

A kinetic study of chelant-assisted remediation of contaminated dredged sediment

A. Poletti^{a,*}, R. Pomi^a, E. Rolle^a, D. Ceremigna^a,
L. De Propris^b, M. Gabellini^b, A. Tornato^b

^a Department of Hydraulics, Transportation and Roads, University of Rome "La Sapienza", Via Eudossiana 18-00184 Rome, Italy

^b ICRAM, Central Institute for Scientific Research Applied to Sea, Rome, Italy

Received 22 November 2005; received in revised form 7 April 2006; accepted 11 April 2006

Available online 25 April 2006

Abstract

A study on the remediation of a real heavy metal-contaminated sediment was conducted using the four chelating agents ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), citric acid and the *S,S*-isomer of the ethylenediaminedisuccinic acid ([*S,S*]-EDDS). Different chelant washing experiments were carried out at a chelant/total metal content of 1 and 10 mol/mol for treatment durations from 0.5 to 48 h to study the extraction kinetics of trace metals and major cations. The objective was to evaluate the removal efficiency of conventional chelating agents as compared to innovative, biodegradable species. Among the target contaminants, Cd, Cu, Pb and Zn were found to be adequately removed by both EDTA and EDDS, while NTA and citric acid yielded unsatisfactory results in some cases. It was also found that As was a critical contaminant which would require an additional specific treatment step, since the residual concentrations after the washing treatment were still far above the regulatory limit values.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Sediment; Heavy metals; Washing; Chelating agents

1. Introduction

The high amounts of contaminated sediment requiring dredging for the purpose of maintaining or restoring coastal areas claim for technically reliable and cost-effective management strategies in order to produce environmentally compatible materials to be used in naturalistic or civil engineering applications. For most countries, the huge amounts of polluted material indeed make final disposal an unrealistic option, due to both environmental constraints and space availability limitations.

Sediment contamination originates from industrial activities, such as metallurgy, mining, paint and chemicals factories, military operation fields, refineries, shipping as well as contaminants transport by rivers. As a consequence of the variety of pollution sources, contaminated dredged sediment usually contains both heavy metals and organic pollutants, which require the application of a treatment sequence. In this context, soil/sediment

washing may be included in the treatment train with the main target of removing inorganic contaminants. If compared to other treatment processes, the advantage from the application of soil/sediment washing is that relatively simple technology is involved.

Chelating agents have been widely investigated (see, e.g. [1]) as efficient extracting agents to enhance the performance of soil/sediment washing. Chelating agents are widely available reagents, commonly employed in assorted commercial and industrial applications as constituents of several products including detergents, pulp and paper, cosmetics, pharmaceuticals, agrochemicals and textiles. A number of chelating agents are also naturally produced by living organisms to solubilize and transport nutrients in natural ecosystems.

In the present study the use of EDTA and NTA for chelant-assisted washing was compared to the application of two more biodegradable agents, namely citric acid and EDDS. EDTA and NTA are amino-polycarboxylic acids, and are characterized by a large stability as complexing agents. EDTA has been extensively investigated for applications in contaminated soil and sediment remediation, due to its high extraction efficiency for most heavy

* Corresponding author. Tel.: +39 06 44 585 037; fax: +39 06 44 585 037.
E-mail address: alessandra.poletti@uniroma1.it (A. Poletti).

