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Technical Note

Assessment of EDTA heap leaching of an agricultural soil highly contaminated with heavy metals

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HIGHLIGHTS

- EDTA heap leaching exhibited efficient metal removal rates from soils.
- EDTA leaching changed soil properties and inhibited plant growth.
- Soil amendment and aging after EDTA leaching recovered the soil properties.
- EDTA leaching plus soil amendment and aging is feasible for soil remediation.

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ABSTRACT

The efficiency of heavy metal removal from soil by EDTA leaching was assessed in a column leaching experiment at the laboratory scale and field heap leaching at the pilot scale using a sandy loam sierozem agricultural soil contaminated with Cd, Cu, Pb, and Zn. Soil amendment and aging were conducted to recover leaching soils. The percentages of Cd, Cu, Pb, and Zn removed by column leaching were 90%, 88%, 90%, and 67%, respectively, when 3.9 bed volumes of 50 mM EDTA were used. At the pilot scale, on-site metal removal efficiencies using the selected leaching procedure were 80%, 69%, 73% and 62% for Cd, Cu, Pb and Zn, respectively. EDTA leaching decreased soil CEC, total P, total K and available K concentrations but increased organic matter and total Kjeldahl N concentrations. The subsequent amendment and soil aging further reduced the DTPA-extractable heavy metals in the leached soils. Growth of the first crop of pak choi in the leached soil was inhibited but the second crop grew well after the soil was aged for one year and the concentrations of Cd and Pb in the edible parts were below the Chinese statutory limits. The results demonstrate the potential feasibility of the field leaching technique using EDTA combined with subsequent amendment and soil aging for the remediation of heavy metal-contaminated agricultural soils.

1. Introduction

Soil washing is one of the few treatments available for the permanent removal of metals from soils, especially highly contaminated soils (Dermont et al., 2008; Makino et al., 2008). A number of chelating agents (mostly aminopolycarboxylic acids) have been tested for soil washing. The EDTA is the most commonly used chelant because it has a strong chelating ability for cationic heavy metals, EDTA leaching can be used to treat a broad range of soil types, and the EDTA is recoverable (Dermont et al., 2008). A number of previous studies have investigated the optimum operational parameters of soil washing with EDTA, including dosage, washing cycle, post-wash rinses (Andrade et al., 2007), regeneration of EDTA leachate (Di Palma et al., 2005; Lo and Zhang, 2005; Finzgar and Lestan, 2008; Cesaro and Esposito, 2009), and EDTA degradation (Finzgar and Lestan, 2008; Pociecha and Lestan, 2012; Voglar and Lestan, 2012a).

Most studies of EDTA washing have focused on the effectiveness of toxic metal removal from soils at industrial sites and there are few reports in the literature on studies dealing with the ecological toxicity of agricultural soils after remediation (Jelusic et al., 2014).

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EDTA is a biologically stable chelant and it is very difficult for unacclimated microbial cultures to degrade (Hong et al., 1999). After EDTA leaching some metal-EDTA complexes are retained in the soil by the formation of bonds with soil iron oxides and especially goethite (Nowack and Sigg, 1996). Some of these bound complexes may be released and washed from the soil with irrigation water (Jelusic et al., 2013). Moreover, soil dissolution and mineral nutrient leaching may also occur during the removal of potentially toxic metals (Tsang et al., 2007b). It was recently reported that batch extraction with EDTA substantially removed Cd, Pb, and Zn from contaminated soil and then reduced the concentrations of these metals in plants. However, the yields of plants grown on remediated soil were depressed comparing to control soil, possibly due to the toxic effects of metal-EDTA complexes, lack of metal micronutrients and changes in soil physical properties during the washing process (Jelusic et al., 2013, 2014). Batch extraction, especially intensive mixing of the soil slurry and soil compression after dewatering, would be expected to result in significant deterioration of soil physical properties (Voglar and Lestan, 2012a; Zupanc et al., 2014). Field leaching (or column leaching) may have numerous advantages over batch washing such as equally good or even better metal removal effectiveness (Hauser et al., 2005). Soil structure remains intact during field leaching but not during batch extraction. Field leaching may also be more practical and economical when applied on a large scale (Heil et al., 1999; Finzgar and Lestan, 2006).

