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Evolution of Bioavailable Copper and Major Soil Cations in Contaminated Soils Treated with Ethylenediaminedisuccinate: A Two-Year Experiment

Michael Komárek · Zuzana Michálková · Jiřina Száková · Aleš Vaněk · Tomáš Grygar

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Abstract This study evaluates the long-term behavior of metals in soils treated with ethylenediaminedisuccinate for remediation purposes. The addition of the chelant led to a significant increase of water-extractable copper, iron, aluminum contents and their uptake by poplar. Increased concentrations of the metals were present in the soil solution even after the 2 years of the experiment (up to a 30-, 170- and 270-fold increase for copper, iron and aluminum, respectively). Therefore, soils treated with chelants must be monitored not only for the targeted metal concentrations but also for major soil cations originating from chelant-induced dissolution of soil oxides.

Keywords Soil remediation · Chelating agent · Metal · Bioavailability

Chelating agents, such as EDTA (ethylenediaminetetraacetate) and its biodegradable structural isomer EDDS ([*S*,*S*]-ethylenediaminedisuccinate), have been extensively studied as amendments enhancing metal extraction from contaminated soils (soil washing and flushing) or the uptake of metals by plants grown on such soils (enhanced phytoextraction) (Leštan et al. 2008). However, there are several disadvantages of these methods, including the competition of major soil cations for the ligand, e.g., Fe, Mn and Al from chelant-enhanced dissolution of soil oxides, which lowers significantly the efficiency of the process (Nowack et al. 2006; Komárek et al. 2009, 2010). Furthermore, there is only limited information about the long-term evolution of the (bio) available pool of metals in soils treated with EDDS, either after soil washing/flushing or after enhanced phytoextraction. Therefore, the aim of this study is to describe the evolution of (bio) available Cu (as the target contaminant) and Fe, Mn, Al (originating from the dissolution of soil oxides) in soils treated with EDDS during a two-year experiment conducted on two contrasting soils contaminated with Cu-based fungicides. This paper is extending our previous study (Komárek et al. 2010) conducted on the same soils to a two-year experiment.

Materials and Methods

The two soils used in this study originated from an active vineyard (soil V) and a hop field (soil H) contaminated with Cu-based fungicides (Table 1). Samples were collected from the superficial layer (0–20 cm), air-dried, homogenized and sieved through a 10-mmstainless sieve prior to further processing. Soil samples used for basic physico-chemical characteristic determination were further sieved through a 2-mm stainless sieve. Pseudo-total metal concentrations were determined using the *aqua regia* digestion (USEPA method 3051a). In order to determine the chemical fractionation of Cu in the studied soils, the sequential extraction procedure by Rauret et al. (2000) was

M. Komárek (✉) · Z. Michálková · J. Száková
Department of Agro-Environmental Chemistry and Plant Nutrition, Czech University of Life Sciences Prague, Kamýcká 129, 16521 Prague 6, Czech Republic
e-mail: komarek@af.czu.cz

A. Vaněk
Department of Soil Science and Soil Protection, Czech University of Life Sciences Prague, Kamýcká 129, 16521 Prague 6, Czech Republic

T. Grygar
Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 25068 Řež u Prahy, Czech Republic

Table 1 Basic physico-chemical characteristics of the studied soils

	Soil H (Chernozem)	Soil V (Cambisol)
Clay (%)	12.7%	10.2%
TIC (mg kg^{-1})	0.25	<0.01
TOC (%)	3.00	2.16
CEC (cmol kg^{1})	11.7	4.12
pH_{KCl}	7.35	5.48
Total metal concentrations (n = 3)		
Cu (mg kg^{-1})	204 ± 2	166 ± 6
Fe (g kg^{-1})	37.8 ± 0.4	31.6 ± 1.2
Mn (g kg^{-1})	0.61 ± 0.02	0.70 ± 0.02
Al (g kg^{-1})	33.8 ± 3.7	19.0 ± 0.2

performed. The approximate content of poorly crystalline/amorphous oxides in the soils was determined using the acid-oxalate extraction and confirmed using voltammetry of microparticles (Grygar and van Oorschot 2002). Concentrations of the analyzed elements in the extracts and digests were determined using ICP-OES (Vista Pro, Varian, Australia; limits of detection were well below the analyzed concentrations: 4.00 μg Al L^{-1}, 0.50 μg Cu L^{-1}, 0.10 μg Fe L^{-1}, 0.03 μg Mn L^{-1}). All chemicals used were of analytical grade (Fluka, Germany; Merck, Germany).