metals and high stability [1–12]. However, EDTA is currently under scrutiny due to possible adverse health and environmental effects, including eutrophication of water caused by calcic and ferric phosphate dissolution, interaction with photosynthetic organisms through inhibition of cellular division, chlorophyll synthesis as well as algal biomass production, inhibitory effects over plants, resistance to bacterial biodegradation [13]. NTA, despite its biodegradability under specific conditions, is suspected to induce kidney toxicity and tumors, the latter upon prolonged exposure to high dosages, as revealed by sub-acute toxicity studies [14]. Citric acid is a carboxylic acid with three –COOH groups and behaves as a tetradentate ligand. It is naturally produced by the metabolism of almost all living organisms as it represents an intermediate in the citric acid cycle. Citric acid is commonly biodegradable and non-toxic. EDDS is a structural isomer of EDTA and is made up of two fragments of amino acid aspartate, containing two chiral carbon atoms resulting in the existence of three optical isomers, [S,S]-EDDS, [R,R]-EDDS, [R,S]-EDDS. Among these three isomers, only [S,S]-EDDS is readily and completely biodegraded, as evidenced by studies on activated sludge systems [15]. Vandevivere et al. [16] have also investigated the biodegradability of metal–EDDS complexes, showing effective biodegradation of Ca–EDDS, Cr(III)–EDDS, Fe(III)–EDDS, Pb–EDDS, Al–EDDS, Cd–EDDS, Mg–EDDS, Na–EDDS and Zn–EDDS, as opposed to Cu–EDDS, Ni–EDDS, Co–EDDS and Hg–EDDS complexes. Moreover, [S,S]-EDDS exhibits low toxicity to fish and *Daphnia* [15].

In the design of a washing process, treatment duration is an issue of major concern, with a direct influence on reactor size and treatment cost. For a certain contamination level, the time required to attain a given removal efficiency is recognized to be largely dependent on type, age and history of contamination, which affect the interactions between the contaminants and the solid matrix constituents as well as their speciation. This generally leads to significantly higher contact times required for naturally contaminated soil/sediment if compared to spiked materials [1,10–12,17]. To study the applicability of the selected chelants for the treatment of a real contaminated sediment, different aspects were investigated in the present study, including: (1) the time required to reach extraction equilibrium for the different target contaminants, (2) the extent of re-adsorption phenomena of contaminants onto the solid matrix, and (3) the competition between trace metals and major cations for complex formation. The results from the kinetic experiments allowed for the determination of the optimal treatment duration, which is one of the key factors in full-scale application of the washing process. A more detailed study concerning the influence of a number of parameters, including solution pH, on metal removal yield by means of chelant-assisted sediment washing is the subject for another paper [18].

2. Materials and methods

Samples of dredged sediment taken from a heavily contaminated Italian harbour site were homogenized and thereafter stored in the laboratory at 4 °C until the time of testing to prevent biodegradation of the organic matter. The material was

analyzed for the following physical and chemical properties: grain size distribution, water content, pH, total organic carbon (TOC), elemental composition, as well as metal fractionation. All the analyses were performed in triplicate. Water content, pH and TOC were measured according to the standard methods prescribed by the Italian Ministry of Agriculture and Forests [19]. Metal content was determined using atomic absorption spectrometry after sample digestion performed through lithium tetraborate fusion at 1050 °C in platinum melting pots. Determination of Hg involved hot digestion with a 1:1 concentrated HNO₃ + H₂SO₄ mixture in a reflux device [20], while measurement of As and Sb implied digestion with a 10:1:4 concentrated HNO₃ + H₂SO₄ + HClO₄ mixture [20]. Metal speciation in sediment was estimated through the sequential extraction procedure proposed by Campanella et al. [21], which consists of five extraction steps accomplished using the following agents: 1 M NH₄OAc (fraction A: exchangeable and carbonate-bound), 1 M NH₂OH·HCl + 25% AcOH (fraction B: bound to Fe/Mn oxides), 0.1 M HCl (fraction C: bound to organic matter), 0.5 M NaOH (fraction D: bound to humic acids) and 8 M HNO₃ (fraction E: sulphides).

The values derived from the physico-chemical characterization are as follows: humidity = 66.7%, pH = 7.84, TOC = 2.7% dry weight. The grain size distribution of the material (see Fig. 1) revealed a bimodal curve with higher amounts of particles in the diameter ranges 5–8 and 57–150 μm. According to the AASHO classification system, the sediment was found to be composed of 2% gravel, 28% sand, 63% silt and 7% clay, thus belonging to the silty loam textural class.