It is still not clear whether or not EDTA field leaching is a feasible technique for the remediation of highly contaminated agricultural soils, how soil properties and nutrients may change and if soil structure and function can be recovered through amendment and soil aging. The objective of the study was therefore to test pilot scale EDTA field leaching for the simultaneous removal of the heavy metals Cd, Cu, Pb, and Zn from a contaminated agricultural soil based on a comparison with laboratory column studies. Soil properties, especially soil nutrients and metal phytoavailability, were determined to evaluate the influence of EDTA leaching on soil quality. Furthermore, the effects of amendment with phosphate and organic matter and of soil aging on soil recovery were assessed by growing vegetables on the remediated soil to evaluate the environmental feasibility of EDTA leaching.

2. Materials and methods

2.1. Soil

The field site investigated is located in the watershed of Dongdagou, Baiyin city, Gansu Province, northwest China (104°16′E, 36°29′N). The soil is highly contaminated with Cd, Cu, Pb, and Zn after decades of irrigation with sewage from mining and smelting factories (Nan and Zhao, 2000). The soil is classified as a sierozem with a sandy loam texture. Samples were collected from the top 20 cm of the soil profile. Selected soil physico-chemical properties were: sand 53%, silt 30% and clay 17%, pH 7.34, organic matter 2.64%, and CEC 9.48 cmol (+) kg^{-1}. The total Cd, Cu, Pb, Zn concentrations in the soil used for column leaching were 24.2, 444, 552, 854 mg kg^{-1}, and for pilot scale field leaching were 17.8, 359, 391, and 599 mg kg^{-1}, respectively.

2.2. Column leaching procedure

Plexiglas (acrylic) columns 5.5 cm in internal diameter and 30 cm in height were used. A sheet of filter paper and a 2-cm-deep layer of silica sand were placed in the bottom of each column. Air dried soil (500 g) sieved to <2 mm was placed in each column with a bulk density of approximately 1.3 g cm^{-3} and bed volume (BV) of 385 cm^3. The soil columns were placed on plastic saucers and wetted with deionized water from the bottom. They were kept at room temperature for 1 wk to reach steady state conditions before the leaching experiment.

Two concentrations of Na_2-EDTA, 5 and 50 mM, were used in column leaching and each was set up in triplicate. Leaching solution was added manually once every 6–12 h and leachates were allowed to flow out of the bottom under gravity. Collection of leachates was carried out every 12 h. The volumes and heavy metal concentrations of the leachates were determined. Leaching was terminated when the total leachate volume reached 1500 mL (i.e. 3.9 BV). The duration of the whole leaching procedure was 12 d.

2.3. Field leaching procedure

Pilot scale leaching was conducted under field conditions at Dongdagou, Baiyin city. The ground at the leaching site had a slope of 0.15 and was lined with double-layer plastic impermeable material. Contaminated surface soil was excavated and heaped to form piles on the leaching site. Each pile contained approximately 65 kg soil and was formed into a heap with a rectangular base 1 × 0.5 m in size and with an average height of 10 cm (bed volume of 50 dm^3). Leaching solution was sprinkled manually on the dished pile top surface to maintain a water layer of ~2 cm throughout the leaching procedure. Leachate was led to a channel and finally collected in a sump. The leaching procedure is shown in Table 1. There were four treatments and each was composed of several phases with different concentrations or volumes of EDTA solution and rinsing water. Each treatment was set up in duplicate. The duration of the whole leaching procedure was 20–25 d.

