Remediation of heavy metal contaminated soil washing residues with amino polycarboxylic acids

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ABSTRACT

Removal of Cu, Pb, and Zn by the action of the two biodegradable chelating agents [S,S]-ethylenediaminedisuccinic acid (EDDS) and methylglycinediacetic acid (MGDA), as well as citric acid, was tested. Three soil samples, which had previously been treated by conventional soil washing (water), were utilized in the leaching tests. Experiments were performed in batches (0.3 kg-scale) and with a WTC-mixer system (Water Treatment Construction, 10 kg-scale). EDDS and MGDA were most often equally efficient in removing Cu, Pb, and Zn after 10–60 min. Nonetheless, after 10 d, there were occasionally significant differences in extraction efficiencies. Extraction with citric acid was generally less efficient, however equal for Zn (mainly) after 10 d. Metal removal was similar in batch and WTC-mixer systems, which indicates that a dynamic mixer system could be used in full-scale. Use of biodegradable amino polycarboxylic acids for metal removal, as a second step after soil washing, would release most remaining metals (Cu, Pb and Zn) from the present soils, however only after long leaching time. Thus, a full-scale procedure, based on enhanced metal leaching by amino polycarboxylic acids from soil of the present kind, would require a pre-leaching step lasting several days in order to be efficient.

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1. Introduction

The release of heavy metals and other pollutants in society has made soil contamination one of the most important environmental problems. Heavy metals cannot be mineralized or decomposed, unlike organic contaminants, and must therefore be removed from the soil or be physically and/or chemically contained [1]. The large quantities of polluted soils make landfill disposal an unrealistic option, due to environmental constraints and space limitations. One commonly used method for remediation of contaminated soil is soil washing, which is a technique that uses water to separate fine soil components (clay and silt) from the coarse components (sand and gravel) in a mechanical process. The volume of contaminated soil is reduced, since the contaminants tend to bind to the small soil particles. Soil washing can be used on both organic and inorganic contaminants, but the main target contaminant group is heavy metals [2,3]. In the design of a washing process, treatment duration is of major concern. The time required to arrive at a given clean-up goal is depending on the nature of the metal retention mechanism and the influence of factors such as pH, soil type (composition, exchange properties, etc.), the presence of natural organic matter, age of the contamination, and the presence of other inorganic contaminants [2,4]. Synthetic complexing agents, chelators in particular, are sometimes used in combination with soil washing to further enhance the removal of metals. However, many of these chelators have long degradation times in soil, resulting in toxicity and stress to the community of soil-living microbes and eco systems [5–7].

There are many factors to consider when deciding whether an artificial chelating agent can be used in full-scale remediation or not. The chelating agents need to be added in excess in relation to the contaminant concentration, since they generally are non-selective and form complexes with most of the major polyvalent cations present in the soil (i.e., Fe, Mn, as well as Ca, Mg, etc.). The chemical state of the metals in the soil also affects the efficiency of the chelators, since metals in recently contaminated soils, as well as in artificially contaminated laboratory system, are more labile and accessible than metals in soils that are historically contaminated [2,6]. Furthermore, the chosen agent must be biodegradable but at the same time has a high metal binding capacity. It is also desirable that the chelator can be recovered and used several times, consid-

ering the economy of a full-scale process using chemicals that are expensive.

In the past, EDTA (ethylenediamineacetic acid) has been the most widely used chelating agent for extracting metals from contaminated soils [7–16]. EDTA has a high capacity for metal complexation and extraction but a comparably low biodegradability in the environment [7]. EDTA is also quite mobile in soils and can thereby be transported to the groundwater, together with the mobilized metals [7,8]. In several previous studies, EDDS ([S,S]-ethylenediaminedisuccinic acid) has been proposed as an environmentally friendly and safe chelant [14,17–23]. MGDA (methylglycinediacetic acid) is another example of a more environmentally friendly chelator [14,17]. Mineral acids like nitric acid could be used to produce a low pH that would lead to a release of adsorbed hydrolyzed (cationic) metals from the soil. However, in a technical scale it would be an advantage if a metal mobilization could be achieved at a near neutral pH. Solutions with low pH have negative effects on the soil washing equipment in terms of corrosion, and also lead to irreversible damage to the soil constituents.

The aim of this study was to test the capacity of some biodegradable complexing agents for removal of metals remaining in the soil after a conventional soil wash procedure. A batch study using solutions (neutral pH) with the two chelating agents EDDS and MGDA, and citric acid as a reference for comparison, was performed. EDDS, with four carboxylic groups and two potentially binding nitrogen positions in the molecule, is similar to EDTA in structure. MGDA, with three carboxylic groups and one nitrogen position in the molecule, is similar to NTA (nitrilotriacetic acid). Citric acid contains three carboxylic groups, as well as a hydroxy group (not complexing at low or near neutral pH). The same chelators were tested in a 10 kg-scale using equipment designed for soil washing (Water Treatment Construction), WTC-mixer, which can be used in a full-scale process in combination with a conventional soil washing technique. The key issues were: (1) Can metals remaining in contaminated soil, after conventional soil-wash that has removed the metal carrying fine-fraction, be released due to the action of the selected biodegradable amino polycarboxylic acids? (2) How do these agents compare with citric acid in terms of metal removing capacity? (3) Is it feasible to design a full-scale remediation process based on soil-wash, combined with a subsequent leaching step using biodegradable strong complexing agents? Thus, the aim is neither to establish the complexing capacity of EDDS and MGDA, which is already well-documented, nor to compare results from unique contaminated soils of various origin or compile data from different cases in a review of the performance of EDDS and MGDA. The main purpose is to find out if the metal fraction remaining after soil-wash, in some selected soils from sites with old and aged metal contamination, can be removed with EDDS/MGDA, and if the WTC-procedure, giving short leaching times, can be utilized in a one-step soil-wash remediation procedure.

