

Column Extraction of Heavy Metals from Soils Using the Biodegradable Chelating Agent EDDS

LUKAS HAUSER, SUSAN TANDY, RAINER SCHULIN, AND BERND NOWACK*
Institute of Terrestrial Ecology (ITO), Swiss Federal Institute of Technology (ETH), Universitätsstrasse 16, CH-8092 Zurich, Switzerland

A possible remediation strategy for metal polluted soils is washing with chelants. Here, we compare the efficiency of batch and column extraction of Cu, Zn, and Pb from three soils using the biodegradable chelant EDDS. A total of 53–80% of Cu was extracted in batch and 18–26% in column extraction. For Zn, the extractability was 16–50% in batch and 20–64% in columns and for Pb 25–52 and 18–91%, respectively. Column leaching was therefore equally or better suited for Zn and Pb removal. The longer extraction time in the column resulted in more formations of Fe(III)EDDS by slow dissolution of iron oxides. Zn was uniformly washed from the column, while Cu and Pb were extracted in the top layers and deposited in the bottom layers, presumably by biodegradation of the metal–EDDS complexes and slow dissolution of iron oxides. Between 18 and 42% of the applied EDDS was lost through biodegradation after 7 weeks. In short time experiments, only 6% of EDDS was degraded. Using EDDS concentrations in excess of available heavy metals caused pronounced leaching of organic matter and clogging of the column. Our results prove that heap leaching using EDDS is a promising approach to reduce the heavy metal content of polluted soils.

Introduction

The extraction of heavy metals from soils using chelants has been studied extensively (1). The most often proposed chelant is EDTA, the most widely used chelant in the world (2). Because EDTA is very recalcitrant to microbial degradation (3), it is quite mobile in soils and readily transported to the groundwater together with the mobilized metals (4). EDDS (ethylenediaminedisuccinic acid) has received much attention in the past few years as a potential replacement for EDTA (5). The S,S-isomer of EDDS (in this paper, for simplification, it is referred to as EDDS) is produced by some bacteria and fungi (6) and is easily biodegradable, while the R,R- and S,R-isomers are not (7–9). Industrial EDDS is produced via chemical synthesis either as a racemate or as a pure S,S-enantiomer. EDDS has received some attention in recent years in soil washing and chelant-enhanced phytoextraction (10–14). In soil washing, EDDS has been found to be superior to EDTA around neutral pH in extracting metals from soils because the competition with Ca is much less important (10).

Most studies about chelant extraction of metals from soils report results from laboratory batch experiments looking at

the influence of chemical and soil chemical factors on the removal. Although these suspension-based extraction techniques could be upscaled to treat larger amounts of soils (15), it may be more practical and economical to leach the soil by either column or heap leaching. Heap leaching is used in the mining industry for the extraction of precious metals and has the potential for an economical treatment of large amounts of soils (16). Only a few studies have dealt with column extraction of heavy metals (11, 17–19) or have compared batch and column leaching (4, 20).

Normally, batch extraction studies are carried out in pure water with added background electrolytes. For an upscaling of the extraction procedure, it would be more economical to use natural water such as tap or river water for the extraction. Natural waters normally contain Ca and Mg, which are able to affect the extraction of metals in a different way than the normally used Na-background electrolytes (21).

The ratio of soil/water changes drastically when changing from batch to column extraction. Whereas suspension studies normally employ soil-to-solution ratios of 1:50 to 1:5 (1), the momentaneous ratio during the column extraction is about 2:1. So far, it has been found that the solid/water ratio does not affect the extraction efficiency of metals during batch extraction (22, 23). However, in these studies, the metal/chelant ratio was also changing, and excess chelant was used.

The aim of this work was to test the potential use of the environmentally friendly chelant EDDS for column extraction of heavy metals from polluted soils. Comparing column to batch extractions, we investigated in particular the influence of the background electrolyte and the soil/solution ratio on extraction efficiency. We also analyzed the concentration of EDDS in the eluates because we expected biodegradation to occur. Speciation calculations were used to distinguish between the different metal complexes in the leachate solutions.

