.5 |
| Soil C | 6.3 | 5.91 | 31.85 | 62.02 | 6.13 | 3767.3 | 2506.1 | 1023.5 | 94.7 | 280.4 | 56.7 |

the stable 1:1 metal–EDTA complexes, the formation constants of which could reach to 19.0, 17.5, 19.7 and 17.4 for Pb–EDTA, Zn–EDTA, Cu–EDTA and Cd–EDTA, respectively [17]. The average extraction efficiencies for Pb, Zn, Cu and Cd in Soil C were 42.1%, 42.9%, 41.1% and 61.3%, respectively; while in Soil Y, they were 27.3%, 45.4%, 40.3% and 46.6%, respectively. Percentage extractabilities of metal followed the sequence of Cd > Zn > Cu > Pb. The extraction efficiencies by EDTA for Pb, Cu and Cd in Soil C were higher than that in Soil Y. While in the case of Zn, the extraction efficiencies by EDTA in Soil Y were higher than that in Soil C. This may be correlative to the higher pH (6.3) of Soil C. Previous studies showed that pH influenced the extraction of HMs by EDTA only in the acidic range (pH < 5) [18,19]. The removal of greater amounts of toxic metals has most often been observed at lower pH levels [20]. However, Vandevivere et al. reported that a slightly alkaline pH was optimal for the removal of Pb, Zn and Cd with [S, S]-EDDS [21]. The formation of complexes in soils is controlled by the kinetic of all complexation reactions, adsorption in soil solid phases, mineral dissolution and the possible degradation of the chelating agent or its metal complexes [22]. These interactions are difficult to predict and depend on the contaminants and soil conditions.

From Fig. 2, quite remarkable differences were presented between the soil column depth and the extraction efficiencies by EDTA for Pb, Cu, Cd in both tailing soil samples ($p < 0.01$), which proved that the HMs was removed through soil column from up to bottom.

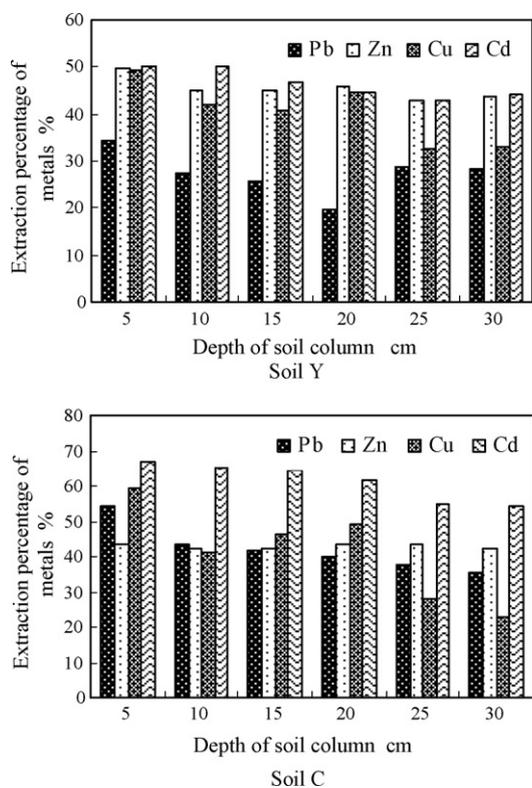


Fig. 2. Extractability of Pb, Zn, Cu and Cd in soil columns by EDTA (0.05 mol/l of EDTA concentration).

