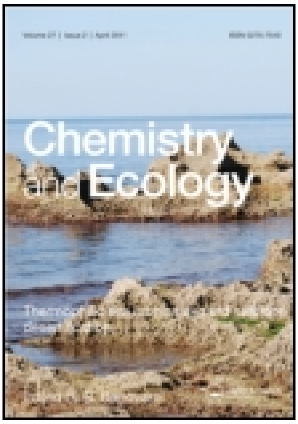

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# Chelant-assisted pulse flushing of a field Pb-contaminated soil

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Laboratory experiments on a lead-contaminated soil were carried out to test the effects of chelant addition on metal leachability using column tests. Tests were aimed at studying metal mobilisation upon application of two different chelating agents (ethylenediaminetetraacetic acid [EDTA] and ethylenediaminedisuccinic acid [EDDS]). Column operation was arranged to simulate a flushing treatment in which the chelating agent is applied in a pulse mode to the soil for one bed volume, while deionised water was continuously introduced for the rest of the experiment. Two different concentrations (3 and 5 $\text{mmol} \cdot \text{kg}^{-1}$ respectively) of the two chelating agents and a control solution (deionised water) were tested in separate experiments; pH, total organic carbon and the total concentrations of Pb, Zn, Fe, Cd, Cu and Ni were monitored during each run. A seven-step sequential extraction procedure was used to evaluate metal partitioning and concentration in the contaminated soil after treatment as a function of depth. The results showed the effect of the nature of flushing solution on the hydraulic behaviour of the columns. Metal concentrations in the leachate increased considerably upon the application of chelants, thus indicating their suitability for metal extraction from contaminated soils. In view of full-scale application of soil flushing, particular concern should also be devoted to ensuring a homogeneous distribution of the solution within the contaminated area and an efficient collection of the exhausted extracting solution, as well as to recovering and recycling the chelating agent used.

**Keywords:** soil flushing; contaminated soils; chelating agents; lead; column experiments

## 1. Introduction

Soil contamination has become a major environmental concern worldwide due to rapid industrialisation, increased urbanisation, intensive agricultural practices and inappropriate waste disposal methods. As a consequence, the need for soil remediation is growing and the development of new low-cost, efficient and environmentally friendly remediation technologies has generally become one of the key research activities in environmental science and technology [1].

With a view to metal contamination, factors affecting metal retention in soils include pH, particle size distribution, mineralogical composition, cation-exchange capacity, natural organic matter, the nature and age of contamination and the presence of interfering species [2]. All such

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factors affect the chemical speciation of contaminants in soils, which is in turn related to their solubility and potential bioavailability [3].

The technologies available for the remediation of metal-contaminated soils can be divided into two main groups, namely, immobilisation methods and separation/concentration methods. According to the former technique, contaminants are immobilised to limit their leaching and prevent potential impacts on groundwater. The latter remediation principle relies on either removing the contaminants from the soils or separating the highly contaminated soil fraction [4].

Soil flushing is an *in situ* soil-washing technique applicable to sandy soil or sediment with high hydraulic conductivity, especially when the contaminated area is located on top of a low-permeability layer which allows the process to be operated in a pump-and-treat mode [5].

To improve the contaminant extraction capacity, chelating agents have been widely tested for use in soil-flushing applications to metal-contaminated soils [6]. The co-extraction of soil minerals and organic matter during chelant-enhanced flushing, which can alter both the physical structure and the chemical properties of the soil, might however be detrimental to future land use and deserves considerable attention [7].

This study was carried out to test the effects of two different chelating agents, namely the biodegradable EDDS and the recalcitrant EDTA, on metal extraction from a field-contaminated industrial soil in a soil-flushing remediation process [8].

EDTA is an amino-polycarboxylic acid characterised by a large stability as a complexing agent; it has been extensively investigated for applications in contaminated soil and sediment remediation, due to its high extraction efficiency for most potentially toxic metals and the high stability of the formed metal complexes [9,10]. However EDTA is recalcitrant to biodegradation and is, therefore, characterised by a high environmental persistence [11], so that it is currently under scrutiny due to possible adverse health and environmental effects [12].

EDDS is a structural isomer of EDTA and is made up of two fragments of the amino acid aspartate, containing two chiral carbon atoms, resulting in the existence of three optical isomers, [*S*,*S*]-EDDS, [*R*,*R*]-EDDS and [*R*,*S*]-EDDS. Among these three isomers, only [*S*,*S*]-EDDS is readily and completely biodegraded [13,14] and exhibits low toxicity to fish and *Daphnia* [13]. Metal–EDDS complexes including Ca–, Cr(III)–, Fe(III)–, Pb–, Al–, Cd–, Mg–, Na– and Zn–EDDS have also been found to show successful biodegradation, as opposed to Cu–, Ni–, Co– and Hg–EDDS complexes [15]. The metal-chelating ability, accompanied by the short activity time span in the soil due to rapid biodegradation, could make this substance a promising substrate for use as a soil amendment for soil flushing or enhanced phytoextraction purposes [16].