The elemental composition of sediment is shown in Table 1 along with the values calculated for the standard deviation of measurements as well as the limit concentrations prescribed by the Italian regulation for soil (residential and industrial sites) and sediment (column C of the Venice lagoon Act). The critical elements contributing to the contamination of sediment were found to be As (exceeding the limit concentration by 3.6 times), Cd (1.5 times), Hg (1.7 times), Pb (1.8 times) and Zn (1.5 times); Cu was also considered among the target contaminants as its total content in sediment was still relatively close to the limit concentration.

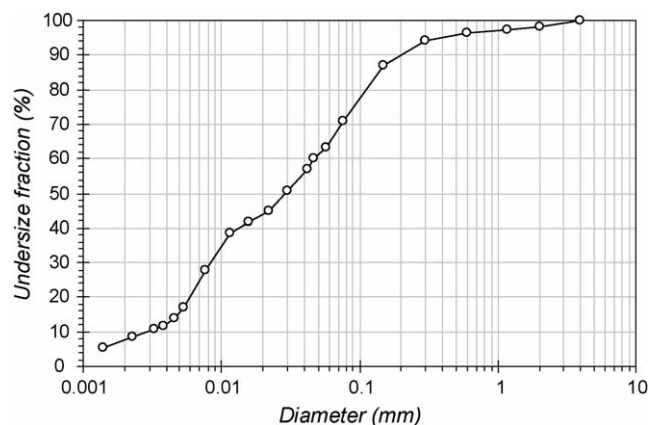


Fig. 1. Grain size distribution of sediment.

Table 1
Elemental composition of sediment and comparison with limit values

Element	Concentration (mg/kg dry wt.)	S.D. (mg/kg dry wt.)	Limit concentration (mg/kg dry wt.)		
			Soil (resid.)	Soil (ind.)	Sediment (Ven.)
Al	59590	3930	–	–	–
As	180.9	9.5	20	50	50
Ca	94080	2590	–	–	–
Cd	30.7	1.9	2	15	20
Cr	108.1	9.5	150	800	1000
Cu	323.0	4.5	120	600	400
Fe	41110	650	–	–	–
Hg	17.3	3.1	1	5	10
K	13420	300	–	–	–
Mg	28790	1190	–	–	–
Mn	411.3	3.4	–	–	–
Mo	209.0	42.1	–	–	–
Ni	83.1	17.3	120	500	150
Pb	886.2	51.0	100	1000	500
Sb	7.7	0.1	10	30	–
Si	141190	1830	–	–	–
Zn	3723.0	222.4	150	1500	2500

Metal partitioning among the different sediment fractions is reported in Fig. 2. In general, an appreciable portion of total metal content (from 25 to 85% depending on the metal under concern) was associated to fractions A and B (exchangeable+carbonate-bound and Fe/Mn oxides-bound). An exception was represented by Ni and Cr, which were mainly associated to the residual fraction of the material. This is expected to affect the efficiency of the washing treatment.

Samples of 60 °C oven-dried sediment were subjected to lab-scale washing experiments using ethylenediaminetetraacetic acid (EDTA) in the form of the Na₂ salt, citric acid (Cit), nitrilotriacetic acid (NTA) and the *S,S*-isomer of the ethylenediaminedisuccinic acid ([*S,S*]-EDDS) in the form of Na₃-*N,N'* salt as the washing agents. Different experiments were carried out in order to study the kinetics of metal extraction, as well as the influence of chelant type and concentration on metal removal efficiency. The washing treatment was performed at a liquid-to-solid ratio of 20 l/kg on duplicate samples rotated on an end-over-end tumbler for different times, namely 0.5, 1, 2, 24 and 48 h. The chelating agents were applied at two different concentrations, 0.02 and 0.2 M, corresponding to a chelant dosage of 1 (stoichiometric) and 10 mol/mol of total metal content, respec-

tively. Total metal content included major metal cations (Ca, Fe, K and Mg), which were accounted for in calculation of chelant dosage since they are reported to compete with heavy metals for chelant–metal aqueous complexes formation [3,11,12,17,22]. At the end of each contact period, the slurries were centrifuged at 6000 rpm. The liquid solution obtained was then filtered on 0.45- μ m membrane filters and then acidified with 1:1 HNO₃ for subsequent chemical analysis; the solid material was oven-dried at 60 °C and thereafter subjected to the sequential extraction procedure to estimate the speciation of residual contaminants.