Poplar (*Populus nigra* L. cv. Wolterson) was used for the two-year pot experiment as a fast growing metal-tolerant tree species for directly evaluating metal bioavailability. Cuttings with a similar diameter originating from one specimen were chosen for the experiment. Each pot contained 5 kg of air-dried and sieved (10-mm sieve) soil. Two poplar cuttings were planted in each pot. Each pot was fertilized at the beginning of each vegetation period with 0.5 g of N as NH_4NO_3; 0.16 g of P and 0.4 g of K as K_2HPO_4. The pots were kept in an outdoor weather-controlled vegetation hall and watered using deionized water. EDDS was applied in three doses at the beginning of the first vegetation season at total concentrations of 3 and 6 mmol kg^{-1} (Komárek et al. 2010). The EDDS concentrations were chosen to represent approximately molar EDDS/Cu ratios of 1/1 and 2/1 without being phytotoxic (Evangelou et al. 2007). A control variant treated with deionized water was included.

Soil samples were taken from pots before and after the first and the second vegetation season. Water-soluble metals and dissolved organic carbon (DOC) were determined using ICP-OES and a fully automated segmented flow C analyzer with IR detection (SAN^{++} system, Skalar, Netherlands). Due to its high degradability (half life of 2.5–7.5 days; Meers et al. 2008), it is possible to assume that no EDDS was present in the soils during the second vegetation season. During each harvest, poplar stems and leaves were carefully separated. The biomass was washed carefully using deionized water, dried at 60°C until constant weight and finely ground prior to decomposition. Samples were decomposed using the dry ashing procedure according to Miholová et al. (1993). Metal concentrations in the digests were determined using ICP-OES. The analytical procedures were evaluated analyzing the certified reference materials Light Sandy Soil 7002 (Analytica, Czech Republic) and IAEA-V-10 Trace Elements in Hay (International Atomic Energy Agency, Austria).

Results and Discussion

Total Cu concentrations reached 204 and 166 mg kg^{-1} in soil H and V, respectively, and are the result of the intensive application of Cu-based fungicides. Soil H exhibited a higher CEC value which can be related to the higher TOC, Fe-oxide and clay contents (Tables 1 and 2). Nevertheless, the chemical fractionation of Cu was similar in both studied soils: while only a small portion (<2%) of Cu was present in the most labile exchangeable fraction, the majority of Cu (>50%) was present in the so-called residual fraction. Copper present in the reducible (19–21%) and oxidizable (23–27%) fractions was distributed in both soils according to their TOC and Fe-oxide contents. Soil H can be characterized by a majority of poorly crystalline Fe oxides (mainly ferrihydrite, $5Fe_2O_3 \cdot 9H_2O$ and/or lepidocrocite, γ-FeOOH) and nanocrystalline goethite (α-FeOOH) and/or hematite (Fe_2O_3). In contrast, soil V is predominantly enriched with well crystalline goethite and hematite. Only a minor amount of poorly crystalline (or nanocrystalline) Fe oxides was identified in soil V (Fig. 1).

Table 2 Oxalate-extractable Fe, Mn and Al in the studied soils before and after the two-year plant experiment (n = 3)

		Fe (g kg^{-1})	Mn (g kg^{-1})	Al (g kg^{-1})
Soil H	Initial	5.90 ± 0.94	0.41 ± 0.06	1.02 ± 0.11
	0 mmol EDDS kg^{-1}	15.2 ± 1.2	1.13 ± 0.16	3.01 ± 0.36
	3 mmol EDDS kg^{-1}	14.6 ± 0.9	1.02 ± 0.03	2.56 ± 0.03
	6 mmol EDDS kg^{-1}	15.3 ± 0.6	1.21 ± 0.05	2.86 ± 0.11
Soil V	Initial	3.27 ± 0.20	0.71 ± 0.09	1.58 ± 0.24
	0 mmol EDDS kg^{-1}	4.62 ± 0.76	0.86 ± 0.10	2.71 ± 0.38
	3 mmol EDDS kg^{-1}	4.10 ± 0.09	0.69 ± 0.02	2.19 ± 0.03
	6 mmol EDDS kg^{-1}	4.31 ± 0.16	0.69 ± 0.09	2.26 ± 0.20