Because of their strong chelating capacity, the application of both EDTA and EDDS to soils may change the amount and distribution of metals among their various chemical forms [17]. This can be estimated through selective extractive techniques aimed at exploring the geochemistry of metal contaminants in soil [18].

In this study, the metal mobilisation effect exerted by the two chelating agents during a soil-flushing treatment operated in a pulse mode was evaluated on a field-contaminated soil sample through laboratory-scale experiments. The metal-extraction capacity of EDTA and EDDS as a function of the amount of solution passed through the soil was evaluated, and the distribution of the residual contamination after treatment was also estimated. Because applications of flushing treatments to field-contaminated soils are much scarcer than those to spiked soils, the results of the present study are believed contribute to a widening of the data inventory on the process performance when operated on contaminated aged soils.

The main issues addressed during the study included: (1) the variation of hydraulic conductivity of the soil during the flushing process; (2) the mobilisation effect produced by the flushing solutions under different operating conditions (chelant type and dosage); and (3) the changes in metal distribution in soil upon flushing, to provide information on the residual metal-leaching potential of the flushed soil.

## 2. Materials and methods

### 2.1. *Materials*

The soil sample used for the experiments was obtained by mixing three different soils, including a highly Pb-contaminated soil from an abandoned industrial site located in the area around Enna (Italy), a sandy soil from a sandpit and a silty clay collected from the 100–150 cm top layer in an agricultural area in the area around Catania (Italy). The contaminated soil was a field soil exposed to natural ageing conditions for several years after the contamination event. The other two mixture constituents were added to attain a final soil hydraulic conductivity suitable for application of the flushing process. Prior to mixing, each sample was oven-dried at 105 ± 5 °C to constant weight and crushed to pass to a 2-mm sieve.

The soil mixture was characterised for a number of physical and chemical properties. Electrical conductivity (EC) and pH were measured on the soil slurry obtained by contacting the soil with deionised water at liquid-to-solid (L/S) ratios of 10 and $5\,\mathrm{L} \cdot \mathrm{kg}^{-1}$, respectively. The total metal content was determined by ICP-OES (Perkin–Elmer Optima 4300 DV) analysis of the liquid solutions obtained from acid digestion (1:3 v/v concentrated $HNO_3 + HCl$ solution). Total organic carbon (TOC) was analysed through a Shimadzu TOC-V CSH/CSN analyser.

The results from the initial characterisation of the soil is reported in Table 1.

### 2.2. *Experimental set-up*

The soil-flushing experiments lasted for more than 300 days and were carried out on five laboratory-scale (8.0 cm inner diameter, 50 cm height) polyethylene columns using either deionised water or a chelating agent as the flushing solutions. The columns were filled (from bottom to top) with: (1) 1 cm of acid-washed gravel (<5 mm); (2) 2 cm of acid-washed sand (<1 mm); and (3) 40 cm of dry soil (∼2900 g). Care was taken in compacting the soil layers in order to attain a uniform degree of compaction, with a final bulk density of $1.4\,\mathrm{g} \cdot \mathrm{cm}^{-3}$.

The flushing solution was fed into the column from the top layer, while the effluent solution was recovered from the bottom. Feeding was gravity controlled by a constant-head tank in which the liquid level was maintained constant throughout the experiment by means of an overflow weir.

The soil columns were exposed to room temperatures ($T = 20$–26 °C) during the operation. Each experiment was run on a single replicate.

One of the five columns continued to be flushed only with deionised water to be used as a control for comparison purposes. Each of the other columns was operated to simulate a flushing treatment in which the chelating agent was applied in a pulse mode to the soil for one bed volume stopping the flux to allow a contact time of 48 hours. Deionised water was continuously introduced

Table 1. Chemical and physical characteristics of the soil sample (dry weight basis).

| Parameter | Value | Elemental composition ($\mathrm{mg} \cdot \mathrm{kg}^{-1}$) | Concentration |
|---|---|---|---|
| pH | 7.0 | Pb | 2882 |
| Electric conductivity ($\mathrm{mS} \cdot \mathrm{cm}^{-1}$) | 2760 | Cd | 1.0 |
| Bulk density ($\mathrm{g} \cdot \mathrm{cm}^{-3}$) | 1.41 | Cu | 21.0 |
| TOC (%) | 1.81 | Fe | 8790 |
| Particle size distribution (%): | | Mn | 281 |
| Sand ($\Phi > 0.05$ mm) | 70 | Ni | 9.0 |
| Silt ($0.01 \leq \Phi \leq 0.05$ mm) | 18 | Zn | 28.0 |
| Clay ($\Phi < 0.01$ mm) | 12 | | |

Table 2. Characteristics of the experimental set-up.