2. Materials and methods

2.1. Soil characterization

The soil residues after conventional soil washing of three heavy metal contaminated soils (A–C) were used:

A: A sandy soil, low in natural organic matter; from an industrial site with mixed contaminants (metals as well as hydrocarbons).

B: A sandy coarse-grained moraine with minor amounts of organic matter; from a shooting-range.

C: A clay-dominated soil with minor amounts of organic matter; from a steel works site.

Table 1
Total acid leachable[a] metal concentrations (mg kg^{-1}), pH[b], and ignition residue[c], LOI (%) in soils A, B and C. $N = 3$, mean ± SD. MKM = Limits for soil usage on areas that are less sensitive, established by the Swedish Protection Agency [23].

	Soil A	Soil B	Soil C	MKM
Al	14600 ± 820	7930 ± 380	6160 ± 190	
Cr	56 ± 14	67 ± 14	370 ± 57	150[d]
Cu	230 ± 9.0	400 ± 75	84 ± 60	200
Fe	23100 ± 480	23500 ± 3270	55200 ± 5480	
Mn	300 ± 37	370 ± 74	680 ± 59	
Ni	38 ± 8.0	39 ± 4.0	250 ± 57	120
Pb	2370 ± 260	2520 ± 1040	480 ± 27	400
Zn	200 ± 5.0	790 ± 270	170 ± 80	500
pH	6.9 ± 0.1	7.0 ± 0.2	5.8 ± 0.1	
LOI	12.0 ± 0.1[e]	1.5 ± 0.3	1.1 ± 0.2	

[a] Microwave digestion with 7 M HNO_3.
[b] Water to solid 1:5 (v:v).
[c] 550 °C, 2 h.
[d] Not exceeding 1% Cr(VI).
[e] Including some 10 mg kg^{-1} hydrocarbons.

The three soils come from different locations, but all are similar in composition: moraine, rich in feldspars and quartz (sand) with minor fractions of natural organics, and usually low levels of clays (less than 5%, except for soil C).

After the conventional soil washing, most of the fine-fraction (including essentially all of the clay) was removed. Soil washing is merely separation of the fine-fraction of the soil from the course material by suspension in water and removal of the water phase that carries the suspended particulate and colloidal matter [25]. Particles with diameters below 0.1 mm are to a large extent separated from the rest of the soil. This size fraction generally carries most of the metal contamination. The remaining residues (soils A–C) were highly heterogeneous with respect to the size distribution with particle sizes ranging from 0.1 to 2 mm, with larger grains up to 5 mm, and with visible metallic residues (soil C). Grains above 2 mm in size were removed from the soils prior to the leaching tests.

The cation exchange capacities of the soils were not measured. However, they are all sandy and fairly coarse-grained with minor amounts of clayish materials remaining (after the soil washing that removed the clay fraction with its associated exchangeable metals). The exchange capacity would not be expected to exceed 25 meq kg^{-1}, considering the general composition of the soils [24]. However, the major mechanism for adsorption of the metals in this study (Cu, Zn, Pb, as well as Fe) would be surface complexation of hydrolyzed species, rather than electrostatic interaction (ion-exchange), as well as co-precipitation with Fe (and possibly Al) constituting a hydroxide carrier phase.

The present leaching experiments were performed on the residues that still carried considerable levels of heavy metals, i.e., did not reach the desired remediation levels (MKM—limits for soil usage on areas that are less sensitive, c.f. Table 1), that are established by the Swedish Environmental Protection Agency (SEPA) [26]. The total metal concentrations of the soil residues (acid digestion, 7 M HNO_3) are given in Table 1, and the distribution of metals, as defined by sequential leaching, is given in Fig. 1, based on the Tessier procedure [27], slightly modified.