3. Results and discussion

Investigation of sediment washing kinetics provided useful information on the relationship between metal extraction yield and contact time. Figs. 3 and 4 depict the results from chelant-assisted washing in terms of concentrations of extracted metals as a function of contact time. Wide variations in metal removal efficiency were observed depending on both the metal under concern and the chelating agent used.

Among the investigated metals, Ni (not reported graphically here) and Cr were the most difficult to extract from the sediment matrix, as could be anticipated by metal partitioning among the different sediment fractions as reported in Fig. 2. In particular, Ni concentrations in the final solutions were lower than the analytical detection limit, while Cr displayed maximum removal yields of about 18% (0.2 M Cit) and 11% (0.2 M EDTA). Low removal efficiencies for Cr were indicated by other authors as well [2].

After 48-h washing, As was removed by ~35% with 0.2 M NTA and 0.2 M Cit and by ~20% with 0.2 M EDTA and 0.2 M EDDS. At the lower dosage no chelating agent was capable of extracting more than 10% of the initial As content. This behaviour is consistent with the findings of other authors [23] which indicated that chelating agents are not effective in extracting As; this is related to the anionic forms of both As(III) and

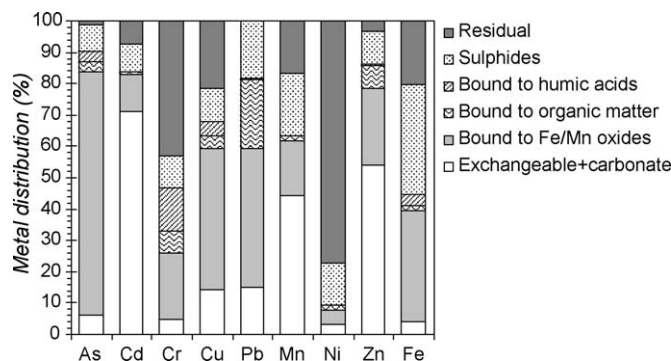


Fig. 2. Metal speciation in sediment.