2.4. Soil sampling and cropping after field leaching

After pilot scale field leaching the soil in each treatment was collected to determine the residue heavy metals. In addition, leached soil from treatment 4 was collected for soil properties analysis and cropping. The cropping was conducted in pot experiments in a greenhouse. There were four treatments: (1) initial soil without leaching, (2) leached soil, (3) leached soil amended with 2% calcium magnesium phosphate (Leached soil + CaMgP), and (4) leached soil amended with 2% calcium magnesium phosphate and 0.5% organic fertilizer (Leached soil + CaMgP + Organ. Fert.). Each treatment was set up in four replicate pots and each pot contained 0.55 kg soil. Each pot was supplied with 0.05 g N, 0.05 g P_2O_5 and 0.05 g K_2O (in the form of urea, calcium superphosphate and potassium sulfate, respectively) as basic nutrients. Soils were incubated at room temperature and about 70% of soil water-holding capacity for 2 wks. Then soil samples were taken in each pot for phytoavailability assessment. The first crop rotation was conducted from January to February, 2013. Pak choi (*Brassica rapa* L. ssp. *chinensis*) was grown in the soils with four seedlings in each pot. The first and second top-dressings were conducted 20 and 40 d after sowing and on each occasion the pots were supplied with 0.05 g N, 0.05 g P_2O_5 and 0.05 g K_2O. After 50 d the edible parts of the pak choi were harvested to determine their biomass and heavy metal concentrations. After harvest soil was left to continue aging in the greenhouse for around one year until the second crop. The second crop rotation was conducted from January to February, 2014. Soil in each pot was again supplied with 0.2 g N, 0.2 g P_2O_5 and 0.2 g K_2O (in the form of urea, calcium superphosphate and potassium sulfate, respectively) as basic nutrients. Pak choi was grown in the soils with four seedlings in each pot. After 55 d the edible parts were harvested to determine biomass and heavy metal concentrations and the soil samples were taken for phytoavailability assessment.

Table 1
Scheme for pilot-scale field heap leaching.

Treatment	1st phase		2nd phase		3rd phase		4th phase	
	Leaching solution	BV	Leaching solution	BV	Leaching solution	BV	Leaching solution	BV
Treatment 1	5 mM EDTA	2.6	50 mM EDTA	1.3	Water	2.6		
Treatment 2	50 mM EDTA	2.6	50 mM EDTA	1.3	Water	2.6		
Treatment 3	5 mM EDTA	2.6	50 mM EDTA	1.3	50 mM EDTA	2.6	Water	2.6
Treatment 4	50 mM EDTA	2.6	50 mM EDTA	1.3	50 mM EDTA	2.6	Water	2.6

2.5. Soil and plant analytical

The analysis of soil properties and plant samples followed the methods of Bao (1996). Briefly, soil pH was determined using a 1:2.5 soil to water ratio. Soil CEC was determined by the NH_4OAc–NaOAc methods. Soil organic matter was determined by heating the dried samples at 350 °C for 5 h. Soil dissolved organic carbon (DOC) was extracted with 0.5 M K_2SO_4 and determined with an SSM-5000A solid sample module with a TOC-Vcs/cp analyzer (Shimadzu, Japan). Soil total Kjeldahl N was determined by Kjeldahl digestion and distillation. Soil available N was measured by the alkaline-hydrolysis diffusion method. Total P (P_2O_5) was determined by $H_2SO_4/HClO_4$ digestion and available P was extracted with 0.5 M $NaHCO_3$ by the Olsen method. P was analyzed by the molybdenum blue method. Available K (K_2O) was determined by flame photometer after extraction with 1 M NH_4OAc. Soil total K and total metal concentrations were determined after digestion with HCl/HNO_3 (1:1 v/v). Phytoavailability of metals in soil was assessed by DTPA extraction following the standard method released by The Ministry of Agriculture of the People's Republic of China (2005). The DTPA extraction solution was prepared by mixing 0.005 M DTPA, 0.01 M $CaCl_2$, and 0.1 M triethanolamine and the solution adjusted to pH 7.3. Plant samples were dried and digested with HNO_3/H_2O_2 (5:2 v/v). Heavy metal analysis of leachates and digests was performed using a flame atomic absorption spectrophotometer (Varian SpectrAA 220FS).

2.6. Statistical analysis

Statistical analysis was performed using the SPSS version 16.0 for Windows software package (SPSS, Chicago, IL). Data are presented as mean values ± standard deviation (SD) or standard error (SE) of 4 or 3 replicates. Means were compared by t test or by one-way analysis of variance followed by Duncan's multiple range test at the 5% level.