F1   Water-soluble (water; 20 °C)
F2   Cation exchangeable (1.0 M NH$_4$Ac, pH 7; 20 °C)
F3   Carbonates and hydroxides (1.0 M NH$_4$Ac, pH 5.0; 85 °C)
F4   Hydrous oxides (0.043 M NH$_2$OH–HCl in 25% acetic acid (v/v); 85 °C)
F5   Labile organics and amorphous metal sulfides (0.02 M HNO$_3$ and 30% H$_2$O$_2$ (3:5, v/v), pH 2.0; 85 °C); after completed leaching 3.2 M NH$_4$Ac in 20% HNO$_3$ + water was applied
F6   Consolidated organics, metal sulfides and residual fraction (microwave digestion in 7 M HNO$_3$)
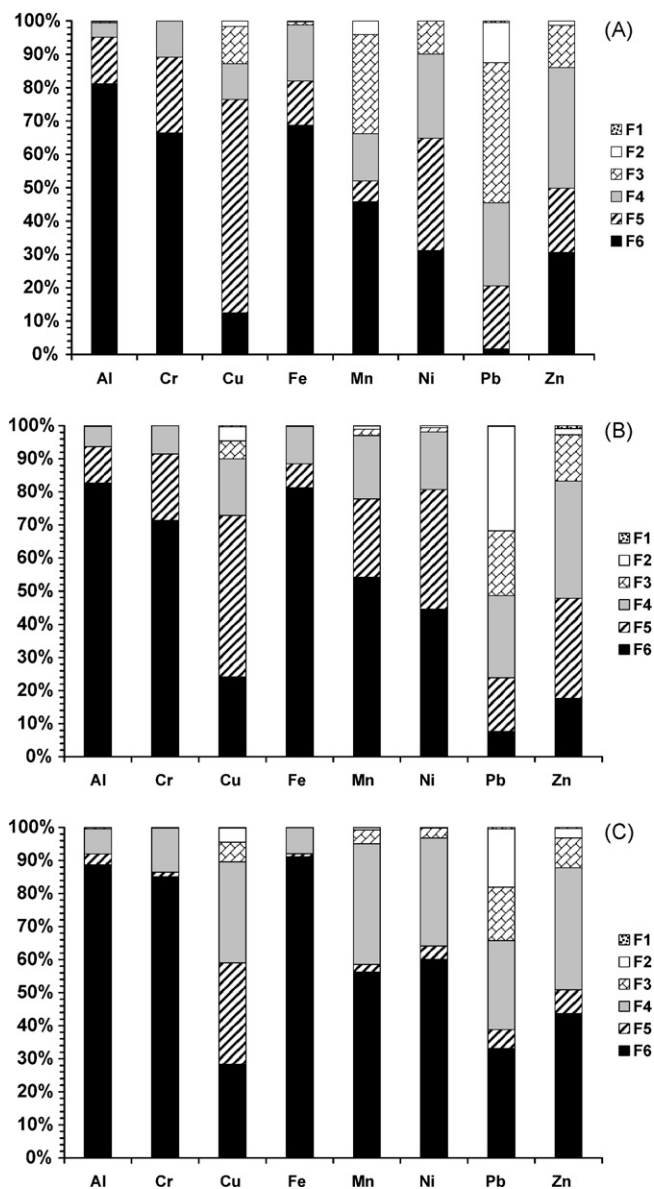
Fig. 1. Sequential extraction of metals (Al, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) from soils A, B and C: Six extraction steps, modified from [24]. F1 = Water-soluble; F2 = cation exchangeable; F3 = carbonates and hydroxides; F4 = hydrous oxides; F5 = labile organics and amorphous metal sulfides; F6 = consolidated organics and metal sulfides (residual). The fractions represent mean values, N = 3.
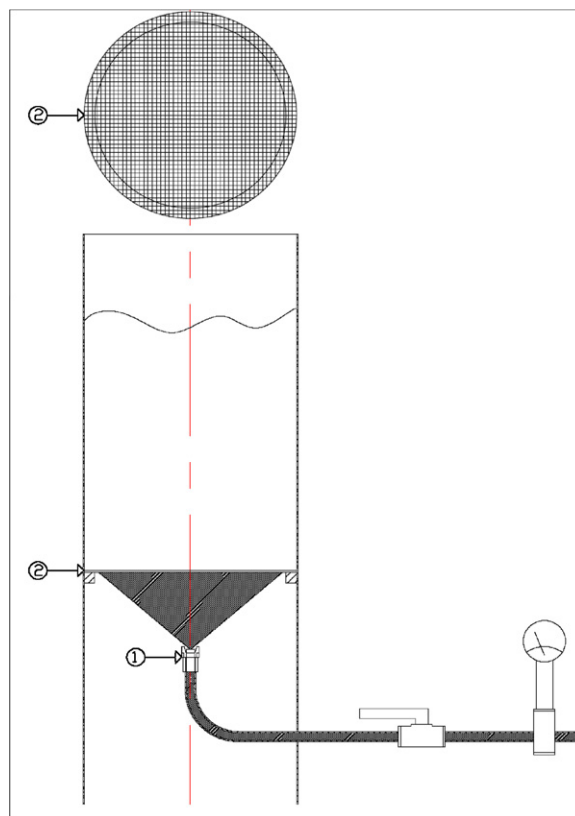

Fig. 2. Schematic illustration of the WTC-mixer system. The fluid phase comes from a die (1), designed to create the right drop size. The pressure of the fluid creates droplets that hit the soil material (grains) that is placed on a net (2).

2.3. Dynamic washing—the WTC-system

The WTC-mixer [28] is schematically illustrated in Fig. 2. The fluid phase (water) comes from a die, specially designed to create the right drop size (point 1 in Fig. 2). The pressure of the fluid creates highly energetic droplets and these droplets hit the material (grains) that is placed on the net (point 2 in Fig. 2). The solid material on the net is exposed to a bombardment of distinct droplets. Pressure, droplet size, flows and temperature in the mixing zone can be varied. These parameters were fixed throughout all of the experiments to allow for a direct comparison with the batch experiments.

The two amino polycarboxylic acids used in the batch studies (0.18 M EDDS and MGDA, pH 7), together with tap water (pH 8.2) as a control, were used also in the WTC-system (10 kg of soil flushed with 10 or 20 L solution). The applied pressure was 2.5 MPa. The water solutions were collected in 50 L containers and were continuously agitated by a metal blade rotor (100 rpm) during the flushing. When no soil was left inside the WTC-mixer (after less than a minute), the agitation was terminated. Samples (triplicates) of the slurries were collected after 10, 20, 30, and 60 min, 24 h, and 10 d (without agitation). The samples were centrifuged for 6 min (4000 rpm) and the supernatants were acidified with 1% HNO_3 and stored at 4 °C prior to metal analysis. The slurries were pH-adjusted with HNO_3, when needed, in order to maintain a constant pH during the 10-d experiment.

2.4. Analysis of metals

Metal concentrations in all solutions were analyzed by ICP-OES (Plasma 4000 DV, PerkinElmer, USA). Eight elements were quantitatively determined: Al, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. Data

2.2. Batch experiments

The soil residues (A, B, and C) were exposed to solutions with complexing agents: 0.18 M EDDS (pH 7), 0.18 M MGDA (pH 7), and 0.18 M citric acid (pH 7). Tap water (pH 8.2) was used as a control. The chosen molarity of the chelating agents was about one order of magnitude above the total levels of the metals Cr, Cu, Ni, Pb and Zn in the soils, c.f. Table 1. 300 g of soil was continuously agitated (200 rpm) together with 300 mL solution in 2.5 L plastic containers. Samples (triplicates) of the slurries were collected after 10, 20, 30, and 60 min, 24 h, and 10 d. The samples were centrifuged for 6 min (4000 rpm) and the supernatants were acidified with 1% HNO_3 and stored at 4 °C until metal analysis. A constant pH of 7 was maintained throughout the experiment (adjustments with HNO_3 and/or NaOH).

evaluation was carried out with the PerkinElmer WinLab32 software, and quantification and identification were achieved by using standard solutions (0.02–7 mg/L) with calibration curves for each element. All solutions were acidified with 1% HNO_3 before analysis.