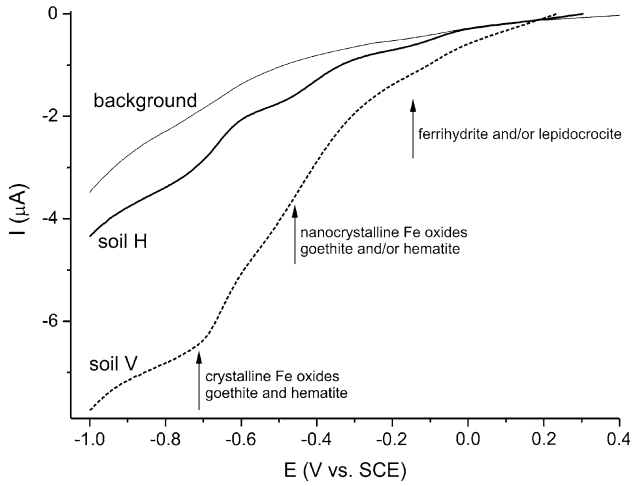

Fig. 1 Voltammetric curves of soil samples with assignment of (*negative*) voltammetric peaks. Individual *arrows* indicate potential ranges of pure Fe(III) oxide species

The presence of plants significantly increased oxalate-extractable Fe, Mn and Al contents in both soils (with the only exception of Mn in soil V; Table 2). This can be possibly attributed to the presence of root exudates capable of solubilizing these metals from various soil phases (e.g., poorly crystalline and/or amorphous oxides). Furthermore, increasing water-extractable metal concentrations were observed during the two-year experiment in the absence of EDDS. These facts are in accordance with increasing water extractable C in the control treatment during the 2 years (Fig. 2). On the other hand, no significant changes were observed after the addition of EDDS. This fact can be explained by the much stronger nature of the acid-oxalate extraction compared to the EDDS addition.

The addition of EDDS further led to a significant increase of water-extractable metals and increased concentrations of the metals were present in the soil solution