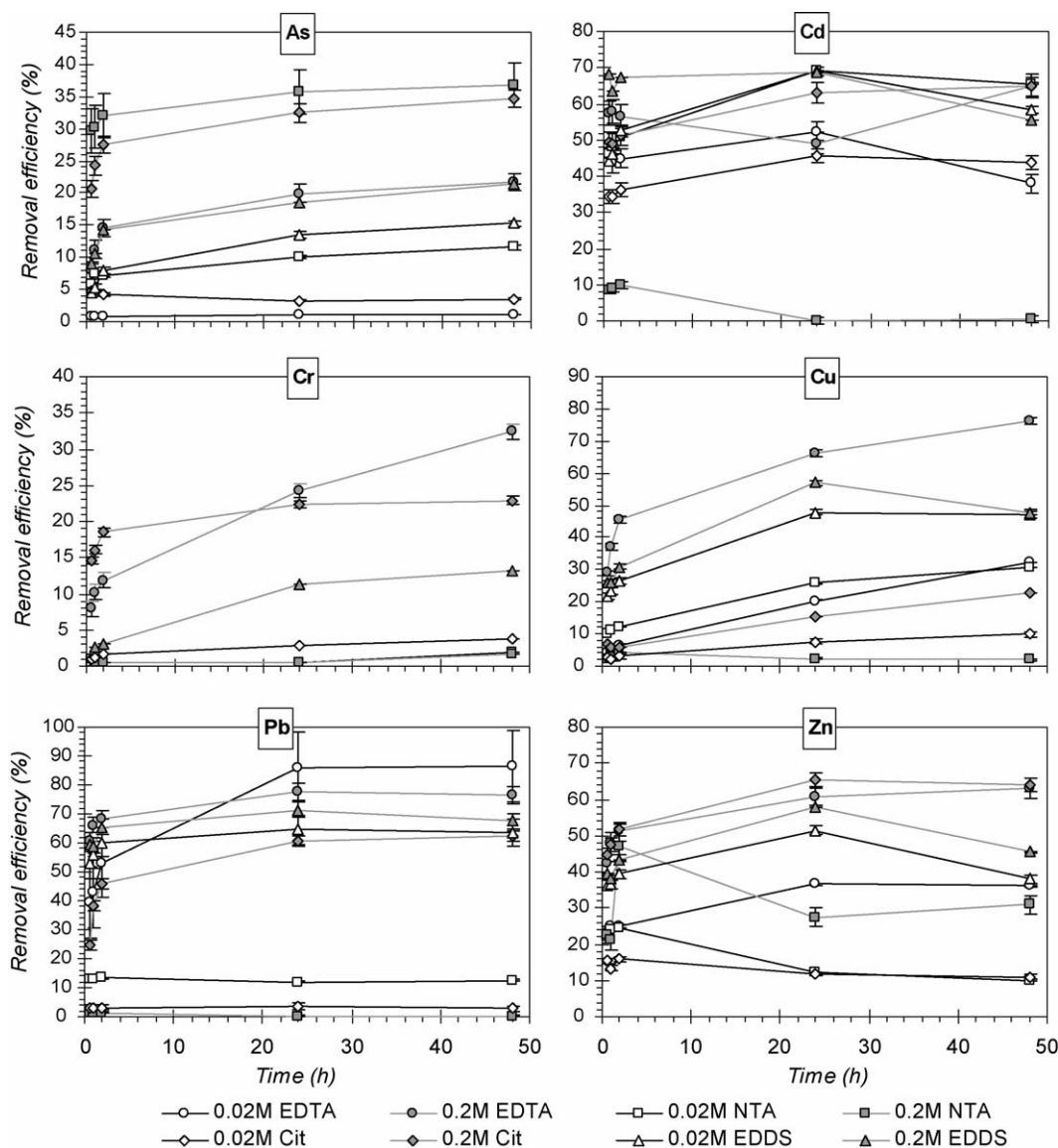


Fig. 3. Extraction kinetics (heavy metals).

As(V), which do not allow the formation of stable chelant complexes. Arsenic in soil and sediment is reported to be mainly bound to Al and Fe oxides and clay minerals through sorption mechanisms [23,24], and this was also the case of our study as indicated by Fig. 2. However, in the case under investigation As mobilization from sediment appeared not to be related to the release of Fe (see below for details on this metal). This apparent contradiction may be explained considering that As released following solubilization of Fe (hydr)oxides could afterwards be precipitated into stable arsenate forms, which are oxidized As species of generally low solubility. This was also confirmed by the analysis of As speciation in sediment after 2-h washing. While the amount of As associated to the Fe/Mn oxides fraction was 78% in the untreated material, it decreased considerably after treatment, reaching levels in the range 5% (0.2 M NTA)–15% (0.2 M EDTA).

Among the investigated heavy metals, Pb exhibited the highest removal yield (up to about 78–86% in the case of 0.02 and

0.2 M EDTA), followed by Cu (76% with 0.2 M EDTA and 57% with 0.2 M EDDS) and Zn (65% using 0.2 M Cit and 63% using 0.2 M EDTA). Similar results for Pb were also obtained in other studies (see, e.g. [7]), which showed good complexation efficiencies of this metal using chelating agents (especially EDTA) in the case of both spiked and real soils.