2.5. Statistical analysis

All soil experiments were performed in triplicates, and the results are presented as mean ± standard deviation, SD. Statistical analysis was performed with MINITAB 15 for WINDOWS (Minitab Inc., USA).

A general linear model (GLM) multivariate analysis was used to test for effects of experimental solutions (EDDS, MGDA, and citrate) for the different soils (A, B, and C) on metal mobilization (Cu, Zn and Pb) over time (10, 20, 30, 60 min, 24 h, and 10 d). The post hoc test used for multiple comparisons for observed means was Tukey's test at the 5% level of significance. Pair wise comparisons were made both between the soils (metal leaching over time between soils A, B, and C) and within each soil (metal leaching over time within soil A, B, and C, respectively) and also between batch and WTC-mixing studies.

3. Results and discussion

All three soils contained high levels of Pb and Zn, as well as Cu (A and B) and Cr and Ni (C) (Table 1). The standard deviations (three replicates) were high for some of the soil systems, particularly for Pb in soil B (soil from shooting-range containing minor particles of metallic Pb), as well as for Cu and Cr in soil C (refractory particles of alloys containing these elements, as well as Ni and Zn). The presence of these particles makes the soils heterogeneous with respect to the loads of contaminating metals, although the soil matrix is fairly uniform. The initial mobilization (10 min to 24 h) of Cu, Pb, and Zn from the soils is illustrated in Figs. 3–5, and the total acid leachable fraction of metals and the release of metals after 10 d are presented in Figs. 6–8. Concentrations of Cr and Ni in the leachates from soil C were low, corresponding to releases of less than 3 mg/kg, and are not presented. Water (control system) was not able to release more than 0.5% metals (after 10 d), in both the batch experiments and WTC studies. The results from the control systems are therefore not further presented or discussed.

3.1. Release of Cu

The release of Cu from the three soils (batch as well as WTC) is illustrated in Fig. 3.

Less than 10% of the Cu was released from the soil with the highest Cu-level (B) after 10 min, but increasing to around 20% after 24 h in the EDDS and MGDA-systems, and with a similar release in the citrate system. A larger fraction of the Cu was released by EDDS and MGDA from soil A (second highest initial Cu-load), going from around 20% (after 10 min) to above 40% (24 h), with the citrate system 5–10% lower. The release from soil C (lowest initial Cu-level) was similar, going from less than 20% (10 min) to some 30% (after 24 h) for EDDS and MGDA, the citrate giving a lower release. Results from the WTC-systems were similar, although a slightly lower release after 24 h (no agitation). The copper in soil A is predominantly released in extraction step F5—labile organics and amorphous metal sulfide (c.f. Fig. 1), in contrast to soils B and C, which could be an explanation to the difference in leachability between A and the other two soils after short leaching times.

After 10 d, the releases of Cu were of the order 80% or higher for soils B and C (EDDS and MGDA, Figs. 7 and 8) but only reaching some 50% in soil A (Fig. 6). The effects of longer exposure times were minor in the citrate systems. However, the results after 10 d demonstrate the opposite from the short extraction times: Higher
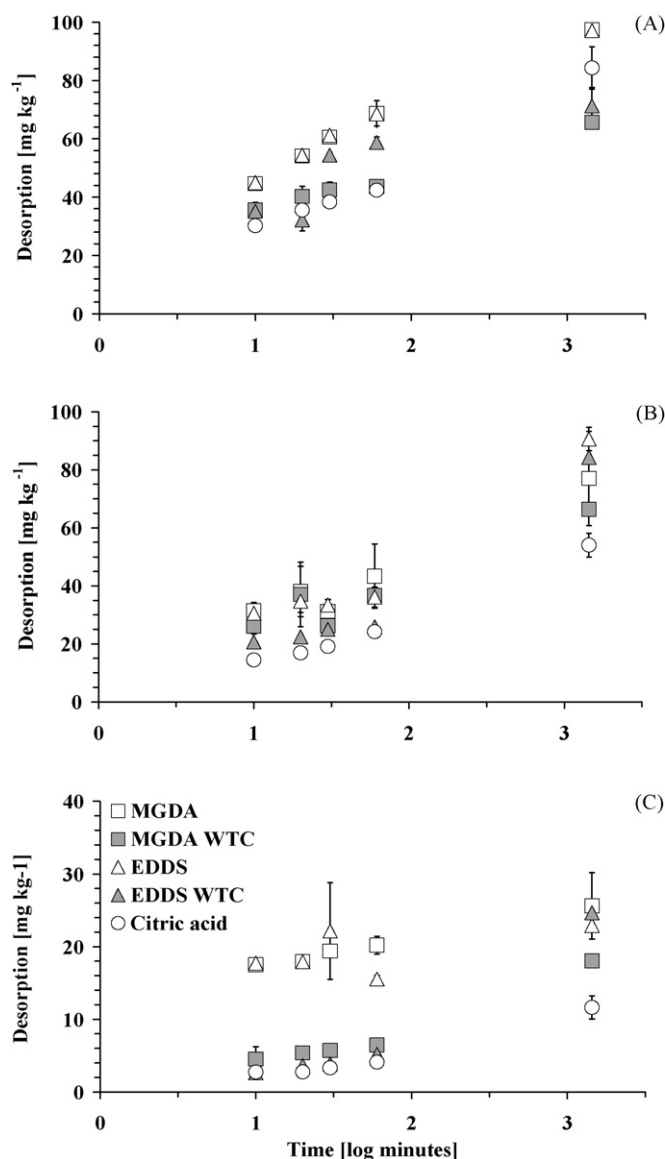

Fig. 3. Mobilization of Cu from soils A, B and C (mg kg^{-1} desorbed metal) by the complexing agents MGDA, EDDS and citric acid (0.18 M, pH 7) as a function of reaction times (10, 20, 30, 60 min, and 24 h (log min)). Symbols represent mean ± SD, $N = 3$. Total concentration (mg kg^{-1}) of Cu in soil A = 230 ± 9, soil B = 400 ± 75; soil C = 84 ± 60.

leaching from soils B and C than from soil A. This illustrates the qualitative nature of the arbitrary definitions of leaching mechanisms in the sequential leaching scheme [27]. There are evidently copper species that are leachable with complexing agents from soils B and C, but not from A, given time enough.