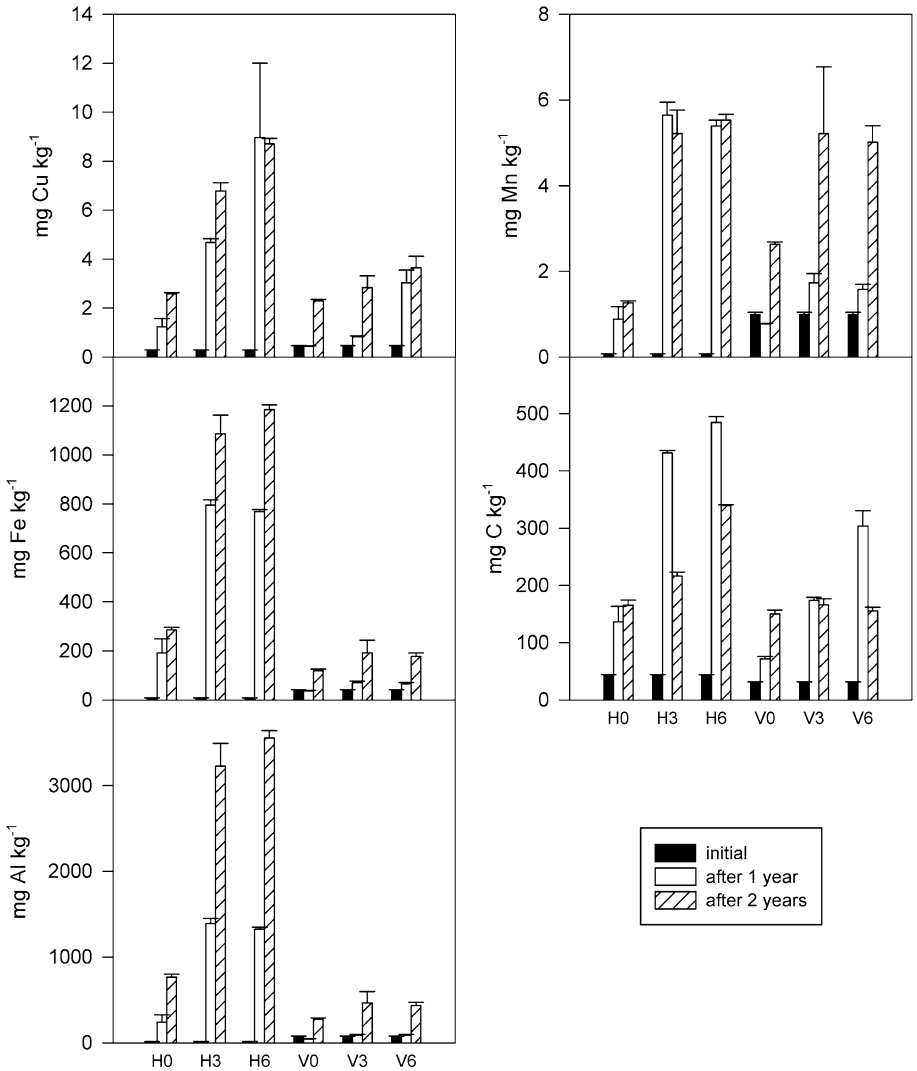

Fig. 2 Water-extractable metals and C in studied soils H and V before, after 1 year (Komárek et al. 2010) and 2 years of the experiment (this study) and after the addition of 0, 3 and 6 mmol EDDS kg^{-1} in the first year (n = 3)

even after the 2 years of the experiment (e.g., up to a 30-fold increase for Cu, 170-fold increase for Fe, 270-fold increase for Al in soil H; Fig. 2). It is needed to point out that no EDDS was added during the second year. This highlights the possible leaching and toxicological risks associated with the use of chelating agents (even biodegradable ones) in soil washing and phytoextraction processes. The application of EDDS did not influence the mobility of Ca in both soils and this metal does not have to be regarded as a direct competitor for the EDDS ligand at the studied soil pH values (Tandy et al. 2004). In the soils treated with EDDS, water-extractable C decreased after the second year. This is mostly due to EDDS degradation (Meers et al. 2008); however, some of its degradation products must have remained in the soils (Chen et al. 2010).

The biomass production of poplar stems and leaves grown on both soils after the first and the second vegetation season is presented in Fig. 3. There were no significant differences of biomass yields between different EDDS treatments and control variants during the first season. However, poplar cuttings did not grow on soil V treated with the highest EDDS dose (6 mmol kg^{-1}) in the second year, even when the cuttings were replanted. This could have been caused by increased concentrations of mobilized metals (Cu, Fe, Al) after the application of the highest EDDS dose which were kept in the soil solution due to the acidic character of the soil. Despite this fact, higher biomass production (especially on soil V) was obtained during the second year compared to the first one (except for soil V treated with 6 mmol EDDS kg^{-1}). In our previous study concerning a similar two-year experiment with EDTA and poplar (Komárek et al. 2008), an opposite trend was observed—the biomass production decreased in the second year. This can be attributed to the different nature of the chelating agents. While EDDS is a biodegradable chelant, the persistent and more toxic EDTA kept the metals mobilized in the soil solution throughout the 2 years making them available for plant uptake. From this point of view, EDDS is a much more environment-friendly mobilizing agent.

The application of EDDS significantly increased Cu uptake by poplar during the first year and enhanced Cu translocation from stems to leaves. Nevertheless, due to EDDS degradation, possible Cu precipitation, re-adsorption and depletion of the bioavailable pool, significantly lower Cu concentrations were observed in poplar biomass after the second year of growth. On the contrary, when EDTA was studied as the mobilizing agent, increased target metal concentrations were observed during the second year, especially due to EDTA persistence in the soil (Komárek et al. 2008). In the case of the major soil cations studied (Fe, Mn, Al), their increased uptake by poplar from soil H was observed during the second year (Fig. 4; data for Mn are not shown). This was due to the increased dissolution of soil Fe, Mn and Al oxides in the presence of EDDS (Komárek et al. 2009) and subsequent redistribution of the metals in the soil sorption complex. These results are in a good agreement with the oxalate-extractable Fe, Mn and Al concentrations (Table 2). An opposite trend was observed in soil V, where lower metal concentrations were observed after the second year compared to the first one.