Materials and Methods

Soils. The soils used in this study were taken from two polluted sites in Switzerland. Two soils were taken from an area in Dornach, which had been heavily contaminated with Cu, Zn, and Cd for about a century by particulate emissions from an adjacent brass smelter (24). The two soils differed in their carbonate content and pH. The third soil (Rafz) originated from an agricultural field in Northern Switzerland contaminated with Zn, Pb, and Cd due to past sewage sludge applications (25). The soil samples were taken from the top 20 cm, dried at 40 °C, and sieved to <2 mm. Soil properties are displayed in Table 1. The molar sum of the heavy metals Zn, Cu, Pb, Cd, and Ni was between 18.3 and 20.2 $\mu\text{mol g}^{-1}$ in all three soils.

Batch Extractions. Batch extractions were carried out with 0.01 M NaNO_3 and tap water (0.7 mM Mg, 2 mM Ca, pH 7.9). The soil/solution ratio was set to 1:50, 1:10, and 1:2 by mixing 0.8, 4, or 20 g of air-dried soil with 40 mL of NaNO_3 or tap water in 50 mL polypropylene centrifuge tubes. The pH was adjusted with HNO_3 or NaOH to 7.0 48 h prior to addition of EDDS. For each soil/solution ratio and soil, three replicates were made. EDDS was added at a concentration of 20 $\mu\text{mol g}^{-1}$ soil. S,S-EDDS was obtained from Procter and Gamble. The samples were shaken at 350 rpm on a rotary shaker. After 24 h, the pH of the extraction solution was measured, and the suspensions were centrifuged for 15 min at 3000 rpm and filtered (cellulose acetate, 0.45 μm , Sartorius). Cu, Zn, Pb, Fe, Al, Ca, and Mg were measured in the extracts by means of flame AAS (Varian AA400). The extraction solutions

* Corresponding author phone: +41 (0)44 633 61 60; fax: +41 (0)44 633 11 23; e-mail: nowack@env.ethz.ch.

TABLE 1. Soil Properties

soil	pH	CaCO ₃	C _{org}	Ca	Fe	Zn	Cu	Pb	sum heavy metals
		(%)		g kg ⁻¹			mg kg ⁻¹		μmol g ⁻¹
Dornach 1	7.0	13.8	5.7	58	31	667	527	60	19.8
Dornach 2	6.2	0.6	7.3	10	28	659	449	76	18.3
Rafz	5.5	0.5	3.4	10	18	987	73	732	20.2

from the Rafz soil in tap water at the soil/solution ratio of 1:50 were also analyzed for dissolved EDDS.

Column Extractions. Extractions were carried out using packed soil columns. Two 50 mL polypropylene centrifuge tubes were stuck on top of each other. The top column was filled with 50 g of soil, and the bottom tube served as a collector of the leachate. To prevent the soil from being washed out from the upper tube, nylon mesh (mesh size 60 μm) was placed on the bottom of the tube. Triplicate columns were prepared for each soil. Before the start of the experiment, 50 mL of tap water was added to each column to ensure that the soil was soaked thoroughly. After drainage, the water holding capacity was determined to be 373, 470, and 364 g kg⁻¹ for soil Dornach 1, Dornach 2, and Rafz, respectively.

EDDS was applied at 20 μmol g⁻¹ soil (EDDS: heavy metals = 1; 10 mL of 0.1 M solution for 50 g of soil). For Rafz soil, an additional series was run in which a 10-fold amount of EDDS (200 μmol g⁻¹ soil) was applied. The pH of the EDDS solution was adjusted to 7.5. EDDS was added in two portions at the beginning of the experiment. The first 5 mL was added on day 0 of the experiment and the second 5 mL on day 4. Thereafter, starting at day 7, the columns were watered twice a week with 5 mL of tap water. The leachates were collected once a week and weighed to determine the quantity of the extracts. The leachates were filtered (cellulose acetate filter, 0.45 μm, Sartorius). For determination of Fe, the extracts were filtered through a 0.05 μm nitrocellulose filter (Sartorius) for colloid removal (preliminary experiments indicated that high concentrations of iron pass through the 0.45 μm filter). Seven leachate samples were collected for every column during a total of 7 weeks. A total of 100 μL of formaldehyde (Fluka) was added to the bottom tubes to inhibit microbial growth. The columns were kept in the dark to prevent photodegradation of EDDS.