The release of Cu was of similar magnitude for EDDS and MGDA during the initial phase (10 min to 24 h), but possibly higher for EDDS than for MGDA after 10 d (for soils A and B, but not C), and significantly higher than for the citrate systems (all soils). There was no clear correlation with the stability constant for the Cu-complexes (log k_1 = 3.50, 18.4 and 13.88 at I = 0.1 for citric acid, EDDS and MGDA, respectively [6,29]), except that the citrate systems generally gave the lowest release.

3.2. Release of Pb

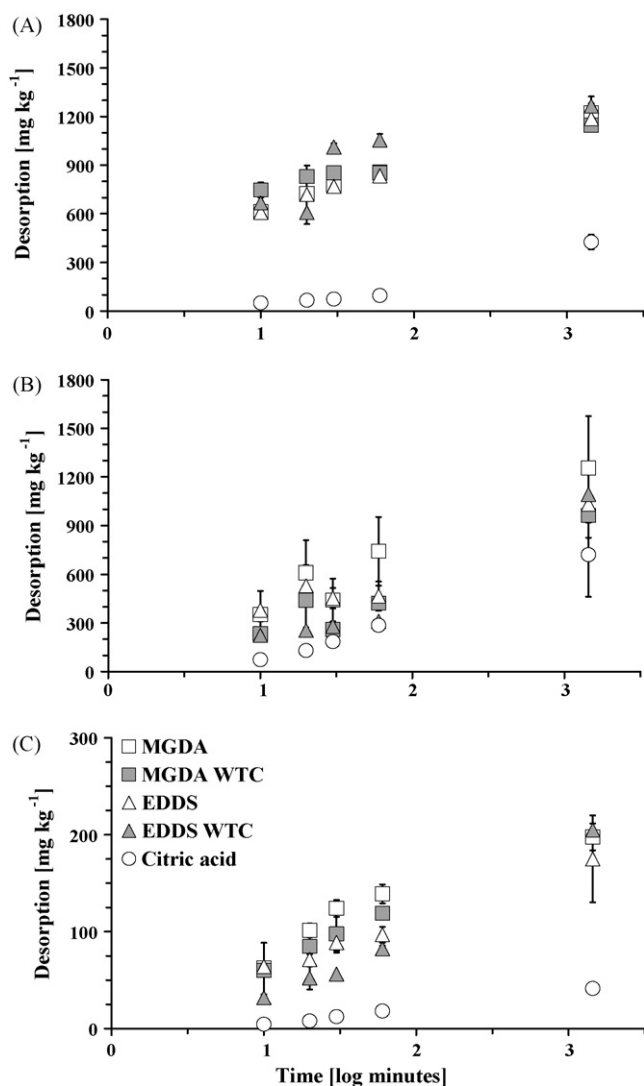The release of Pb from the three soils (batch as well as WTC) is illustrated in Fig. 4.

Fig. 4. Mobilization of Pb from soils A, B and C (mg kg^{-1} desorbed metal) by the complexing agents MGDA, EDDS and citric acid (0.18 M, pH 7) as a function of reaction times (10, 20, 30, 60, and 24 h (log min)). Symbols represent mean ± SD, $N = 3$. Total concentration (mg kg^{-1}) of Pb in soil A = 2370 ± 260, soil B = 2520 ± 1036; soil C = 480 ± 27.

3.3. Release of Zn

The release of Zn from the three soils (batch as well as WTC) is illustrated in Fig. 5.

Less than 5% of the Zn was released from the soil with the highest Zn-level (B) after 10 min, but increasing to around 10% after 24 h in the EDDS and MGDA-systems, and lower in the citrate system. The release from soils A and C by EDDS and MGDA was similar, less than 5% after 10 min and increasing to maximum 10% after 24 h. Results from the WTC-systems were similar, although a slightly higher release after 24 h for soils A and B.