The results obtained from this two-year experiment suggest that the use of chelating agents in chemically enhanced phytoextraction or soil washing can result not only into a long-term solubilization of the targeted metals (Cu), but also of those metals originating from the dissolution of soil oxides, i.e., Fe, Mn, Al. Especially in the case of soils containing high amounts of amorphous/poorly crystalline Fe and Al oxides (such as soil H), increased leaching and plant uptake of these major soil cations cannot be neglected. For this reason, soils treated with chelating agents, including biodegradable ones such as EDDS, have to be subsequently monitored not only for the targeted metal concentrations but also for major soil cations originating from chelant-induced dissolution of soil oxides.

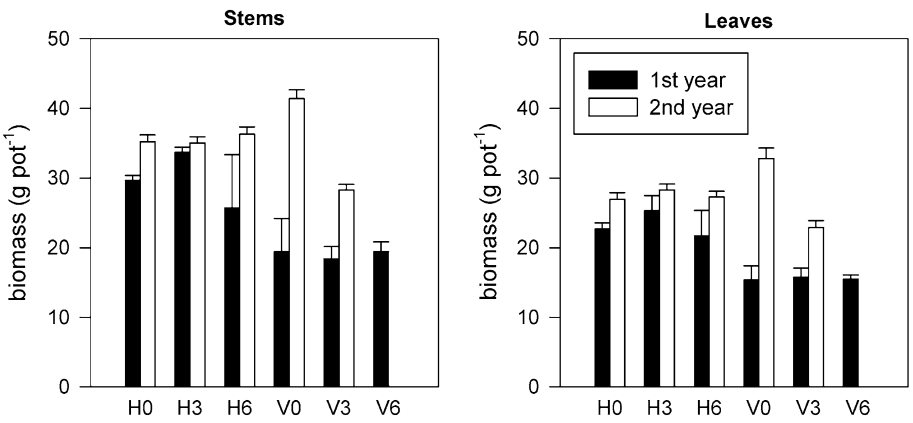

Fig. 3 Biomass yields of poplar plants grown in soils H and V obtained after the first year (Komárek et al. 2010) and second year of the experiment (this study) and after the addition of 0, 3 and 6 mmol EDDS kg^{-1} in the first year (n = 3)