It was also found that, as reported elsewhere in the literature, Cu displayed by far the slowest extraction kinetics. It has been proposed [17] that the slower extraction rate may be related to the fact that in soil and sediment Cu is commonly associated to organic matter or other oxidizable species. Nevertheless, this is objectionable in the case under study, considering that the relatively low amount (~19%) of Cu associated to the oxidizable fractions of sediment could not account for the increase in Cu removal efficiency with time observed from Fig. 3. Furthermore, since the speciation of Cu in the untreated sediment was very similar to Pb (see Fig. 2) but the extraction kinetics was not, quite unlikely may the observed behaviour of Cu be related to

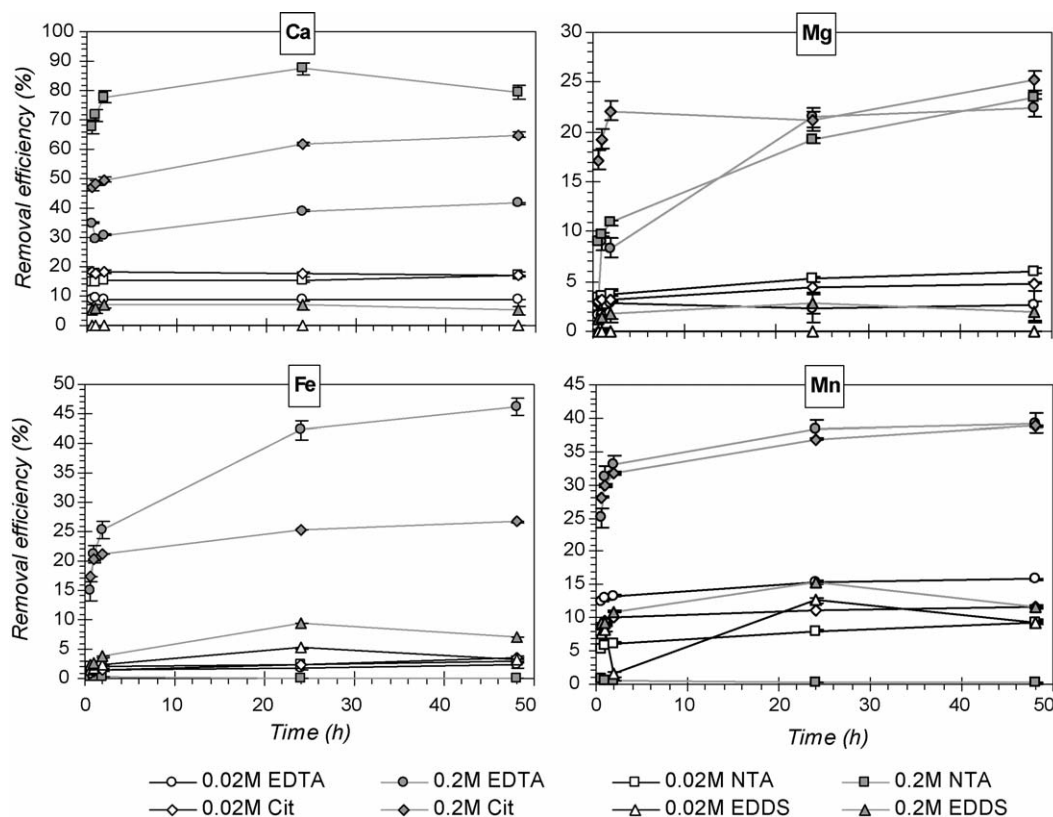


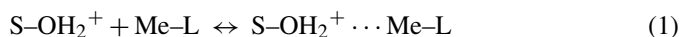
Fig. 4. Extraction kinetics (major cations).

its initial chemical speciation in sediment. Rather, it is tempting to hypothesize that the slower extraction kinetics was related to the lower rate of Cu complexes formation.

The effect of the washing process on Cd was almost comparable for all the chelating agents studied (removal efficiency after 48 h: 55–65%), with the exception of 0.02 M Cit and 0.02 M EDTA (removal efficiency after 48 h: 38–44%) as well as 0.2 M NTA (removal efficiency after 48 h: <1%).

For both Zn and Cd a reduction in soluble metal concentration was observed for long treatment durations (48 h). Although a similar decrease was observed occasionally for other metals, in the case of Zn and Cd the reduction in extraction efficiency upon prolonged contact with the chelating agents appeared both to be more relevant and to occur more systematically.