A second set of experiments was carried out with a much faster addition of water to the column. This experiment was only made with Dornach 2 soil and an EDDS concentration of 20 μmol g⁻¹ soil. On the first day, 10 mL of EDDS (0.1 M) was added in two portions. The columns were watered twice a day with 5 mL of tap water. Six eluates were collected within 10 days.

All sample extracts were acidified with one drop of concentrated HNO₃ (65%) prior to analysis. The heavy metals Zn, Cu, and Pb as well as Fe, Ca, Mg, and Mn were determined by flame-AAS. At the end of the experiment, the soil material in the columns was frozen and separated from the tubes. After defrosting, the soil was sliced horizontally into six sections of equal size. Total metal concentrations in the soil samples were analyzed by energy-dispersive X-ray fluorescence analysis (X-Lab 2000, Spectro, Germany).

EDDS Analysis. EDDS was analyzed according to the method of Tandy et al. (26). The sample was derivatized with FMOC (fluorenylmethyl chloroformate), and the fluorescing product was separated by HPLC on a Lichrosphere 100-RP-18 column (length 12.5 cm, diameter 4 mm, Merck). A Jasco high performance liquid chromatograph (PU-980) equipped with a fluorescence detector (Spectroflow 980; excitation wavelength: 265 nm; emission cutoff filter: 320 nm) was used. The mobile phases were 0.1 M phosphate (pH 6.8) and acetonitrile. The detection limit was 0.01 μM.

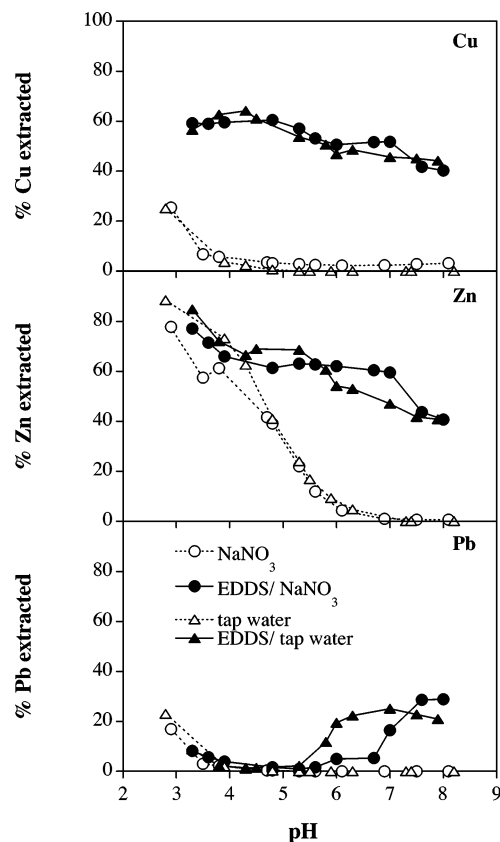


FIGURE 1. Influence of the background electrolyte (tap water vs 0.01 M NaNO₃) on batch extraction of Cu, Zn, Pb, and Ca from Rafz soil in the absence and presence of EDDS (ratio chelant/metal = 1).

Speciation Calculations. All speciation calculations were performed using the program ChemEQL (27). The stability constants for metal-hydroxy complexes, for metal-EDDS complexes, and protonation of EDDS were taken from ref 28 and adjusted to 0.01 M ionic strength. Because the concentrations of Fe, Cu, Zn, and Pb in the absence of EDDS were very low and because EDDS was in excess of total metals, almost all metals in the presence of EDDS were chelated. Therefore, the inorganic speciation of metals by other anions (e.g., HCO₃⁻, Cl⁻) did not influence the speciation and could be neglected. The speciation calculations were performed for the column leachates from week 3. Input variables were the measured pH, total concentrations of cations (Ca, Mg, Mn, Al, Fe, Cu, Zn, and Pb), and total EDDS.