| | Flushing solution | | | | |
|---|---|---|---|---|---|
| Run name | Type | Chelant dosage | Initial pH | Bed volume (mL) | Pore volume (mL) |
| Control | Deionised water | — | | 799 | 304 |
| EDTA3 | EDTA | $3\,\text{mmol} \cdot \text{kg}^{-1}$ soil | 4.60 | 879 | 334 |
| EDTA5 | EDTA | $5\,\text{mmol} \cdot \text{kg}^{-1}$ soil | 5.42 | 867 | 330 |
| EDDS3 | EDDS | $3\,\text{mmol} \cdot \text{kg}^{-1}$ soil | 9.30 | 955 | 363 |
| EDDS5 | EDDS | $5\,\text{mmol} \cdot \text{kg}^{-1}$ soil | 9.35 | 845 | 321 |

for the rest of the experiment. The disodium EDTA salt dihydrate ($C_{10}H_{12}N_2Na_2O_8 \cdot 2H_2O$) and the [*S*,*S*] isomer of EDDS ($Na_3$-N,N′ salt: $C_{10}H_{13}N_2Na_3O_8$) were used in the tests; two different concentrations (3 and 5 mmol kg$^{-1}$ of soil, respectively) of the two chelating agents were tested in separate experiments. Prior to the onset of the experiments, the columns were saturated with deionised water as the feeding solution for an equilibration period of 10 days.

The characteristics of the columns used during the experiments are reported in Table 2.

### 2.3. *Eluate analysis*

A number of parameters including pH, dissolved organic carbon (DOC) (Shimadzu TOC-V CSH/CSN analyser) and the total concentrations of Pb, Zn, Fe, Cd, Cu and Ni were measured at the outlet of each column to monitor the behaviour of contaminants during the soil-flushing treatment.

### 2.4. *Metal distribution in the soil after treatment*

Metal fractionation in the soil after the flushing treatment was estimated using the sequential extraction procedure proposed by Zeien and Brümmer [19], which is based upon seven extraction steps accomplished using the extraction agents indicated in Table 3. Details of the extraction method are also provided in the same table, which indicates the operational definition of both individual fractions and related components extracted.

The extraction procedure was applied to soil samples after treatment taken at two different depths, in order to evaluate the changes occurred in metal distribution in the soil along the column resulting from the flushing process applied.

## 3. Results and discussion

### 3.1. *Lead and DOC extraction*

As indicated in Figure 1, different hydraulic behaviours were observed for the five columns during the flushing process. The first part of the curves depicted Figure 1, where the average flow velocity was observed to increase with time, is related to the initial column operation, which implied the progressive saturation of the soil, then chelant solutions were added to four of the five columns. After ∼1 bed volume flushed through the columns, the flow velocity was found to decrease at different rates depending on the flushing solution; the decrease was more pronounced for EDDS than EDTA, and for higher chelating agent dosages. This reduction in soil permeability has also been reported in other studies [20,21]. Clogging represents a major problem in view of the application of chelant-enhanced flushing. This was attributed to soil dispersion [22], or the reverse of coagulation [23]. Besides, porosity and diffusion path for sorption and transport processes may

Table 3. Details of the sequential extraction procedure.

| Fraction no. | Operational definition of fraction | Operational definition of components extracted | Extractants | Extraction conditions |
|---|---|---|---|---|
| 1. | Mobile | Water-soluble and exchangeable metals, soluble metallorganic complexes | 1 M $NH_4NO_3$ (unbuffered) | 24-h shaking |
| 2. | Easily mobilisable | Specifically adsorbed, occluded close to particle surface, bound to carbonates, extracted from low-stability metal organic complexes | 1 M $NH_4OAc$ (pH 6) | 24-h shaking |
| 3. | Occluded in Mn oxides | Occluded in Mn oxides, specifically adsorbed, small portions of organically-bound metals | 0.1 M $NH_2OH$-HCl + 1M $NH_4OAc$ (pH 6) | 30-min shaking |
| 4. | Organically bound | Bound to organic matter | 0.025 M $NH_4$-EDTA + 1M $NH_4OAc$ (pH 4.6) | 90-min shaking |
| 5. | Bound to poorly crystalline Fe oxides | Occluded in poorly crystalline Fe oxy-hydroxides | 0.2 M $NH_4$-oxalate buffer (pH 3.25) | 4-h shaking in darkness |
| 6. | Bound to well crystalline Fe oxides | Occluded in well crystalline Fe oxy-hydroxides | 0.1 M ascorbic acid + 0.2 M $NH_4$-oxalate buffer (pH 3.25) | 30-min boiling |
| 7. | Residual | Residual | Microwave acid digestion | |

change upon aggregate breakdown. All these influences on soil physical and chemical properties may potentially limit the subsequent use of the treated soil.

The mode of EDTA and EDDS addition was a significant factor controlling the observed behaviour of metal leaching [24]. The concentrations of Pb and DOC in the column effluents are shown in Figure 2 as a function of the flushed volumes. It can be observed that for all the columns, Pb mobilisation peaked at a level which depended on the type and concentration of the flushing solution. The Pb extraction yield, attained using deionised water, was considerably lower than that observed for the other runs, as evident from the cumulative Pb release values in the different experiments.