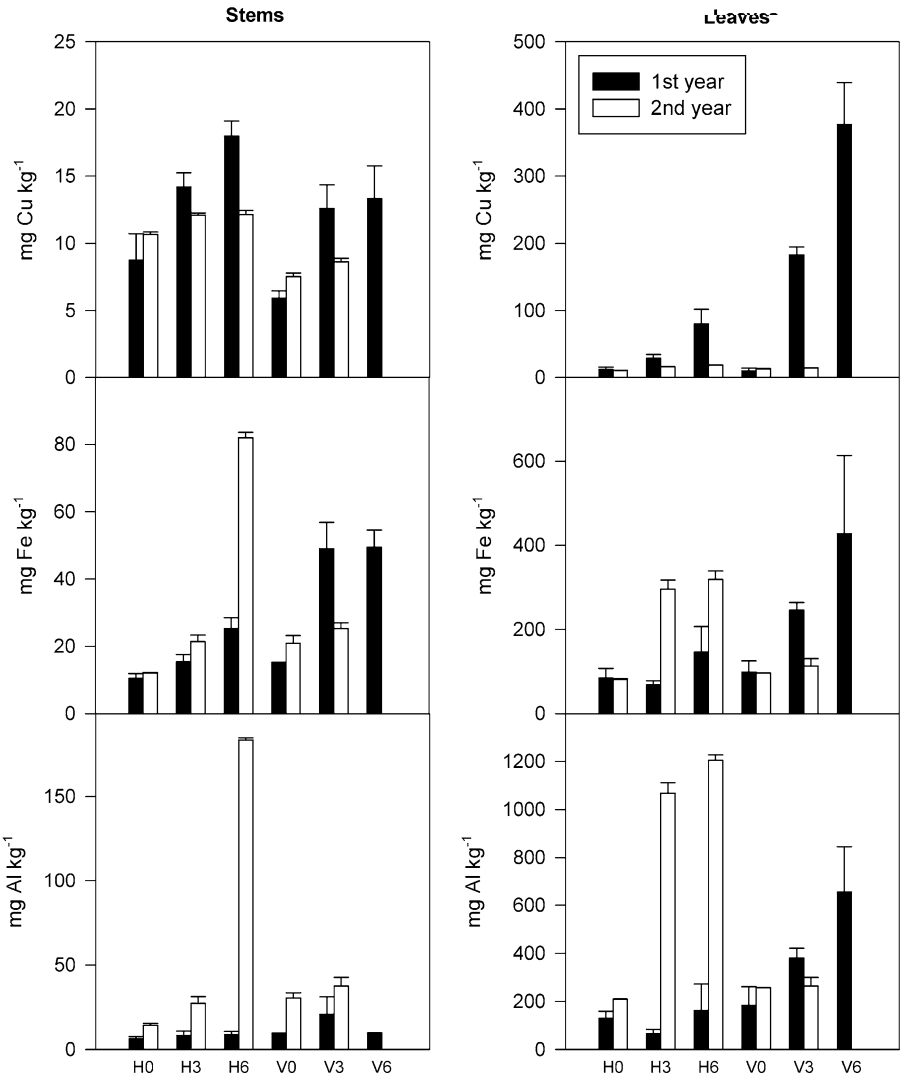

Fig. 4 Cu, Fe and Al concentrations in poplar plants grown on soil H and V after the first year (Komárek et al. 2010) and second year of the experiment (this study) and after the addition of 0, 3 and 6 mmol EDDS kg^{-1} in the first year (n = 3)

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References

Chen LT, Liu T, Ma C (2010) Metal complexation and biodegradation of EDTA and S, S-EDDS: a density functional theory study. J Phys Chem A 114:443–454

Evangelou MWH, Ebel M, Schaeffer A (2007) Chelate assisted phytoextraction of heavy metals from soil. Effect, mechanism, toxicity, and fate of chelating agents. Chemosphere 68:989–1003

Grygar T, van Oorschot IHM (2002) Voltammetric identification of pedogenic iron oxides in paleosol and loess. Electroanalysis 14:339–344

Komárek M, Tlustoš P, Száková J, Chrastný V (2008) The use of poplar during a two-year induced phytoextraction of metals from contaminated agricultural soils. Environ Pollut 151:27–38

Komárek M, Vaněk A, Száková J, Balík J, Chrastný V (2009) Interactions of EDDS with Fe- and Al-(hydr)oxides. Chemosphere 77:87–93

Komárek M, Vaněk A, Mrnka L, Sudová R, Száková J, Tejnecký V, Chrastný V (2010) Potential and drawbacks of EDDS-enhanced phytoextraction of copper from contaminated soils. Environ Pollut 158:2428–2438

Leštan D, Luo CL, Li XD (2008) The use of chelating agents in the remediation of metal-contaminated soils: a review. Environ Pollut 153:3–13

Meers E, Tack FMG, Van Slycken S, Ruttens A, Vangronsveld J, Verloo MG (2008) Chemically assisted phytoextraction: a review of potential soil amendments for increasing plant uptake of heavy metals. Int J Phytoremediat 10:390–414

Miholová D, Mader P, Száková J, Slámová A, Svatoš Z (1993) Czechoslovakian biological certified reference materials and their use in the analytical quality assurance system in a trace element laboratory. Fresen J Anal Chem 345:256–260

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

Rauret G, López-Sanchez JF, Sahuquillo A, Barahona E, Lachica M, Ure AM, Davidson CM, Gomez A, Lück D, Bacon J, Yli-Halla M, Muntau H, Quevauviller P (2000) Application of a modified BCR sequential extraction (three-step) procedure for the determination of extractable trace metal contents in a sewage sludge amended soil reference material (CRM 483), complemented by a three-year stability study of acetic acid and EDTA extractable metal content. J Environ Monitor 2:228–233

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