Results and Discussion

Batch Extraction: Influence of Background Electrolyte. In the absence of chelants, low levels of Cu and Pb were extracted below pH 3.5, while high levels of Zn were extracted below pH 6 (Figure 1). The addition of EDDS resulted in a significant increase in the extractability of Cu and Zn at all pH values, while Pb extraction was only increased above pH 6. Replacing the NaNO₃ background electrolyte with tap water had no significant effect on the extraction of Cu and Zn by EDDS (Figure 1). The presence of higher concentrations of Ca in

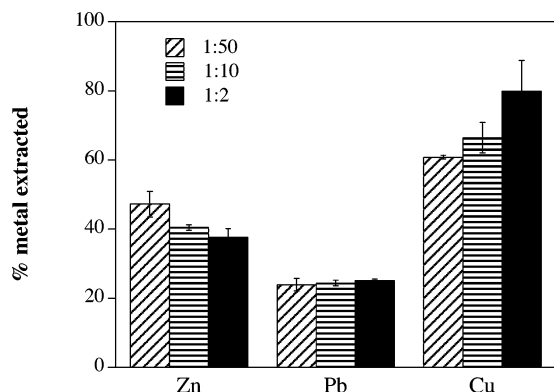


FIGURE 2. Influence of the soil/solution ratio on Zn and Pb extraction from Rafz soil and Cu extraction from Dornach 2 soil using EDDS at a chelant/metal ratio of 1. Conditions: background electrolyte tap water, pH 7, ratio chelant/metal = 1.

the tap water (3 mM as compared to 0.3 mM in the NaNO_3 extract at pH 7) therefore did not significantly affect the extractability of Cu and Zn because the CaEDDS complex was very weak ($\log K = 4.6$ (28)). Extraction of Pb was slightly enhanced by EDDS between pH 5 and 7 in the presence of tap water. EDDS forms only very weak complexes with Pb ($\log K = 12.7$ for Pb as compared to 18.4 for Cu (28)). The experiment thus leads to the conclusion that tap water is a well-suited solvent for soil washing with EDDS. Additional benefits of tap water or other freshwaters such as river or lake water include low cost, simplification of the washing process, and good availability.

Batch Extraction: Influence of Soil/Solution Ratio. The three metals Cu, Zn, and Pb reacted differently to changes in the soil/solution ratio, when the ratio of chelant/metal was kept constant. Figure 2 shows that the extraction of Zn in the presence of EDDS at pH 7 decreased with increasing soil/solution ratio (shown for Rafz soil). The same trend toward lower Zn extraction was also observed for the other two soils (data not shown). This suggests that the solubility of Zn was controlled by a solid phase or by a change in the concentration of counterions in solution.

For Pb, there was no significant change in extraction efficiency when the soil/solution ratio was altered, but the extraction of Cu increased with increasing soil/solution ratio. This may be due to increasing amounts of organic matter being co-extracted. EDDS, like other chelants, not only complexes heavy metals but also extracts organic matter from the soil (29). Increased amounts of extracted organic matter subsequently lead to higher amounts of extracted Cu because organic matter strongly binds Cu. Sequential extractions have shown that a large fraction of Cu in the studied soils was present in the organic fraction (10).

Column Extraction: Water Percolation in Soil Columns. The amount of water added per week to the columns at the low infiltration rate corresponded to half a pore volume. The soil structure remained intact during this time as judged by visual inspection. In the first few weeks of the experiment, the water percolated through the columns rather quickly within 3–6 h. For EDDS columns, the percolation time increased during the experiment, reaching 3–4 days for some columns. The columns to which high concentrations of EDDS were given (Rafz) clogged about 5 weeks after the start of the experiment. The columns with the fast infiltration also showed decreased percolation toward the end of the experiment.