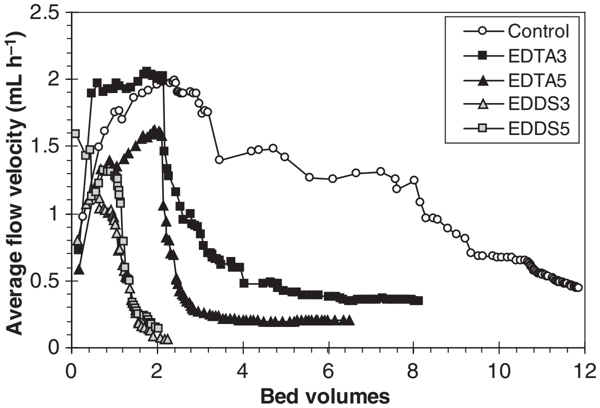

Figure 1. Average flow velocity vesus flushed volumes.

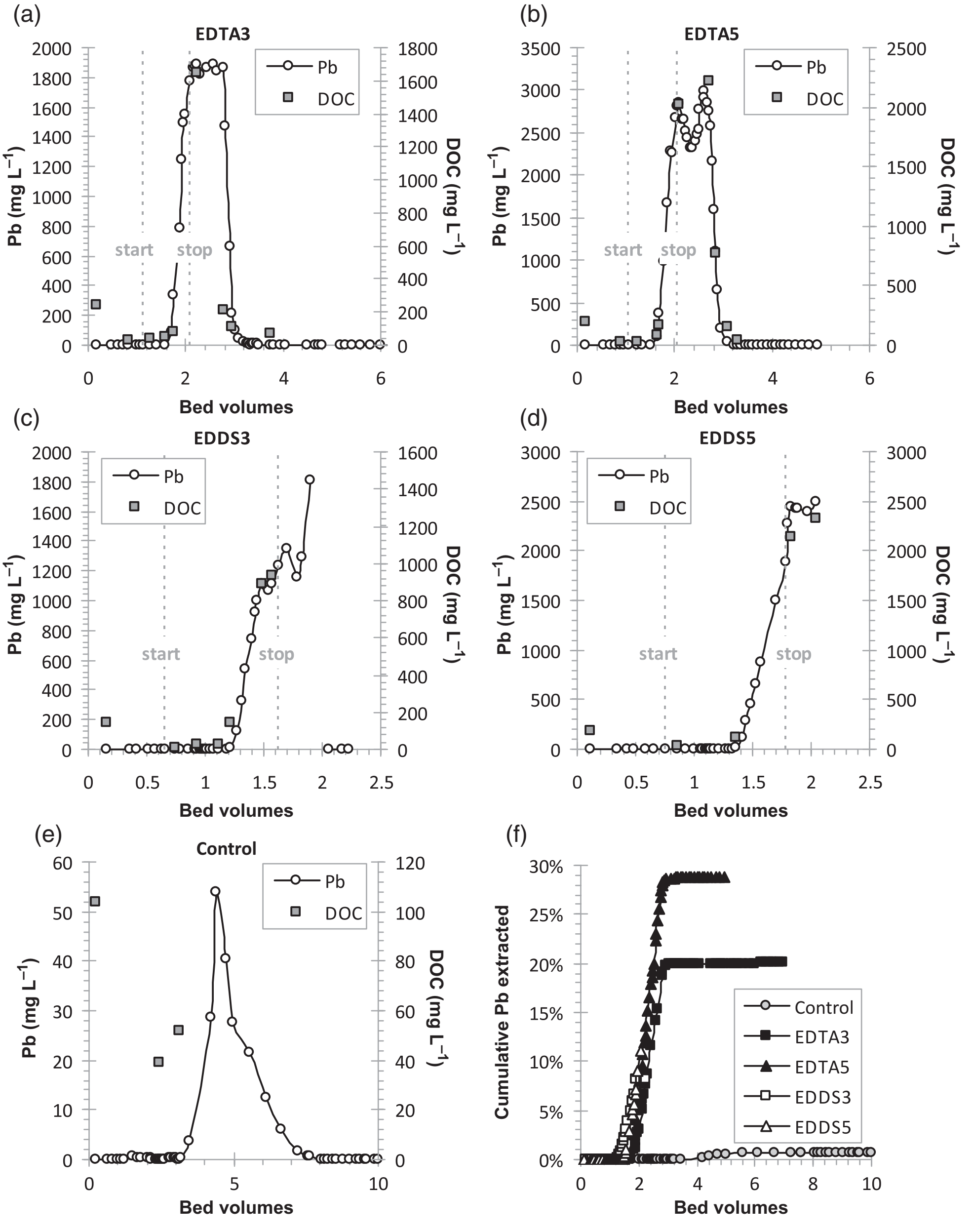

Figure 2. Pb and DOC mobilisation during the flushing treatment: (a) 3 mmol · kg$^{-1}$ EDTA solution, (b) 5 mmol · kg$^{-1}$ EDTA solution, (c) 3 mmol · kg$^{-1}$ EDDS solution, (d) 5 mmol · kg$^{-1}$ EDDS solution, (e) control, (f) cumulative amount of Pb extracted.