Soil types may also contribute to the variation of extraction efficiencies of HMs by EDTA. Li and Shuman found that in the natural coastal-plain soils, Zn concentration was greater in the exchangeable (EXC) and organic matter (OM) fractions, and less in the RES fraction than those in the Piedmont soils, indicating the importance of soil texture in the retention of Zn in soils [23]. Usually, the higher the proportion of the clay and silt content in soil, the lower extraction efficiency of EDTA for metal extraction, because extracted HMs could easily be adsorbed by iron-manganese oxides located on the surface of those soil particles [24]. Li and Shuman also found the concentration of Zn in the Fe and Mn oxide fraction, that was not affected by EDTA, probably due to high association of Zn with the oxides [23]. Our present study also found the same results. The clay and silt content of soil Y were higher than that in Soil C, thus leading to the lower extraction efficiency of EDTA for metal extraction. The amounts of HMs adsorbed on soil particles could be influenced by many other factors, such as the amounts of soil, water losses and their contents in the soils, and were closely related to the contents of soil particles 1–0.02 mm in size [25].

3.3. Fractions of heavy metals before and after EDTA extraction

The extraction efficiency of HMs by EDTA has been reported to be strongly dependent on the source of heavy metal contamination in the soil and on metal distribution among the soil fractions [26]. As seen in Table 3, the RES fraction of Pb, Zn, Cu and Cd in Soil Y were higher than those in Soil C, which could be steadily combined with soil particles and could not be easily extracted by EDTA under formal conditions. Synchronously, the AEX fraction, which could be easily extracted by EDTA, is the major fraction form in Soil C. Therefore, it is easier for metals in Soil C to be extracted by EDTA than those in Soil Y. This conclusion has been supported by many previous researches [27–29]. The release of metals from contaminated soils depends not only on the extraction conditions (e.g. pH, reagent concentration), but also on the modes of metal retention within the soil. Consequently, metal reactivity and behavior towards the extracting solution also depend on the nature of the metal fixation on the soil particles, which can be operationally measured by application of sequential extraction procedures. Weakly sorbed fractions (i.e., exchangeable and carbonate) could be readily extracted, but an effective extraction of strongly sorbed metals in oxide and residual fractions was not always guaranteed within different soil types and contamination sources.

In Soil Y, Pb was mostly accumulated in the RES fraction (57.4% of the total amount) and in the RED fraction (34.8%) before extraction, indicating that the applied Pb may be irreversibly fixed by clay or formed a stable crystal structure with the soil particles. While in Soil C, Pb was mostly accumulated in the RES fraction, RED fraction and AEX fraction, which occupied 37.0%, 28.4% and 26.5% of the total amount, respectively. After extraction, the redistribution of Pb changed dramatically in both soils, an obvious decrease was shown in the concentration of each soil fraction (Table 3). The reducible Pb amounts decreased more in soil Y from 2397.5 to 1340.2 mg/kg than in Soil C (from 1058.4 to 1006.0 mg/kg). There are two main reasons. On one hand, the total amount of Pb was higher in Soil Y; on the other hand, the solubility of Fe and Mn when utilizing EDTA as extractant may cause the decreases in the reducible frac-

Table 3

Concentration of four fractions in different depths after extraction compared to the initial concentration before extraction (mg/kg)