The extracts from all soils were brown, especially the one from Rafz soil at the high chelant/metal ratio, which had the color of black coffee, indicating strong mobilization of organic matter. An additional contribution of the colored

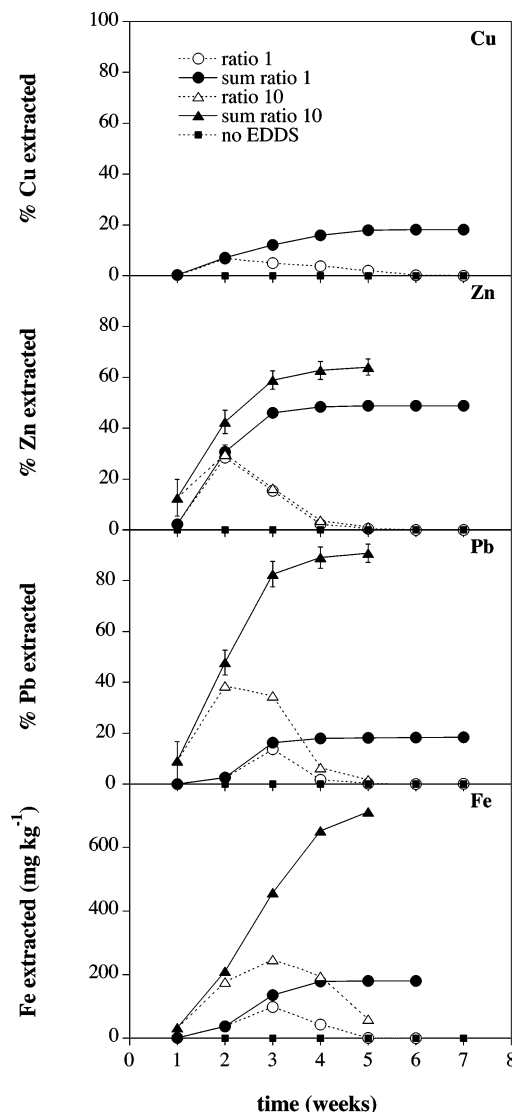


FIGURE 3. Extraction of metals during column leaching with EDDS. EDDS was added at week 0. The empty symbols represent the extracted amount in the leachate, the filled symbol the total extracted amount. The metals leached in the absence of EDDS are shown with squares. Zn, Pb, and Fe data are from Rafz soil at chelant/metal ratios of 1 (circles) and 10 (triangles), and Cu data are from Dornach soil 2 for a chelant/metal ratio of 1 (circles). Error bars are standard deviations for three columns (often smaller than the symbol).

Fe(III)EDDS —complex cannot be ruled out. It is known that in soils, the aggregate stability correlates with organic matter content (30). If organic matter is extracted, soil aggregates break down, and the soil particles are no longer held together. Clogging of soil during washing with high concentrations of chelants has been described before (31).

Column Extraction of Metals. Less than 0.01% Zn and Pb and less than 0.6% Cu were leached from the columns in the absence of EDDS. In the presence of EDDS, metals started to appear in the first extract, had the highest concentration in the second extract, and then decreased to almost background values (Figure 3). The shape of the elution curves of the different metals was very similar. Table 2 shows the amounts of Zn, Cu, and Pb extracted from the column during the experiment. At the chelant/metal ratio of 1, 20–50% of Zn and about 20% of Cu and Pb were extracted from the three soils. More Zn was extracted in the column that was leached at the high rather than the low infiltration rate. The pH of the leachate was between 8.3 and 8.6 for all treatments.

TABLE 2. Comparison of Batch and Column Extraction Efficiency for Cu, Zn, and Pb (Average \pm Standard Deviation, in % of Total Metal) from the Three Polluted Soils^a

metal	soil	chelant/ metal ratio	% of total metal extracted		
			batch	column low infiltration	column high infiltration
Zn	Dornach 1	1	16 \pm 1	20 \pm 1	
	Dornach 2	1	28 \pm 4	28 \pm 2	37 \pm 6
	Rafz	1	38 \pm 3	49 \pm 1	
	Rafz	10	50 ^b	64 \pm 3	
Cu	Dornach 1	1	53 \pm 2	26 \pm 13	
	Dornach 2	1	80 \pm 9	18 \pm 2	17 \pm 1
Pb	Rafz	1	25 \pm 0.5	18 \pm 0.1	
	Rafz	10	52 ^b	91 \pm 4	

^a Ratio chelant: metals = 1; batch data are for a soil/solution ratio of 1:2; pH 7.5; and tap water except where noted. ^b Solid: solution ratio 1:50; ratio chelant/metal: 10; pH 7.5–8; tap water.