For chelant-based flushing, a positive effect of increased chelant concentration on Pb removal was clearly observed. As for the Pb mobilisation capacity of the two chelating agents, in the case of EDDS, the process appeared to be influenced by the lower volumes of solutions that could be flushed through the columns due to the clogging problems occurred: as a matter of fact, although the Pb concentrations in the column effluent were comparable for EDDS and EDTA at the same chelant dosage, the cumulative Pb removal was significantly lower for EDDS as depicted in Figure 2f).

The pH measured in the eluate samples was found to follow quite a stable pattern over time, varying in a relatively narrow range (8.0–8.6) along the individual experiments. While the initial effluent samples from the columns flushed with EDTA and EDDS were slightly more acidic than observed for the control column ($\mathrm{pH} \cong 8.2$), the pH tended to stabilise afterwards, reaching the above-mentioned values after a few fraction ($<0.8$) of the bed volumes eluted.

As for the DOC concentration in the column effluent, for the control run and the other experiments prior to chelant addition the measured values were at levels below $50\,\mathrm{mg \cdot L^{-1}}$, indicating the stability of organic matter under water-flushing conditions, which in turn is related to the ageing history of the investigated soil. Upon application of the chelating agents, the eluate DOC was found to increase with time until a peak value was reached. The peak DOC concentrations attained were $1645\,\mathrm{mg \cdot L^{-1}}$ (EDTA3), $2220\,\mathrm{mg \cdot L^{-1}}$ (EDTA5), $931\,\mathrm{mg \cdot L^{-1}}$ (EDDS3) and $2323\,\mathrm{mg \cdot L^{-1}}$ (EDDS5). Thereafter, the concentrations of DOC in the EDTA leachate solutions declined and remained at a fairly low level ($<70\,\mathrm{mg \cdot L^{-1}}$) after ∼2 bed volumes from chelant addition. Again, when EDDS was used as the flushing agent, the DOC evolution should be interpreted on account of the hydraulic behaviour of the columns. The cumulative amount of DOC eluted from each column was calculated as the integral of the corresponding curve as a function of the bed volumes passed through the column, and compared with the total DOC amount associated with the chelating agent flushed. The difference between the two values was found to be lower than ∼9%, indicating that the natural organic matter in the soil does not significantly contribute to DOC. For this reason, the DOC measured in the effluent solution can be assumed to be an appropriate measure of the chelating agent concentration. As a further verification, the correlation between the Pb and DOC concentrations in the eluates from each column was calculated, yielding correlation coefficient values in the range 0.95–0.99. This allows identification of the effect exerted by the chelating agents on lead extraction from the investigated soil.

### 3.2. *Release of other metals*

The concentrations of the other metals (Cd, Cu, Fe, Ni, Zn) in the column effluent are shown in Figure 3. These were analysed in order to provide information about the extraction capacity of other contaminants or major soil constituents by the chelating agents under study. The curves of metal leaching as a function of flushed volumes had similar shapes to those observed for Pb, with a peak occurring after ∼1 bed volume from chelant addition and a subsequent concentration decline to undetectable levels after additional 2.5–3 bed volumes.

The results of metal extraction reported in Figure 3 show the different metal mobilisation capacity by EDTA and EDDS, with significantly higher extraction yields obtained for most of the investigated metals when EDDS was used as the extracting agent. In particular, EDDS was found to produce a stronger mobilisation of Fe if compared with EDTA, with eluate concentrations peaking at $\sim 110\,\mathrm{mg \cdot L^{-1}}$ at both EDDS dosages after ∼1 bed volume of extracting solution passed through the column, although the overall amount of Fe extracted by EDDS accounted for a very low fraction (∼0.1%) of the total Fe content of the soil. It is well established that chelating agents are able to mobilise elements from major constituents of the solid matrix, including calcite, as well as Fe, Al and Mn (hydr)oxides [3,25–27]. The dissolution of soil minerals is generally associated with ligand exchange reactions where the surface metal–oxygen bonds are broken after the adsorption of the chelating agent on the mineral surface [28,29]. Despite the generally larger stability constants of complexes of trace metals (metals with <0.5% wt. content in soil), compared with those of major elements (elements with >5% wt. content in soil), these may act as strong competitors towards chelant-based complex formation due to their largely higher concentrations in soils, although the extent of competition phenomena is also strongly pH dependent and involves the formation of protonated and/or multidentate chelant complexes [3,10,30]. The fact that in the