3. Results and discussion

3.1. Column leaching of metals

Leaching curves show the dynamics of Cd, Cu, Pb and Zn concentrations in leachate against the cumulative volumes in the column experiment (Fig. 1). When the soil was leached with 5 mM EDTA the Cd peak (22.7 mg L^{-1}) in the leachate appeared at the first collection, i.e. at a cumulative volume of about 70 mL. The Cu and Zn peaks appeared later than Cd at a cumulative volume of about 200 mL. Lead was the least mobile of the four metals. Its concentrations in the leachates continued to increase after the peaks of Cu and Zn. The Pb peak had occurred and reached maximum value at a cumulative volume of about 350 mL. This is consistent with our previous BCR fraction results in which 76% of the total Cd in the soil was in acid soluble forms with values of 23% and 44%, respectively, for Cu and Zn but only 6% for Pb (Yang et al., 2013). The different properties of the metals and their different mechanisms of release result in the differences in their mobility during soil washing (Sun et al., 2001; Zhang et al., 2010a). Nevertheless, when 50 mM EDTA was used as the leaching solution all four metals showed similar elution curves that reached their peak concentrations at the first collection at a cumulative volume of about 60 mL and then their concentrations decreased dramatically during the first 250 mL. This indicates that elevated concentrations of EDTA increase the dissolution of Cu, Zn and Pb.

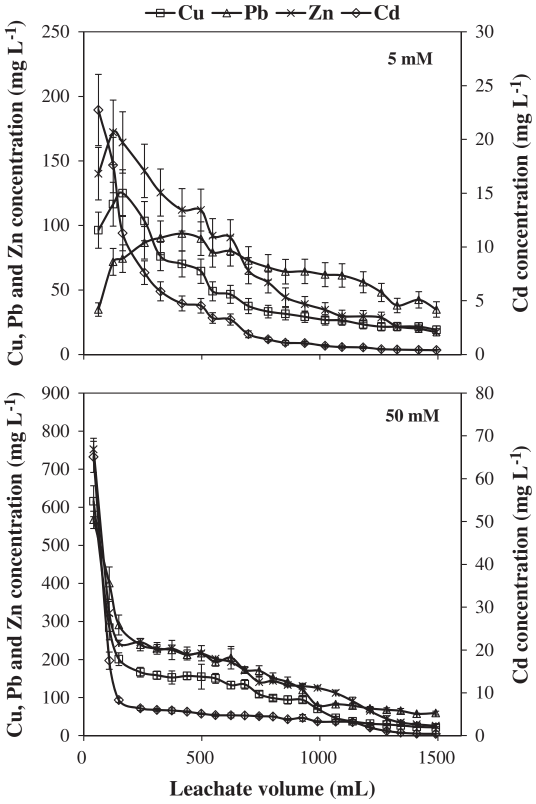

Fig. 1. Leaching curves for Cd, Cu, Pb and Zn in the column experiment with 5 and 50 mM EDTA. Data are mean values ± SE ($n = 3$).

When 5 mM EDTA (3.9 BV) was used in the present column leaching experiment the percentages of Cd, Cu, Pb and Zn removed from the soil were 61%, 36%, 35% and 27%, respectively. These values are higher than that in our previous batch extraction experiment using the same soils, 5 mM EDTA, a liquid/solid ratio of 2.5 and 3 successive washing cycles, each for 1 h (Yang et al., 2013). This implies that column leaching exhibits higher metal removal efficiency than batch extraction. Similarly, Hauser et al. (2005) found that column leaching with chelating agent was equally or better suited for removal of Zn and Pb from contaminated soils. The concentrations of the four metals in leachates in 50 mM EDTA were much higher than in 5 mM EDTA. The percentages of Cd, Cu, Pb and Zn removed from soil increased to 90%, 88%, 94% and 67% when 50 mM EDTA was used. This indicates that increasing the EDTA dosage significantly increased metal removal in the present column leaching experiment.