The same amount of EDDS removed equal or more Zn during column leaching than in batch extraction, but removed much less Cu. At a chelant/metal ratio of 10, extraction of Zn and Pb was much more efficient from the column than in batch extraction. A total of 90% of Pb was extracted from the Rafz soil under these conditions. However, even at this ratio, only 64% of total Zn was extracted from soil Rafz. This result confirms previous findings that Zn extraction by chelants is normally not very efficient, even at very high excess of chelant (10). Pb extraction, however, was often found to reach almost 100%.

Column Extraction: EDDS Leaching from the Column.

For the Dornach 1 and 2 soils, 58% of the applied EDDS was found in the extracts and for the Rafz soil 82%. In the eluate from the columns with the high infiltration rate, 94% of the EDDS was recovered. Adsorption of EDDS to the soil matrix might be an explanation for the removal. However, measurements with the Rafz soil showed that at pH 7, only about 1 μ mol of EDDS g^{-1} of soil was adsorbed. This value increased to 2.5 μ mol g^{-1} at pH 3. Increasing adsorption with decreasing pH is expected for an aminocarboxylate such as EDDS (32, 33). A total of 50 μ mol of EDDS could have been adsorbed onto the soil columns according to this result, representing only 5% of total EDDS. Adsorption therefore can only explain a minor part of the observed disappearance of EDDS.

Biodegradation of EDDS probably was the main cause of the lack of full recovery. It explains the dependence of recovery on the infiltration rate. In the column with a high infiltration rate, EDDS was in contact with the soil for a much shorter time, allowing for much less biodegradation to occur than at a low infiltration rate. Uncomplexed EDDS as well as many metal–EDDS species are known to be biodegradable (7). The 7 weeks of the experiment at the low infiltration rate gave sufficient time for microbial population growth and degradation of EDDS. This means that less EDDS was available for extraction of heavy metals than in the batch extractions where no biodegradation of EDDS was observed (10).

EDDS Speciation. In the soils investigated, Zn, Cu, Pb, and Fe were the most important metals with respect to the formation of complexes with EDDS in the leachate. Figure 4 shows how much of the total EDDS was complexed by these four metals in the leachates. In Dornach 1 and 2 soils, the sum of these four metals equaled the EDDS concentration. Given that extraction was limited by EDDS, microbial degradation of EDDS was therefore a relevant factor for the extraction efficiency. This may explain the lower extraction yield for Cu in the column as compared to batch studies. The batch extractions lasted only 24 h, and no significant microbial degradation of EDDS occurred during this time. The degradation of EDDS in the column experiment was

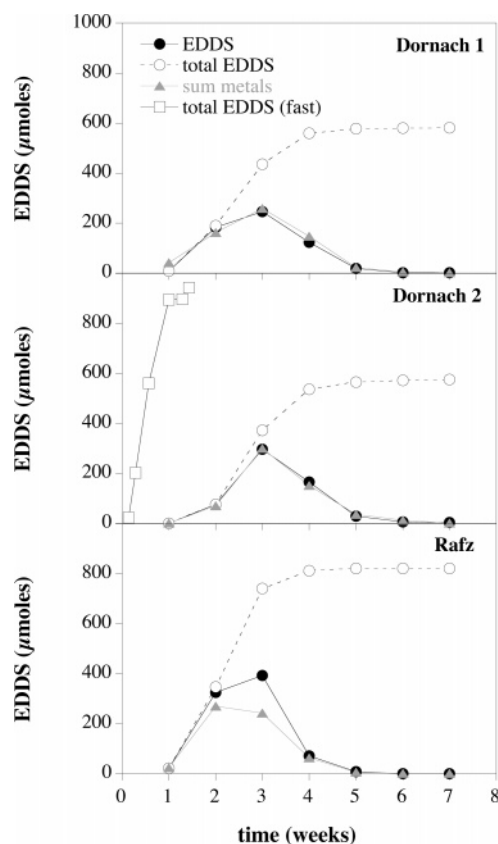


FIGURE 4. Behavior of EDDS during column leaching. The amount of EDDS in the leachates and the cumulative amount is shown. The total EDDS amount from the column with fast leaching is shown for the soil Dornach 2. Also shown is the sum of the metals Cu, Zn, Pb, and Fe in the leachates. Standard deviations were mostly smaller than the symbols.