After 10 d, the release of Zn was only some 35% for soils B (Fig. 7) and C (Fig. 8) with EDDS or MGDA (up to 50% in the WTC-system soil B) and less than 10% in soil A (Fig. 6). The effect of longer exposure time was minor in the citrate systems. There is no evident explanation to the low release, particularly in soil B, which holds a significant load of Zn that cannot represent natural background but must be an external contamination. The fraction represented by leaching step 6 (residual; Fig. 1) is, however, significant, par-
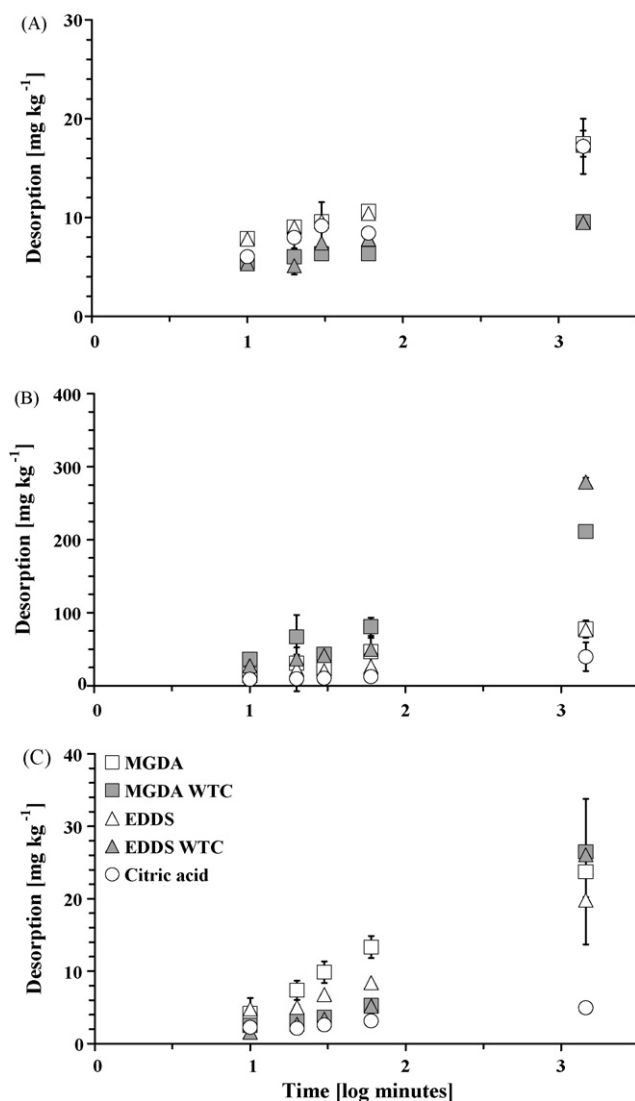

Fig. 5. Mobilization of Zn from soils A, B and C (mg kg^{-1} desorbed metal) by the complexing agents MGDA, EDDS and citric acid (0.18 M, pH 7) as a function of reaction times (10, 20, 30, 60 min, and 24 h (log min)). Symbols represent mean ± SD, $N = 3$. Total concentration (mg kg^{-1}) of Zn in soil A = 200 ± 5, soil B = 720 ± 270; soil C = 170 ± 80.

Above 30% and around 20% of the Pb was released from soils A and B, respectively, with the highest initial loads, by EDDS and MGDA after 10 min. The release increased to 50% and 40%, respectively, after 24 h. The releases from the citrate systems were significantly lower, just as for Cu. The release from the soil with the lowest initial load (C) was lower at the start (10% after 10 min) but increasing to some 40% after 24 h. Results from the WTC-systems were similar.

After 10 d, the release of Pb was almost quantitative from soil B (Fig. 7) and above 80% for soil C (EDDS and MGDA, Fig. 8) but only some 50% from soil A (Fig. 6). There is no evident explanation to this difference between the soils from the sequential leaching results (Fig. 1).

Just as for Cu, the release of Pb was of similar magnitude for EDDS and MGDA during the initial phase, but also after long time (10 d). The stability constants are similar for EDDS and MGDA, but lower for citrate (log k_1 = 4.08, 12.7 and 12.1 at I = 0.1 for citric acid, EDDS and MGDA, respectively [6,29]).
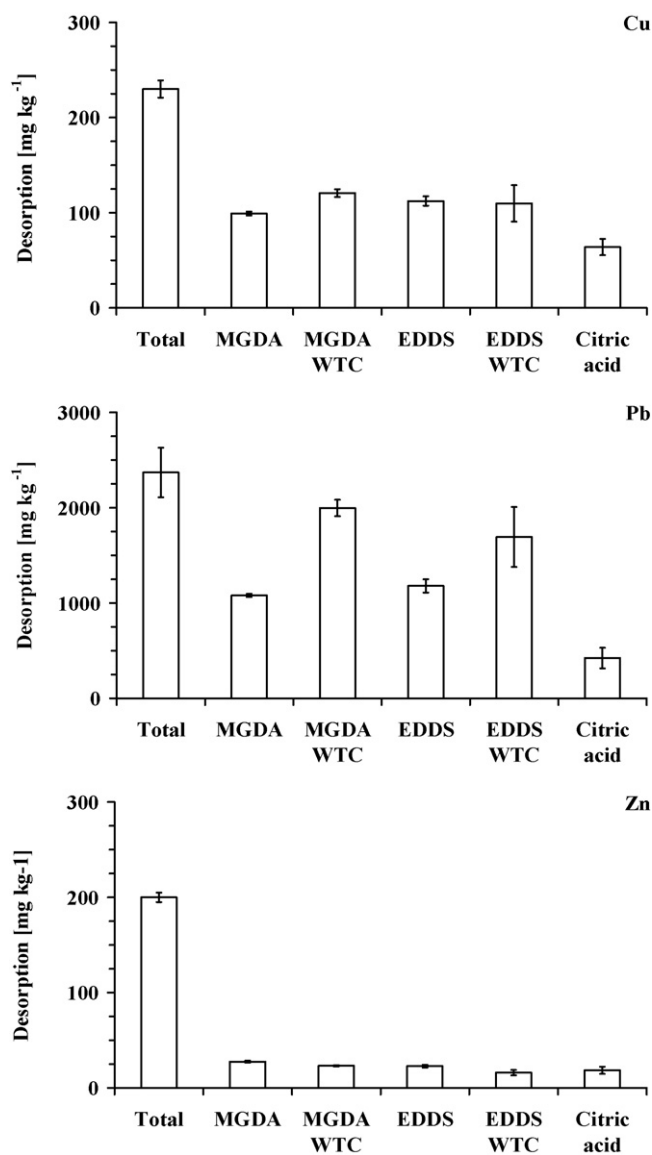
Fig. 6. Total acid leachable fraction (microwave digestion) and mobilization of Cu, Pb, and Zn from soil A (mg kg^{-1} desorbed metal) after 10 d of leaching with 0.18 M chelating agent at pH 7 (EDDS, MGDA and citric acid). Bars represent mean ± SD, N = 3.