Total metal removal in the column leaching experiment was calculated. The whole procedure was divided into three stages based on the volume of leachate and each stage consumed approximately 1.3 BV of leaching solution (Table 2). The amounts of Cd, Cu, Pb and Zn removed from the soil during the first stage were 11.7, 97, 75 and 137 mg kg^{-1} using 5 mM EDTA and 15.6, 220, 257 and 268 mg kg^{-1} with 50 mM EDTA. This stage was much more efficient than later stages regardless of either EDTA dosage or metal species. This can be explained as EDTA-promoted metal dissolution is generally initiated by a fast destabilization where the free and/or complexed EDTA is bound to the metals via surface complexation with subsequent rate-limiting mobilization (Tsang et al., 2007a).

3.2. Metal removal and soil properties changes after field leaching

Based on the laboratory column experiments, combinations of EDTA with two concentrations (5 and 50 mM) were studied in the pilot-scale heap leaching. The scheme is presented in Table 1. The soil after EDTA leaching was rinsed using 2.6 BV of river water to remove free EDTA as well as EDTA mobilized metal species. Based on our preliminary study, rinsing with 1.3 BV of water decreased the metal concentrations in leachate by 95% (data not shown). Table 3 shows the residual metal concentrations in soils after field leaching. In treatment 1, when 2.6 BV of 5 mM EDTA and 1.3 BV of 50 mM EDTA were used the removal efficiencies of Cd, Cu, Pb and Zn were 53%, 41%, 35% and 42%, respectively. Nevertheless, in treatments 2, 3 and 4, when the volume of 50 mM EDTA increased to 3.9 BV or more, metal removal efficiencies increased significantly compared to treatment 1. In treatment 2, i.e. 3.9 BV of 50 mM EDTA leaching and 2.6 BV of water rinsing, the removal efficiencies of Cd, Cu, Pb and Zn were 80%, 69%, 73% and 62%, respectively. The further increasing EDTA dosage in treatments 3 and 4 did not significantly improve the metal removal efficiencies compared to treatment 2. These removal efficiencies in field leaching are comparable with but lower than those obtained in laboratory column leaching at same dosage of EDTA (Table 2). This was expected because many of the factors that influence EDTA leaching efficiency differ between laboratory and on-site conditions. For example, analytical grade EDTA and distilled water were used in the laboratory experiment but at pilot-scale industrial grade EDTA and river water were used. River water may contain larger concentrations of cations such as Ca and Mg which may compete with the EDTA for heavy metals (Hauser et al., 2005). The highest efficiencies of the on-site metal removals were obtained in treatment 4, i.e. 6.5 BV of 50 mM EDTA leaching, in which the residual Cd, Cu, Pb and Zn concentrations in leached soil were 3.3, 112, 107 and 241 mg kg^{-1}, and the removal efficiencies were 82%, 69%, 73% and 60%, respectively. The significant removal of heavy metals from the test soils in the present study suggests that heap leaching with EDTA was efficient when applied at pilot scale.

EDTA washing solution has been reported to dissolve indigenous oxides, carbonates and organic matter which appreciably alters both the soil physical structure and chemical properties (Tsang et al., 2007a). In the present study the leached soil from treatment 4 was collected for soil properties analysis. As shown in Table 4, compared to the initial soil, the soil pH did not change significantly after EDTA leaching, reflecting the buffering capacity of the soil. Soil CEC, total P, total K and available K decreased after EDTA leaching. This may be explained as the non-selective extraction by EDTA of soil cations (except for heavy metals). Soil organic matter and total Kjeldahl N concentrations did not differ from initial soil. Nevertheless, soil DOC and available N and available P increased significantly. This may be due to the partial residues of EDTA. EDTA and metal complexes can be adsorbed onto solid soil phases, especially crystalline iron oxides (Nowack and Sigg, 1996; Voglar and Lestan, 2012b). It is known that the EDTA molecule contains multiple C and N atoms which could contribute to the results when soil organic matter and N concentration are measured. Residual EDTA also explains the significant increases in DOC and available N. As for available P, partial dissolution of soil minerals by EDTA presumably releases P species (Zhang et al., 2013). Generally, EDTA leaching had some influence on soil properties, nutrients and cations as well as heavy metal removal throughout the leaching process in the present study. Nevertheless, the concentrations of nutrients in leached soil were still beyond the levels which would be sufficient for plants (Lü, 2006).

Table 3
Soil residual heavy metals before and after field leaching (mg kg^{-1}).