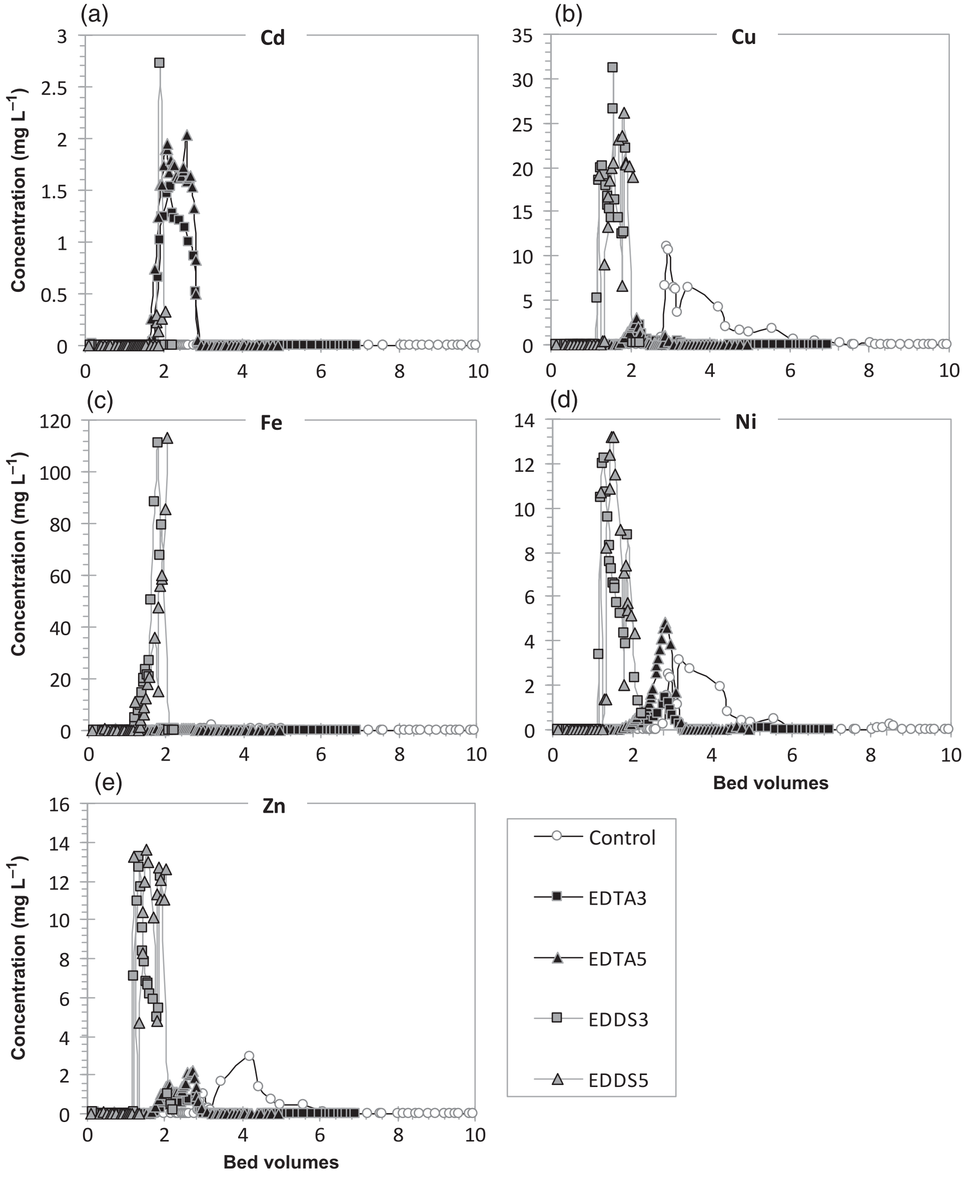

Figure 3. Metal mobilisation during the flushing treatment: (a) Cd, (b) Cu, (c) Fe, (d) Ni, (e) Zn.

present study EDTA did not display any appreciable mobilisation capacity towards Fe may be explained considering the slow dissolution kinetics of Fe (hydr)oxides by EDTA, as reported by a number of investigators [25]. Comparing the results obtained for Fe dissolution by the two chelating agents tested, despite the higher stability constant of Fe-EDTA$^-$ compared with Fe-EDDS$^-$ ($\log K = 27.7$ [31] as opposed to 22.0 [32]), it is believed that the stronger Fe mobilisation capacity by EDDS was related to the increased soil/solution contact time as caused by the lower flow velocity attained. It is likely that the longer contact times for the EDDS-flushed columns allowed for a closer approach to equilibrium conditions for the metal dissolution and complexation reactions.