| Fractions | Soil sample | Before extraction | After extraction | | | | | |
|-----------|-------------|-------------------|------------------|---------|----------|----------|----------|----------|
| | | | 0–5 mm | 5–10 mm | 10–15 mm | 15–20 mm | 20–25 mm | 25–30 mm |
| AEX (Pb) | Soil Y | 335.1 | 94.3 | 220.2 | 256.5 | 294.9 | 324.8 | 349.6 |
| | Soil C | 987.4 | 32.1 | 130.9 | 224.3 | 278.2 | 359.0 | 430.2 |
| RED (Pb) | Soil Y | 2397.5 | 1138.3 | 1286.5 | 1342.5 | 1410.8 | 1462.5 | 1400.3 |
| | Soil C | 1058.4 | 811.0 | 978.0 | 1054.8 | 1060.8 | 1089.0 | 1042.3 |
| OX (Pb) | Soil Y | 197.0 | 135.6 | 141.0 | 151.1 | 138.9 | 136.8 | 137.7 |
| | Soil C | 303.0 | 62.2 | 103.1 | 71.9 | 72.8 | 69.9 | 83.9 |
| RES (Pb) | Soil Y | 3954.6 | 3164.9 | 3359.0 | 3368.7 | 3669.2 | 2993.0 | 3043.0 |
| | Soil C | 1381.5 | 791.1 | 889.4 | 831.3 | 832.2 | 806.8 | 846.8 |
| AEX (Zn) | Soil Y | 488.0 | 178.4 | 257.9 | 278.5 | 290.2 | 312.2 | 301.2 |
| | Soil C | 586.4 | 17.0 | 51.1 | 58.7 | 56.1 | 54.2 | 67.9 |
| RED (Zn) | Soil Y | 240.9 | 198.9 | 223.6 | 229.4 | 228.0 | 242.3 | 233.8 |
| | Soil C | 189.6 | 167.7 | 175.0 | 172.0 | 160.1 | 170.9 | 173.2 |
| OX (Zn) | Soil Y | 1034.1 | 322.4 | 340.7 | 335.6 | 328.9 | 341.2 | 341.9 |
| | Soil C | 670.4 | 475.7 | 472.2 | 468.5 | 463.8 | 465.5 | 465.3 |
| RES (Zn) | Soil Y | 1185.6 | 784.2 | 795.2 | 777.2 | 753.2 | 787.2 | 781.8 |
| | Soil C | 1110.8 | 781.0 | 775.6 | 770.9 | 763.3 | 762.0 | 774.1 |
| AEX (Cu) | Soil Y | 169.0 | 24.9 | 25.4 | 27.4 | 29.4 | 29.9 | 31.1 |
| | Soil C | 473.5 | 79.3 | 143.9 | 135.1 | 121.9 | 232.9 | 274.4 |
| RED (Cu) | Soil Y | 78.3 | 31.4 | 36.6 | 35.9 | 37.9 | 42.0 | 42.2 |
| | Soil C | 280.4 | 133.0 | 239.8 | 219.5 | 199.3 | 275.0 | 308.3 |
| OX (Cu) | Soil Y | 190.1 | 131.1 | 157.5 | 160.1 | 130.7 | 195.6 | 198.9 |
| | Soil C | 195.1 | 135.4 | 147.9 | 135.8 | 140.6 | 158.4 | 143.9 |
| RES (Cu) | Soil Y | 117.3 | 93.9 | 101.5 | 106.3 | 109.6 | 105.7 | 100.1 |
| | Soil C | 84.8 | 70.2 | 74.3 | 63.4 | 65.0 | 80.4 | 73.3 |
| AEX (Cd) | Soil Y | 11.0 | – | 0.3 | 1.9 | 5.2 | 5.9 | 3.9 |
| | Soil C | 38.4 | 7.1 | 10.7 | 11.4 | 12.5 | 15.4 | 16.1 |
| RED (Cd) | Soil Y | 7.9 | 5.4 | 5.7 | 5.3 | 5.6 | 6.0 | 6.2 |
| | Soil C | 7.2 | 4.2 | 4.2 | 4.5 | 4.9 | 5.0 | 4.9 |
| OX (Cd) | Soil Y | 39.9 | 13.8 | 14.7 | 14.7 | 14.3 | 14.7 | 14.6 |
| | Soil C | 34.1 | 10.5 | 9.4 | 9.2 | 9.5 | 11.2 | 11.1 |
| RES (Cd) | Soil Y | 47.1 | 36.6 | 35.1 | 34.3 | 33.6 | 34.1 | 34.4 |
| | Soil C | 13.1 | 8.8 | 8.0 | 7.9 | 8.5 | 10.1 | 10.2 |

–: not detected.