TABLE 3. Calculated Distribution of EDDS Species in the Leachates from Week 3 (in % of Total EDDS)

EDDS complex	Dornach 1	Dornach 2	Rafz
Cu	2.7	6.0	3.3
Zn	14.3	24.1	29.7
Pb	0.0	0.0	6.2
Fe	80.1	69.2	22.6
Mn	3.1	0.7	29.7
Ca	0.01	0.002	3.6
Mg	0.01	0.01	5.1
free	0.0005	0.0002	0.8

partially compensated for by the longer extraction time. However, this also resulted in very high Fe and Ca concentrations in the extracts (Table 1S, Supporting Information), indicating dissolution of iron oxides by EDDS. The columns with the shorter contact time with EDDS showed much lower Fe concentrations. Free chelants and metal–chelant complexes are able to dissolve iron oxides at neutral pH values (34). This process becomes more important with increasing reaction time. It is therefore much more pronounced in the column leaching than in the much shorter batch extraction.

In the Rafz soil, the sum of Cu, Zn, Pb, and Fe was lower than the total EDDS concentration (Figure 4). This leads to the question as to whether excess EDDS remained complexed or formed complexes with other metals. To find an answer, we performed speciation calculations. Potential metals that might have complexed EDDS were Ca, Mg, and Mn. Table 3 shows the calculated amounts of uncomplexed EDDS and metal complexes in the leachate of week 3. In the Dornach

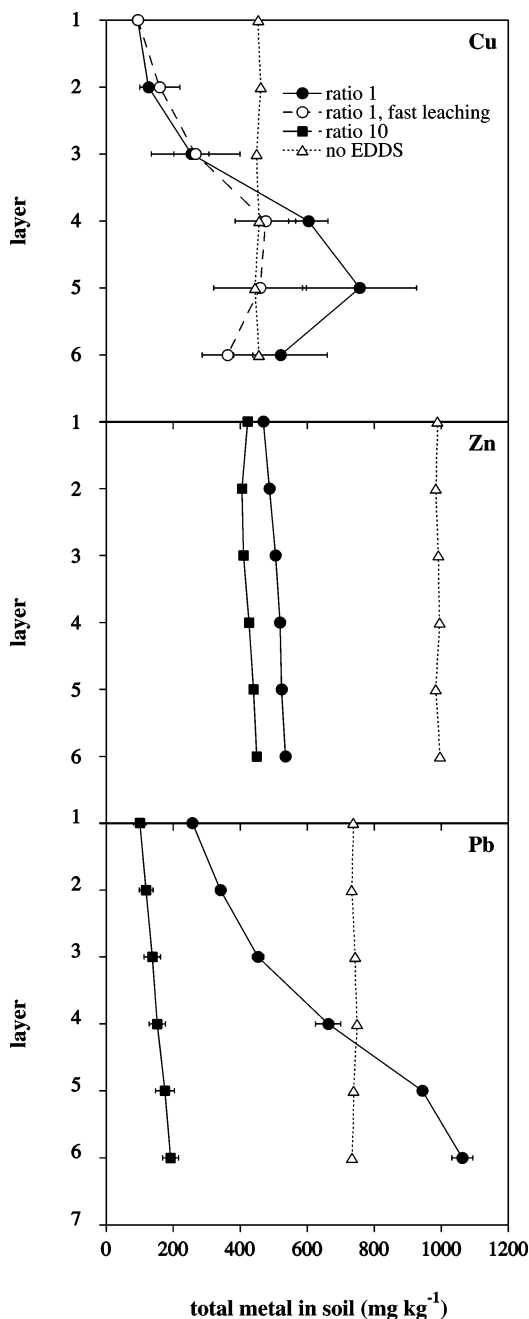


FIGURE 5. Concentration profiles of Cu, Zn, and Pb in the columns after extraction with EDDS. Data are shown for the reference column without EDDS, for the chelant/metal ratio of 1 (all metals), and for the chelant/metal ratio of 10 (Zn, Pb) and the fast leaching rate for Cu. The average and standard deviation from three columns are shown (for the control average of two columns). Data are from soil Rafz (Zn, Pb) and soil Dornach 2 (Cu).

soils 1 and 2, virtually all EDDS was complexed to Cu, Zn, and Fe according to the speciation calculation, with all other metals being of little importance. However, in Rafz soil, Ca, Mg, and especially Mn were very important metals that could have complexed about one-third of the EDDS in the leachate. This would explain the difference between the total EDDS concentration and the sum of Cu, Zn, Pb, and Fe for this soil. Uncomplexed EDDS was negligible in the Dornach soils, and in Rafz it reached close to 1% of the total EDDS.