Likely, such a behaviour is to be ascribed either to sorption mechanisms of the newly formed metal–chelant complexes onto the active sites of sediment particles, or to metal exchange reactions between metal–chelant complexes. Sorption of chelant complexes by the soil matrix has been shown by different investigators [25,26] and described by reactions (1) and (2) involving the formation of ternary complexes through outer-sphere association mechanisms. Indicating the surface sites of solid particles with S, the chelating agent with L and the generic metal ion with Me, sorption of metal complexes by solid particles can be expressed as:

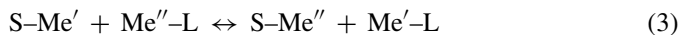


where the surface complex is essentially electrostatically held, i.e. ionic, and



where the surface complex is partly covalently held.

The occurrence of metal exchange reactions in metal–chelant complexes is also reported in the literature [27,28]. Considering two generic metals Me' and Me'', such reactions can be represented by Eq. (3):



Both mechanisms can be thought to play a role in determining the observed concentration patterns of Cd and Zn over time.

When interpreted in overall terms, the results discussed above indicate that the chelating agents with higher extraction capacity were different depending on the specific metal under concern. As a practical implication, this actually complicates the application of the washing process, since for satisfactory remediation efficiencies to be attained for the sediment under study, a treatment based on multiple chelating agents (for instance, applied in different extraction steps) would be required. A number of preliminary results from two-stage chelant-based washing were reported in a previous paper [29].

Further information from kinetic experiments was derived on the behaviour of the major cations Ca, Mg, Fe and Mn (see Fig. 4). In the case of Ca, strong affinity was observed at the 0.2 M level towards NTA and Cit (48-h extraction efficiency of

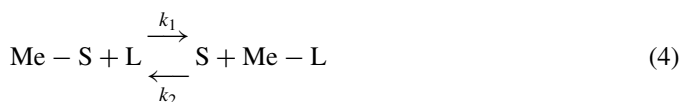
80 and 65%, respectively) with a fast extraction rate, as also reported by other investigators [30]. Like Ca, Mg was better extracted by 0.2 M Cit, 0.2 M NTA and 0.2 M EDTA, although to a lower extent (maximum 25%). In the case of Fe and Mn, 0.2 M EDTA and 0.2 M Cit appeared to exhibit the higher extraction yield. However, in the case of Fe the extraction kinetics was slower if compared to the other major cations Ca and Mn. On the basis of the results from sequential extraction, it is strongly probable that the extraction efficiency of EDTA and Cit is related to their capability of producing the dissolution of Fe and Mn oxides, as reported elsewhere in the literature [28], although other studies report very slow kinetics of oxide dissolution by chelating agents [31]. In this study, sequential extraction on 2-h washed sediment indicated that for the 0.2 M level the residual amount of Fe associated to the Fe/Mn oxides fraction was 2% (Cit), 4% (EDTA), 5% (EDDS) and 18% (NTA) as opposed to 35.5% for the untreated material. In particular, the amount of Fe extracted by EDTA corresponded approximately to that associated to the exchangeable + carbonate and Fe/Mn oxides fractions of the material. In the case of Mn, the extent of solubilization of the corresponding oxides was lower, so that after 2-h washing at the 0.2 M level the amount associated to fraction B was 8% (EDTA), 10% (Cit), 11% (NTA) and 12% (EDDS) as opposed to the initial value of 14%.

Comparing the results from the kinetic experiments described above with those from a previous study on multi-stage washing [29], a 2-h treatment applied in two steps appeared to be more efficient towards metal removal than a single-step treatment at 4 h or more. As a consequence, a more detailed characterization of the 2-h treated material was performed in the present study.