Treatment	Cd	Cu	Pb	Zn
Before leaching	17.8 ± 0.1a	359 ± 17a	391 ± 17a	599 ± 30a
Treatment 1	8.4 ± 0.6b	213 ± 22b	256 ± 14b	347 ± 15b
Treatment 2	3.5 ± 0.5c	113 ± 3c	104 ± 18c	230 ± 17c
Treatment 3	3.4 ± 0.4c	117 ± 7c	114 ± 14c	204 ± 24c
Treatment 4	3.3 ± 0.8c	112 ± 6c	107 ± 22c	241 ± 18c

Data are mean values ± SD ($n = 4$). The same letters in the same column indicate no significant difference ($p > 0.05$).

Table 4
Selected soil properties before and after EDTA field leaching.

Soil property	Initial soils	Leached soils (treatment 4)
pH	7.20–7.43	7.28–7.31
CEC (cmol (+) kg^{-1})	9.5 ± 0.4	8.0 ± 0.2*
Organic matter (g kg^{-1})	26 ± 1	24 ± 0.1
DOC (g kg^{-1})	0.38 ± 0.01	0.92 ± 0.00*
Total Kjeldahl N (g kg^{-1})	1.2 ± 0.1	1.4 ± 0.01
Total P (P_2O_5) (g kg^{-1})	2.7 ± 0.1	2.1 ± 0.1*
Total K (K_2O) (g kg^{-1})	20 ± 0.4	19 ± 0.1*
Available N (mg kg^{-1})	82 ± 5	136 ± 1*
Available P (mg kg^{-1})	64 ± 2	127 ± 11*
Available K (mg kg^{-1})	275 ± 5	123 ± 15*

Data are mean values ± SD ($n = 3$).
* Indicates significant difference between initial soils and leached soils ($p < 0.05$).

3.3. Ecological risk before and after EDTA leaching

Ecological risk assessment of soils before and after leaching and amendment was conducted by growing pak choi, a very popular

Table 2
Removal of heavy metals in column leaching with 5 and 50 mM EDTA (mg kg^{-1}).

Removal	Cd		Cu		Pb		Zn	
	5 mM	50 mM	5 mM	50 mM	5 mM	50 mM	5 mM	50 mM
1st stage	11.7 ± 0.1	15.6 ± 1.6	97 ± 6	220 ± 29	75 ± 4	257 ± 35	137 ± 5	268 ± 22
2nd stage	2.4 ± 0.5	4.7 ± 0.3	37 ± 5	146 ± 25	68 ± 6	184 ± 28	68 ± 10	210 ± 20
3rd stage	0.74 ± 0.01	1.4 ± 0.5	27 ± 2	27 ± 5	50 ± 4	58 ± 6	28 ± 1	77 ± 10
Total removal	15 ± 1	22 ± 2	161 ± 12	392 ± 56	193 ± 15	499 ± 68	233 ± 8	573 ± 47
Removal (%)	61 ± 2	90 ± 9	36 ± 3	88 ± 13	35 ± 3	90 ± 12	27 ± 1	67 ± 6

Data are mean values ± SD ($n = 3$).

Table 5
Soil DTPA-extractable heavy metals before and after EDTA leaching (mg kg^{-1}).

Soil and treatment	Cd	Cu	Pb	Zn
First rotation				
Initial soils	7.8 ± 0.1a	98 ± 1a	90 ± 1a	91 ± 1a
Leached soils	2.3 ± 0.0b	54 ± 1b	69 ± 1b	52 ± 1b
Leached soils + CaMgP	2.0 ± 0.0c	43 ± 1c	53 ± 2c	47 ± 2c
Leached soils + CaMgP + Organ. Fert.	2.0 ± 0.0c	41 ± 1c	53 ± 1c	48 ± 1c
Second rotation				
Initial soils	7.7 ± 0.1a	94 ± 1a	90 ± 1a	90 ± 7a
Leached soils	0.25 ± 0.00b	8.3 ± 0.1b	4.6 ± 0.1b	5.2 ± 0.4b
Leached soils + CaMgP	0.17 ± 0.00c	8.0 ± 0.1b	4.2 ± 0.1b	3.8 ± 0.4b
Leached soils + CaMgP + Organ. Fert.	0.17 ± 0.01c	7.6 ± 0.2b	4.0 ± 0.1b	3.7 ± 0.4b

Data are mean values ± SD ($n = 4$). The same letters in the same column of each rotation indicate no significant difference ($p > 0.05$).