Metal Distribution in the Columns. Total metal analysis in the soil after the extraction revealed that residual Zn was uniformly distributed in the columns (Figure 5). Pb and Cu, however, were removed from the upper parts of the soil

columns and deposited in the lower parts. Leaching of Rafz soil using the high concentration of EDDS led to a uniform removal of Pb. With the high concentration of EDDS, we expect no competition of the metal ions for the chelant molecules since the chelant was available in a large surplus. The Zn profile in the columns with a high infiltration rate exhibited the same uniform removal of Zn from the whole column as at the low infiltration rate. Cu was removed from the upper layers as at the low leaching rate, but there was neither depletion nor deposition of Cu in the lower layers.

The concentration profiles provide evidence that Cu and Pb had been transported through the soil columns and immobilized again. The two possible processes that may explain this behavior are biodegradation of EDDS and metal exchange reactions with Fe(III).

CuEDDS and PbEDDS were found to be biodegradable in soils (11). Degradation of the metal–EDDS complex yields the free ion, a species not soluble at the prevailing pH conditions. Therefore, Cu and Pb would precipitate, leading to an accumulation of the metals in the lower parts of the columns.

A second process that could have led to the liberation of metals from EDDS complexes is the dissolution of iron oxides by metal–EDDS complexes. We can expect that first extraction of Cu, Zn, and Pb took place in the top layers of the column. The slower dissolution reaction later resulted in an exchange of the mobilized metals with Fe(III). A similar process was observed for extraction of Zn by EDDS at a low pH in batch extractions where rapid mobilization of Zn was followed by slow formation of Fe(III)EDDS and a decrease of solubilized Zn (10). Fe(III)EDDS has a much larger stability constant than the other metal–EDDS complexes, and speciation calculations have shown that Fe(III)EDDS can be formed at pH 8.5 in the extraction solutions.

Both processes can explain the distribution of Cu and Pb but not of Zn. Zn should behave in a similar way to the other two metals because it is also biodegradable (7) and able to dissolve iron oxides (10). We would therefore also expect that Zn be deposited in the lower parts of the column. The stability constants of the EDDS complexes follows the order PbEDDS < ZnEDDS < CuEDDS, and solution speciation therefore should favor the solubilization of Cu over Zn. Binding of metals to soils, however, follows the order Zn < Pb < Cu and would favor the immobilization of Pb and Cu over Zn. The combination of both processes obviously resulted in the efficient immobilization of Cu but not Zn in the presence of EDDS onto the soil matrix.

Comparison of Batch and Column Extraction. Compared to batch extraction, column extraction has advantages and disadvantages. The major disadvantage of our leaching procedure was the long flushing time of EDDS from the soil columns, which allowed for substantial biodegradation and dissolution of iron oxides leading to the formation of Fe(III)EDDS and the biodegradation of EDDS. These processes reduced the extraction efficiency because less EDDS was available for complexation. However, extraction yields were still up to 50% Zn at the low chelant/metal ratio and more than 60% Zn and 91% Pb at the chelant/metal ratio of 10. When upscaling the procedure from leaching short columns to heap leaching, the retention time of the extraction solution with the soil and the ratio of chelant/heavy metals had to be optimized. Percolation with a higher flow rate may decrease biodegradation and Fe complex formation while keeping the metal extraction on a high level. The main advantage of column leaching is that the soil structure remains intact, which is not the case for batch extractions. The process can also easily be upscaled, and the technology to do so is available in the mining industry.

Acknowledgments

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Supporting Information Available

Table (1S) with a comparison of batch and column extraction of Ca, Mg, and Fe. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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