For Cu, Ni and Zn, the peak concentrations in the column effluent from the EDDS flushing experiments were appreciably higher (∼2–3 times) than the corresponding values measured in the EDTA runs, indicating a generally stronger mobilisation capacity of EDDS if compared with EDTA. The cumulative amounts of metals extracted at 3 and 5 mmol · kg$^{-1}$ dosages were: for EDDS, 21 and 19% (Cu), 6 and 20% (Ni), 6 and 8% (Zn); and for EDTA, 1 and 2% (Cu), 3 and 8% (Ni), 1 and 2% (Zn). Only in the case of Cd does EDTA display a higher affinity than EDDS, with a cumulative extraction of 36 and 54% as opposed to 7 and 2% at the two chelant dosages adopted. Similar differences in mobilisation patterns by both chelants were observed in a phytoremediation application by Meers et al. [16], where Zn was extracted at roughly comparable levels for both chelants, Cu was mobilised to a larger degree by EDDS than by EDTA, Cd and Pb were mobilised more efficiently by EDTA than by EDDS and the initial mobilisation of Ni was higher for EDDS but was overtaken by EDTA as time progressed. As already discussed in the case of Fe mobilisation, the higher extraction capacity by EDDS that was noted in our experiments for most metals cannot be explained on the basis of the values for the thermodynamic stability constant of metal–chelant complexes. The log K values of EDTA complexes with the investigated metals are indeed higher than the corresponding values for EDDS complexes (Cu–EDTA$^{2-}$, 20.49; Cu–EDDS$^{2-}$, 18.35; Ni–EDTA$^{2-}$, 20.11; Ni–EDDS$^{2-}$, 16.78; Zn–EDTA$^{2-}$, 18.00; Cu–EDDS$^{2-}$, 13.49) [31,32]. Again, it is likely that the higher metal mobilisation capacity displayed by EDDS was caused by the longer contact time between the soil and the flushing solution. In the case of Cd, for which the stability constant of the EDTA complex is eight orders of magnitude higher than that of the corresponding EDDS complex (log K = 18.10 for Cd–EDTA$^{2-}$ and 10.94 for Cd–EDDS$^{2-}$) [31,32], the increase in contact time in the EDDS experiments could probably not outbalance the higher theoretical complexation capacity displayed by EDTA.

### 3.3. *Metal distribution in the soil after treatment*

One of the aims of the present work involved investigating the changes in metal distribution in soil resulting from the application of the flushing treatment. Pb partitioning in the soil was evaluated for the five experimental runs by means of sequential extraction, as described in Materials and Methods. For each column, the procedure was applied on samples taken at the end of each flushing experiment at two different column depths, namely the top and bottom layers; for the control column, the sequential extraction procedure was applied to a single sample, because the low overall extraction efficiency attained was assumed to imply only slight changes in metal distribution with column depth.

The analysis of sequential extraction data for the two major elements Fe and Mn for the control column indicated contents of 1480 mg Fe · kg$^{-1}$ for fraction 5 (occluded in poorly crystalline Fe oxy-hydroxides) and 6090 mg Fe · kg$^{-1}$ for fraction 6 (occluded in well crystalline Fe oxy-hydroxides), corresponding to ∼17 and ∼69% of total Fe, respectively; for Mn the amount associated with fraction 3 (occluded in Mn oxides, specifically adsorbed, small portions of organically bound metals) accounted for 243 mg Mn · kg$^{-1}$, corresponding to ∼86% of total Mn. It was found that in the case of Fe no appreciable reduction in the amount of either fraction 5 (occluded in poorly crystalline Fe oxy-hydroxides) and fraction 6 (occluded in well crystalline Fe oxy-hydroxides) occurred after treatment with the two chelating agents, irrespective of the adopted concentration and the investigated depth. This indicates that under the tested experimental conditions, the flushing solutions were not capable of producing any appreciable mobilisation of Fe oxides. A different behaviour was observed for Mn, with the amount associated with fraction 3 (occluded in Mn oxides, specifically adsorbed, small portions of organically bound metals) decreasing from the initial content of 243 mg · kg$^{-1}$ to 197–219 mg · kg$^{-1}$ when the EDTA solution was used, and 117–148 mg · kg$^{-1}$ when EDDS was the flushing agent. Such results indicate that the chelating agents used resulted in mobilising Mn oxides from the soil. In addition, although the Mn content in fraction 3 (occluded in Mn oxides, specifically adsorbed, small portions of organically bound metals), for columns EDTA3 and EDTA5, did not significantly change from top to bottom, more appreciable changes in Mn concentrations in fraction 3 with column depth were observed for columns EDDS3 and EDDS5. This confirms the previously discussed effect of increased contact time when the EDDS solution was used as the flushing agent.

The sequential extraction data are reported in Figure 4 in terms of Pb amounts associated with each soil fraction. The results for the control column soil show that the major portion of total Pb was associated with the fraction 2, specifically adsorbed, occluded close to particle surface, bound to carbonates, extracted from low-stability metal organic complexes (1705 mg Pb $\cdot$ kg$^{-1}$, corresponding to ∼60% total Pb), or to the fraction 3, occluded in Mn oxides, specifically adsorbed, small portions of organically bound metals (790 mg Pb $\cdot$ kg$^{-1}$, corresponding to ∼28% of total Pb). The other soil fractions contained <13% of total Pb overall. As for the influence of chelant-based soil flushing on Pb distribution, in general, fraction 2 of Pb (specifically adsorbed, occluded close to particle surface, bound to carbonates, extracted from low-stability metal organic complexes) and fraction 3 (occluded in Mn oxides, specifically adsorbed, small portions of organically bound metals) were found to be removed at roughly comparable levels in each experiment. Some Pb mobilisation from the remaining soil fractions was also observed, although with lower removal yields; this confirms previous findings from other literature studies, where chelating agents used for metal extraction from a contaminated soil were shown to be capable of partly dissolving soil matrix constituents including (hydr)oxides of major metals as well as organic matter [3,9,25].