Table 6
Biomass and heavy metal concentrations of the edible parts of pak choi growing in soils before and after EDTA leaching.

Soil and treatment	Fresh weight	Dry weight	Cd	Cu	Zn	Pb
	g pot^{-1}		mg kg^{-1} FW			
First rotation						
Initial soils	26 ± 7a	2.8 ± 0.8a	2.95 ± 0.44a	3.05 ± 0.16a	10.2 ± 0.2a	0.22 ± 0.06a
Leached soils	2.6 ± 0.3c	0.37 ± 0.03c	0.54 ± 0.08b	2.31 ± 0.45b	11.7 ± 1.7a	0.12 ± 0.03b
Leached soils + CaMgP	5.4 ± 1.1c	0.71 ± 0.13c	0.39 ± 0.08b	1.39 ± 0.33c	9.32 ± 2.25b	0.09 ± 0.03b
Leached soils + CaMgP + Organ. Fert.	14 ± 1b	1.7 ± 0.2b	0.25 ± 0.06b	1.07 ± 0.06c	7.06 ± 0.78b	0.09 ± 0.01b
Second rotation						
Initial soils	17 ± 1a	1.2 ± 0.1a	2.07 ± 0.41a	2.31 ± 0.14a	10.6 ± 2.4a	1.76 ± 0.39a
Leached soils	15 ± 3a	1.1 ± 0.2a	0.22 ± 0.02b	0.63 ± 0.09bc	4.88 ± 0.48b	0.20 ± 0.03b
Leached soils + CaMgP	16 ± 2a	1.2 ± 0.1a	0.15 ± 0.01b	0.68 ± 0.03b	4.60 ± 0.25b	0.25 ± 0.02b
Leached soils + CaMgP + Organ. Fert.	15 ± 2a	1.1 ± 0.1a	0.15 ± 0.06b	0.49 ± 0.10c	3.83 ± 0.69b	0.27 ± 0.07b

Data are mean values ± SD ($n = 4$). The same letters in the same column of each rotation indicate no significant difference ($p > 0.05$).

leaf vegetable in China which is usually employed to assess the ecological risk of heavy metals in soils (Zhou et al., 2005). DTPA extraction was used to assess the phytoavailability of soil residual heavy metals. A significant reduction in DTPA-extractable metal concentrations was observed after field leaching (treatment 4) compared to the initial unleached soils (Table 5). This reveals that EDTA leaching did reduce metal mobility to different extents and it was expected that the most labile metals in soils would be removed by EDTA leaching. A similar reduction in metal phytoavailability was obtained through an EDTA-based pilot-scale batch extraction process (Voglar and Lestan, 2012b).

In the present study the amendment with 2% of CaMgP further reduced the DTPA-extractable metals in leached soils (Table 5). DTPA-extractable Cd, Cu, Pb and Zn decreased from 2.3 to 2.0 mg kg^{-1}, from 54 to 43 mg kg^{-1}, from 69 to 53 mg kg^{-1} and from 52 to 47 mg kg^{-1}, respectively. Phosphate is a common amendment to immobilize heavy metals in soils and also provide P as a nutrient (Cao et al., 2003; Chen et al., 2006; Zhang et al., 2010b; Zupancic et al., 2012). Therefore, the subsequent amendment of CaMgP in the leached soils was a useful choice to further immobilize residual metals. Compared to CaMgP the further amendment with organic fertilizer did not change soil DTPA-extractable metals (Table 5). Nevertheless, the application of organic fertilizer could improve soil structure, conserve the nutrients in soil, and enhance the soil microbial biomass, activity and diversity, which in turn improved the crop growth and restrained metal toxicity (Goyal et al., 1999; Jilani et al., 2007; Zhang et al., 2012).