Fig. 7. Total acid leachable fraction (microwave digestion) and mobilization of Cu, Pb, and Zn from soil B (mg kg^{-1} desorbed metal) after 10 d of leaching with 0.18 M chelating agent at pH 7 (EDDS, MGDA and citric acid). Bars represent mean ± SD, N = 3.

3.5. Remediation success in relation to remediation goals

EDDS and MGDA were both efficient in releasing Cu and Pb from all three soils at the level 10–20% after 10 min in the agitated batch systems and increasing to 40–50% after 24 h. The removal was 50–100% after 10 d except for one soil where Cu might be bound as very stable organic species, and Pb was not leachable to the same extent as in the other soils. Citric acid was less efficient, particularly for Pb. The release of Zn was clearly below 5% after 10 min, and still below 10% after 24 h, with maximum release levels of 35% after 10 d. Evidently, a considerable fraction of Zn is present as a strongly adsorbed species (or as a sparingly soluble refractory compound). Major constituents such as Fe and Al were not released, not even after 10 d, with the exception of soil A, where some Fe may be present as an oxy-hydroxide.

Soil C already had an initial Cu concentration below the desired remediation level. A reduction of the Cu concentration close to or below the MKM-value was achieved with MGDA and EDDS in soils A and B, but not with citric acid for soil B. A reduction of the Pb-level close to or below the MKM-value was also achieved for soils B and C, but not A. Reduction of Zn-levels to close to or below MKM

ticularly for soil C (presence of insoluble metal alloys). Stability constants (log k_1 = 4.86, 13.4 and 10.98 at I = 0.1 for citric acid, EDDS and MGDA, respectively [6,29]), are of the same magnitude as for Pb.

3.4. Release of Fe, Al and Cr

The release of Fe, Al and Cr from the three soils (batch as well as WTC), was less than 0.2% of the total inventory after 24 h in all systems and below 1% after 10 d (soils B and C). In soil A, however, as much as 10% of the total Fe was solubilized, which could be an indication of the presence of an oxy-hydroxy phase or some other leachable iron species. The sequential leaching, Fig. 1, rather indicates that Fe, as well as Al and Cr, predominantly appear in the residual fraction. However, fractions F4 and F5 are somewhat larger for soil A than for the other two soils, which possibly would confirm the presence of a fraction that can be leached after long time in soil A, but not in B and C.
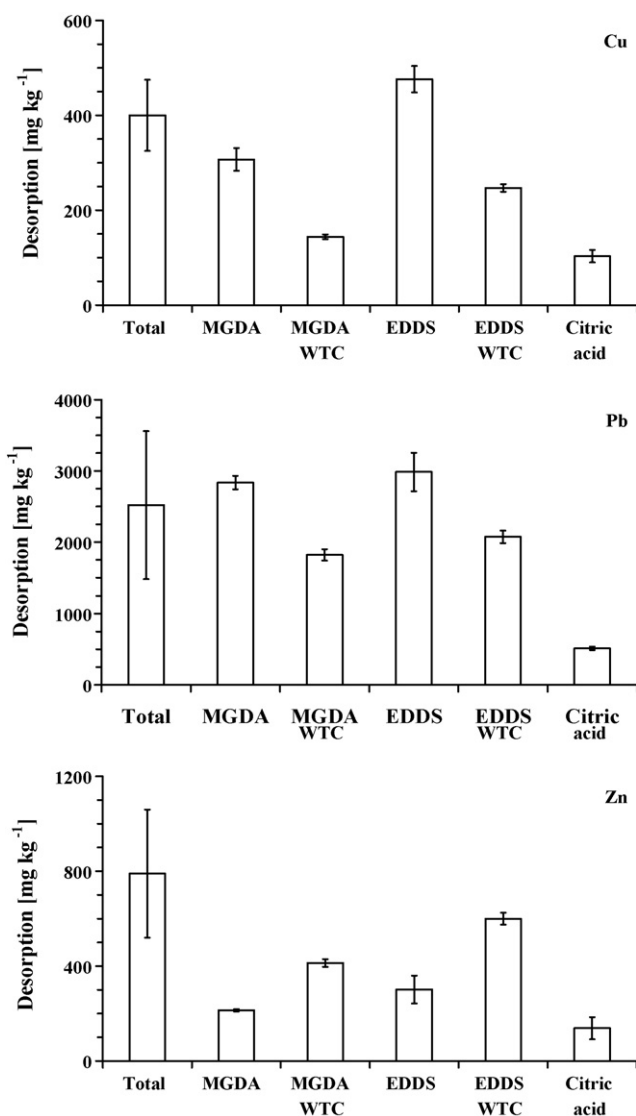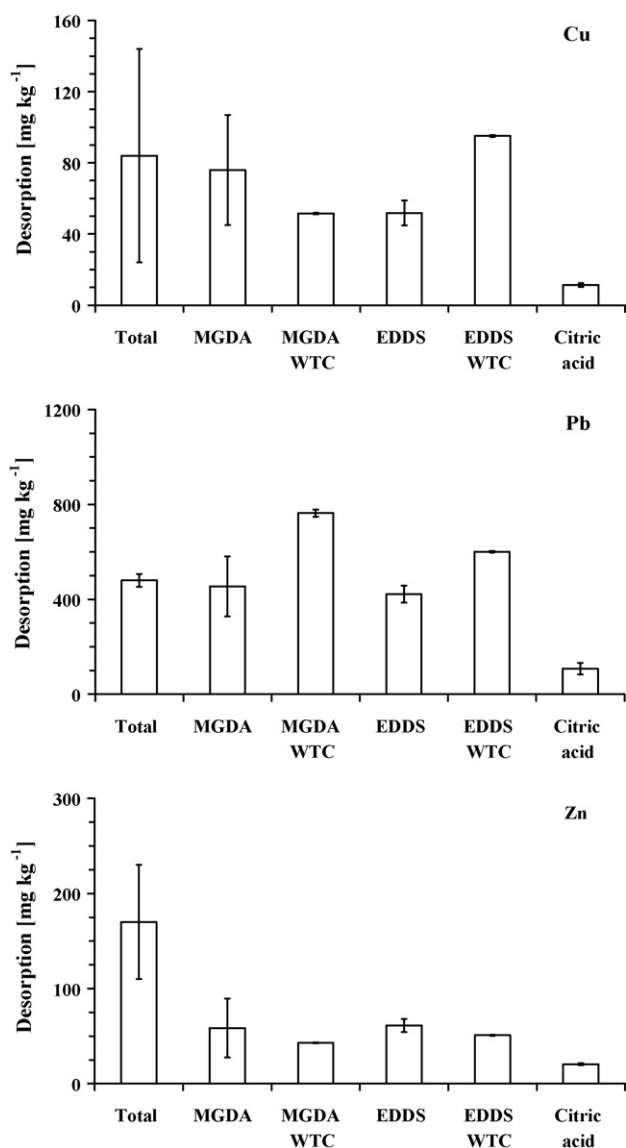
Fig. 8. Total acid leachable fraction (microwave digestion) and mobilization of Cu, Pb, and Zn from soil C (mg kg^{-1} desorbed metal) after 10 d of leaching with 0.18 M chelating agent at pH 7 (EDDS, MGDA and citric acid). Bars represent mean ± SD, $N = 3$.