Another important feature, resulting from the analysis, relates to the observed changes in Pb content with column depth. In particular, the bottom soil layer always had higher Pb contents than the top layer, although with a very similar partitioning among the various soil fractions; in addition, the difference in Pb content between column top and bottom increased with chelant concentration. Such behaviour is believed to derive from the discussed hydraulic effect caused by increased chelant dosages; specifically, as higher chelant additions were associated with stronger decreases in the average flow velocities and prolonged soil/solution contact time, it is likely that the enhanced metal extraction exhausted most of the metal complexation capacity of the chelating agents. This may also explain why the incremental Pb removal from soil at higher chelant dosages

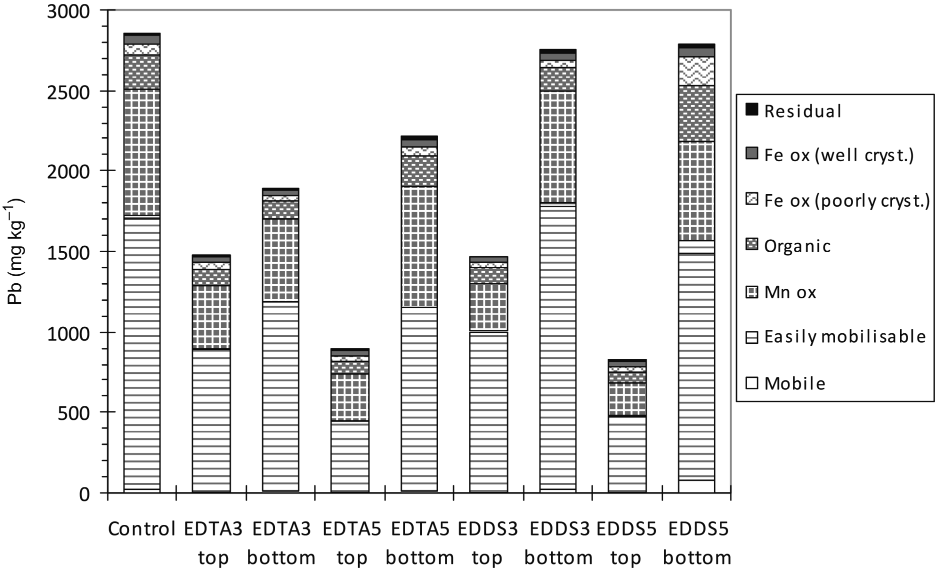

Figure 4. Sequential extraction results (Pb).

could mainly be ascribed to the contribution of the fraction 2 (specifically adsorbed, occluded close to particle surface, bound to carbonates, extracted from low-stability metal organic complexes) of the soil.

The above discussion suggests that longer flushing periods would be required to improve metal removal at greater soil depths, as this would increase chelant availability to lower soil layers. On the basis of the results discussed above, an interesting issue to be further elucidated appears to include the optimisation of chelant dosage and flushing rate as independent operating variables in order to enhance metal removal from soil and keep treatment costs at the lowest level.

## 4. Conclusions

EDTA and EDDS were used as reference chelating agents in laboratory-scale column experiments to investigate the effectiveness of chelant-enhanced flushing of a Pb-contaminated soil. The study aimed at comparing the performance of the biodegradable chelating agent EDDS with that of the recalcitrant EDTA isomer, in terms of both metal mobilisation yield and residual chelant concentration in the effluent solution. An appreciable cumulative mobilisation of Pb (up to 28% in the EDTA treatment) was observed for both chelating agents, with chelant dosage also affecting the extraction yield. In addition, large differences were observed between the two chelating agents in terms of effects on soil, with a sharp decrease in soil permeability when EDDS was used as the flushing solution, in turn affecting the overall performance of the remediation process.

With a view to evaluating the applicability of full-scale chelant-assisted soil flushing, ensuring low levels of residual chelant (either in the free form or as metal complexes) after treatment is deemed critical to prevent subsequent migration of mobile species in the surrounding environment. As a consequence, an overall environmental assessment of soil flushing is claimed accounting for potential side impacts on the environment as well as on human health and safety.

The full-scale application of assisted soil flushing should be cost-effective. To reduce remediation costs while improving the overall environmental profile of the process, recycling of the extracting agent is recommended [1]. This issue has been investigated by a number of authors [2,33–35], however, the chemicals and energy consumption of such recovery processes should also be carefully evaluated if a global life-cycle assessment of the remediation treatment is to be derived.

Because metal contaminants are conservative species being transferred from a solid (the soil) to a liquid phase (the flushing solution) during treatment, the need for appropriate processing and disposal of the effluent is an additional aspect that must be taken into account as far as the treatment cost and the consumption of both natural resources and energy are concerned.

All the mentioned aspects raise important concerns that require further investigation in order to improve the efficacy and the overall environmental profile of the remediation process.

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