In the first rotation plants grown normally in the initial soils contained elevated heavy metals but plants grown in the leached soils showed symptoms of chlorosis and their biomass was significantly inhibited compared with unleached soils (Table 6). Similar results have been reported recently in the literatures (Jelusic et al., 2013, 2014). Possible explanations are that the residual metal-EDTA complexes exerted toxic effects on the plants and/or EDTA leaching altered the soil physical structure and chemical properties to some extent. Moreover, soil macro- and micronutrients such as Fe, Mn, Cu, and Zn can be removed by EDTA leaching which leads to nutrient deficiency (Jelusic et al., 2014). In the present study soil available K was reduced significantly after EDTA leaching (Table 4). These negative changes in leached soils might inhibit plant growth in the first rotation. Nevertheless, amendment with CaMgP and organic fertilizer significantly increased plant growth, although the biomass was still 46% lower than that in the initial soils. Firstly, this may be due to the increase in plant nutrients as the addition of fertilizers. Moreover, amendment with CaMgP in the leached soils reduced the phytoavailability of residual toxic metals and reduced stress on the plants and the amendment of organic fertilizer improved soil structure (Table 5).

In the present study the soils after the first rotation were allowed to age for around one year. Then the second rotation was conducted. Interestingly, plants grew well and got similar biomass (fresh and dry weight) in the initial soils, leached soils, and amended soils (Table 6). This indicates that the soil properties of leached soils had recovered and were fit for plant growth. Several factors may affect the performance of the plants in the EDTA-leached soils after aging of the soil for one year. Firstly, although EDTA is a biologically stable chelant it can be degraded to some extent by soil microbes or chemical attack (Hong et al., 1999). Consequently, the soil residual metal-chelate complexes were also expected to disappear and metals to change to more stable forms. This is confirmed by the remarkable reduction in soil DTPA-extractable metals after one year's soil aging (Table 5). The DTPA-extractable metals in the unleached soils kept constant before and after soil aging. However, the DTPA-extractable metals in the leached soils and amended soils decreased significantly after one year's soil aging. For example, DTPA-extractable Cd, Cu, Pb and Zn in the leached soils decreased from 2.3 to 0.25 mg kg^{-1}, from 54 to 8.3 mg kg^{-1}, from 69 to 4.6 mg kg^{-1} and from 52 to 5.2 mg kg^{-1}, respectively. Similar reduction was also observed in the amended soils. Therefore, soil aging would be critical for the recovery of EDTA-leached soils.

According to Chinese Maximum Levels of Contaminants in Foods (GB 2762-2005) Cd and Pb concentrations should be less than 0.2 and 0.3 mg kg^{-1}, respectively. As shown in Table 6, in the initial soils the Cd concentration in the edible parts of pak choi in the first rotation was 2.95 mg kg^{-1}, which exceeded the official limits 14 times. Cd and Pb concentrations in the second rotation also exceeded 10.4 and 5.9 times. However, in the leached soils and amended soils, Cd and Pb concentrations in the edible parts of the plants decreased significantly compared to the unleached soils. While Cd concentrations in the first rotation of leached soils exceeded the Chinese limits to some extent, Cd and Pb concentrations in the second rotation of leached soils were below the limits. Amendment with CaMgP and organic fertilizer further reduced metal accumulation in plants to some extent. This was expected due to the reduction in heavy metal availability during EDTA leaching and metal immobilization by CaMgP and organic fertilizer as well as metal stabilization during soil aging (Table 5). Similar reduction in heavy metal accumulation in some vegetable after EDTA washing was reported (Jelusic et al., 2013, 2014). Therefore, the remediated soil in the present study could be considered safe for conventional vegetable production.

4. Conclusion

EDTA heap leaching is a feasible method to efficiently remove heavy metals from soil and is easy to be operated at the pilot scale. EDTA leaching had some undesirable influence on soil properties, nutrients and cations. However, the structure and function of EDTA leached soil can be recovered by amendments and soil aging. The remediated soil was fit for plant growth and Cd and Pb concentrations in the plant edible parts were below legislative limits. Therefore, the EDTA heap leaching combined with subsequent amendment and soil aging is technically feasible for the remediation of agricultural soils highly contaminated with metals.

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