was achieved for soil B, with the highest initial loads, the other soils having initial loads below MKM.

Metal release after long contact time could reflect not only desorption of secondary metals but also dissolution of the soil. However, this is probably not an important mechanism under the present conditions (neutral pH); the maximum release of metals by the complexing agents does not exceed the total acid leachable fraction, Figs. 6–8.

In the WTC-system (10 kg-scale), the soil particles were exposed to a flush of droplets, however only for a short period of time (matter of seconds, less than 1 min), followed by a passive exposure to the leachant without agitation. The results in terms of release capacities were in most systems similar to the results from the batch systems, with agitation. Nonetheless, the metal release (Cu, Pb) from the WTC-systems from soil B, was slightly lower than from the batch experiments (continuous agitation for 10 d) and conversely, for soil A, the WTC-systems were slightly more efficient. Soil A contained a visible oily organic fraction that evidently was suspended during the intense leachate flushing in the WTC-

system. This was not observed in the batches despite continuous agitation.

Converting the measured metal concentrations (mg kg^{-1}) in the leaching solutions into a kinetic unit (mg kg^{-1} min^{-1}, not shown), results in extraction rates of metals that are continuously decreasing over time. This indicates that the remediation might arrive at the desired clean-up goal faster if the soil washing had been performed in multiple steps over a shorter period of time. Previous studies with chelator-assisted metal remediation with EDDS [30,31] have indicated that a multiple step treatment with stoichiometric chelator additions would be more efficient in releasing metals than a single-step treatment with higher chelator concentrations Other studies have, however, shown that this is not always feasible [32,33]. These investigations compared multiple step *in situ* soil washing (10 mM EDDS added for each step) with *ex situ* single-step soil washing (40 mM EDDS), were the latter was more efficient in removing Pb from the soil. The explanation to the lower extraction efficiency of the 2nd to 4th cycles in the *in situ* experiments was that the repacking of the soil into the columns reduced the soil volume, structure and porosity, which were most likely vitally important for the Pb extraction efficiency. This should not be a problem in an *ex situ* soil washing. Therefore, the metal extractions might still be more efficient in using multiple extraction steps.

4. Conclusions

Substantial reductions of the metal loads were achieved for all soils (almost quantitative for soil C, after 10 d), which are good results considering the fact that all soils were the residues after conventional soil washing that had already removed the mobile metal fractions. Citric acid was, however, not as efficient as the amino polycarboxylic acids.

Leaching times of 10 min and contact times of 1 h can be achieved in a full-scale technical process, and possibly an exposure of the soil to the leachant during 24 h, but hardly 10 d. The WTC-results are therefore of interest, since the contact times were short (less than a minute), but the metal release still comparable to what was achieved under continuous agitation. Evidently, the spray of solution through the soil will open new surfaces of the soil particles, as well as creating smaller particles due to the physical impact of liquid droplets under high pressure.

The study has demonstrated that the amino polycarboxylic acids perform well after long leaching times and that the short contact time in the WTC-equipment is as efficient as the longer leaching times batch-wise. However, it is simply not possible, and it was not the principal aim of the study, to explain the detailed mechanisms on a molecular level behind the observed metal releases, based solely on measured leaching results. It is probably not possible even with sophisticated analytical methods, considering that the soils are heterogeneous and that the secondary metals have entirely different origin and are present in different chemical states. It is, however, demonstrated that a pre-treatment (or post-treatment) where a leachant containing a strong complexing agent is in contact with the soil for a sufficient time (days) could be effective for the removal of metals that otherwise remain in the soil after conventional soil washing (without additives). The time required for removal of the metals are, in the present cases, too long (days) for a technical procedure unless a two-step sequence is developed: A pre-wash with complexing agents followed by soil-wash (removal of water plus the fine-fraction) or the reversed order, soil-wash followed by extended leaching.

If artificial complexing agents like EDDS and MGDA are used in technical scale it is probably necessary to recover, regenerate and reuse them, considering the economy of a full-scale process, which requires large quantities of quite expensive synthetic chemicals. Two aspects will be studied in the continuation of this project:

(1) Use of the WCT-system, but exposing the soil to the leachant in a circulation system leading to several exposures in sequence, and (2) Regeneration and reuse of the complexing agent in several consecutive leaching cycles.

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