tion [30]. Barona and Romero extracted Pb contaminated soil with EDTA and observed that the amount of Pb that was removed correlated with the amount of Pb associated with the Fe and Mn-oxide and organic matter soil fractions [31]. Wasay et al. studied speciation of metals in polluted soils and found that most of the HMs was found to be bound to Fe–Mn oxides and the organic fraction (30–40%) except for Cd and Zn, which were mainly present on the exchangeable fraction (63–87%) [32]. Pb extraction recovery for Soil C (42.1%) was higher than for Soil Y (27.3%) because of the lower proportion of AEX fraction of Soil Y, which was considered to be easily extracted by EDTA. The results of the present study also indicate that EDTA releases certain amounts of silicate-bound Pb, as residual Pb amounts decreased in both soils [26].

Zinc in the untreated soil was mostly concentrated in the RES fraction, the OX fraction and the AEX fraction (Table 3). Not only the total amounts of Zn, but also the metal distribution before extraction remained similar in both soils. The concentration of zinc in each of the three fraction presented similar decreasing tendency and had the similar ultimate extraction efficiency in both soils, which were 45.4% (in Soil Y) and 42.9% (in Soil C), respectively. Another noteworthy thing was that the concentration of Zn in the RED fraction after extraction remained similar to the results before extraction with EDTA. Li and Shuman also found that the concentration of Zn in the Fe and Mn oxide fractions was not affected by EDTA probably

because of the high association of Zn with the oxides [23]. Adriano demonstrated some trace element cations, like Zn^{2+} , can enter into the crystal lattice of layer silicates through isomorphous substitution or solid-state diffusion into the crystal structure. This process may be irreversible so that some applied metals may be irreversibly fixed by clay [33].

In untreated Soil Y, Cu was mostly concentrated in the AEX fraction (30.5% of the total amount) and OX fraction (34.3%). The OX fraction of Cu accounted for higher percentage (34.3%) of the total than other fractions before extraction and the concentration of which increased with the increasing soil depth after extraction, reflecting the strong-binding of Cu with organic matter in Soil Y. With respect to Soil C, the amount of Cu in the AEX fraction was the largest before extraction with EDTA, which occupied 45.8% of the total amount. After extraction, the measured percentage of Cu in the AEX fraction decreased obviously in shallow soil column. While with the increasing soil depth, the AEX fraction of Cu may be reabsorbed by soil particles, leading to a relatively low extractable efficiency in Soil C (Fig. 1).

The amount of Cd in the OX fraction was the largest in both Soil Y and Soil C before extraction with EDTA, which occupied 37.7% and 36.7%, respectively. Basta et al. [34] concluded that Cd complexation by organic matter was important for Cd retention. In the present study, the amount of Cd in the OX fraction was the largest, attesting

the affinity of this fraction for Cd. However, obvious decreases were found in the concentration of the OX fraction of Cd in both Soil Y and Soil C after EDTA extraction. This phenomenon was mainly caused by the combination of Cd with the sulfide or organic matter in soils, which could be readily extracted by EDTA. Also, EDTA was an effective extractant for the AEX fraction of Cd.

4. Conclusion

EDTA was an effective extracting agent because of its strong chelating ability for different HMs. Percentage extractabilities of metal followed the sequence of Cd > Zn > Cu > Pb. After extraction with EDTA, percentage extractabilities of Pb, Cu and Cd decreased with the increasing depth of the soil column, especially Cu. While in the case of Zn, there was no significant difference between soil column depth and extraction efficiency by EDTA, suggesting that the extracted Zn may not be reabsorbed by soil particles.

The four fractions of metal could be extracted by EDTA and the proportions of Pb, Zn, Cu and Cd in the four fractions varied largely after EDTA extraction. The extraction efficiency of EDTA on the AEX fraction was significant in shallow soil column, while HMs chelated by EDTA was more easily desorbed by soil particles with the increasing depth of the soil columns. In deeper soil column, the decrease of the extraction efficiencies in the RED fraction, the OX fraction and the RES fraction may be related to the decrease of the EDTA concentration.

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