The investigation of metal speciation in the material treated at the 0.2 M level for 2 h revealed a general decrease in the amount of metals associated to fractions A (exchangeable + carbonate-bound) and B (bound to Fe/Mn oxides) if compared to the initial values. This indicates that the chelating agents were capable of extracting, in addition to the easily mobilizable fraction (exchangeable + carbonate-bound), part of other less mobile forms (i.e., Fe oxides and sulphides). In a few cases, an increase in the amount of metals associated to fraction A was observed, presumably as a consequence of the presence of residual metal complexes, as also observed by other authors [32]. Furthermore, the amount of metals associated to fraction C (bound to organic matter) was almost systematically found to increase as a result of treatment, and this was particularly relevant in the case of EDDS for Fe and As. It is tempting to hypothesize that, in addition to the inability of chelants to solubilize such fractions, re-adsorption of chelant–metal complexes or metal ions onto the organic matter fraction of the material may have played a role. Another reason may be found in the inability of the sequential extraction procedure to distinguish sharply between metals bound to organic matter and metals present in the form of low-solubility compounds. For the other metals, EDDS was found to extract the portion associated to fraction A (exchangeable + carbonate-bound), E (sulphides) and partly B (bound to Fe/Mn oxides).

Data from kinetic experiments were also used to describe chelant-assisted mobilization of contaminants from sediment considering the reactions of metal detachment from the solid

particles and subsequent formation of metal–chelant complexes, as reported by Whitworth et al. [33] in the case of EDTA. The competition between metal binding by the surface sites of sediment and metal complexation by the chelating agent can be represented by Eq. (4):



Introducing the rate constants for the forward (k_1) and reverse (k_2) reactions and assuming that the concentration of S is much greater than that of Me–S, according to Eq. (4) the rate of metal–chelant complex formation can be written as:

$$\frac{d[\text{Me} - \text{L}]}{dt} = k_1[\text{Me} - \text{S}] - k_2[\text{Me} - \text{L}] \quad (5)$$

Considering the initial condition that at $t=0$, $[\text{Me} - \text{L}] = 0$, the solution to the differential Eq. (5) is the following:

$$[\text{Me} - \text{L}] = \frac{k_1}{k_1 + k_2} [\text{Me} - \text{S}]_{t=0} [1 - \exp(-(k_1 + k_2)t)] \quad (6)$$

Eq. (6) was used to fit the experimental data through least-squares interpolation. For the fitting procedure, the metal concentrations measured in the extracting solutions were assumed as the corresponding $[\text{Me} - \text{L}]$ values, i.e. the hypothesis was made that soluble metals were only present in the form of aqueous metal–ligand complexes. The validity of such an assumption was assessed by speciation modelling of the extracting solutions after treatment [18], which calculated that more than 95% of soluble metals were in the form of chelant complexes. The quantity $[\text{Me} - \text{S}]_{t=0}$ was assumed to be the total metal amount associated to the non-detrital fractions of sediment, namely fractions A and B as identified by the sequential extraction procedure.

The estimated regression coefficient, R^2 , was higher than 0.9 for all metals and experimental conditions, which implies that data fitting through Eq. (6) was satisfactory. In the case of Cd and Zn, small deviations from the theoretical curve were observed after 48 h, which may be an indication that for the longer extraction periods other mechanisms than metal detachment from the sediment matrix and complexation by chelating agents started playing a role. Presumably, one of such mechanisms is sorption of the newly formed metal–chelant complexes onto the active sites of the solid matrix (see Eqs. (1) and (2)), leading to a decrease in soluble metal concentration. However, the extent of such interfering phenomena was not very pronounced, as demonstrated by the high R^2 values of the fitting curves.

In general, for trace metals including Cd, Cu, Pb and Zn, EDTA and EDDS were found to be kinetically favoured, displaying higher k_1 and lower k_2 values if compared to the other chelating agents. In the case of EDDS, the k_1 values for Ca, Mg and Fe were always considerably lower and the k_2 values remarkably higher than for EDTA and the other chelating agents, which means reduced competition between major cations and trace metals for complex formation in the case of EDDS. This is an additional valuable advantage of using EDDS, implying that for relatively low treatment durations the amount of competitive cations extracted is minimized. This behaviour also reflects the

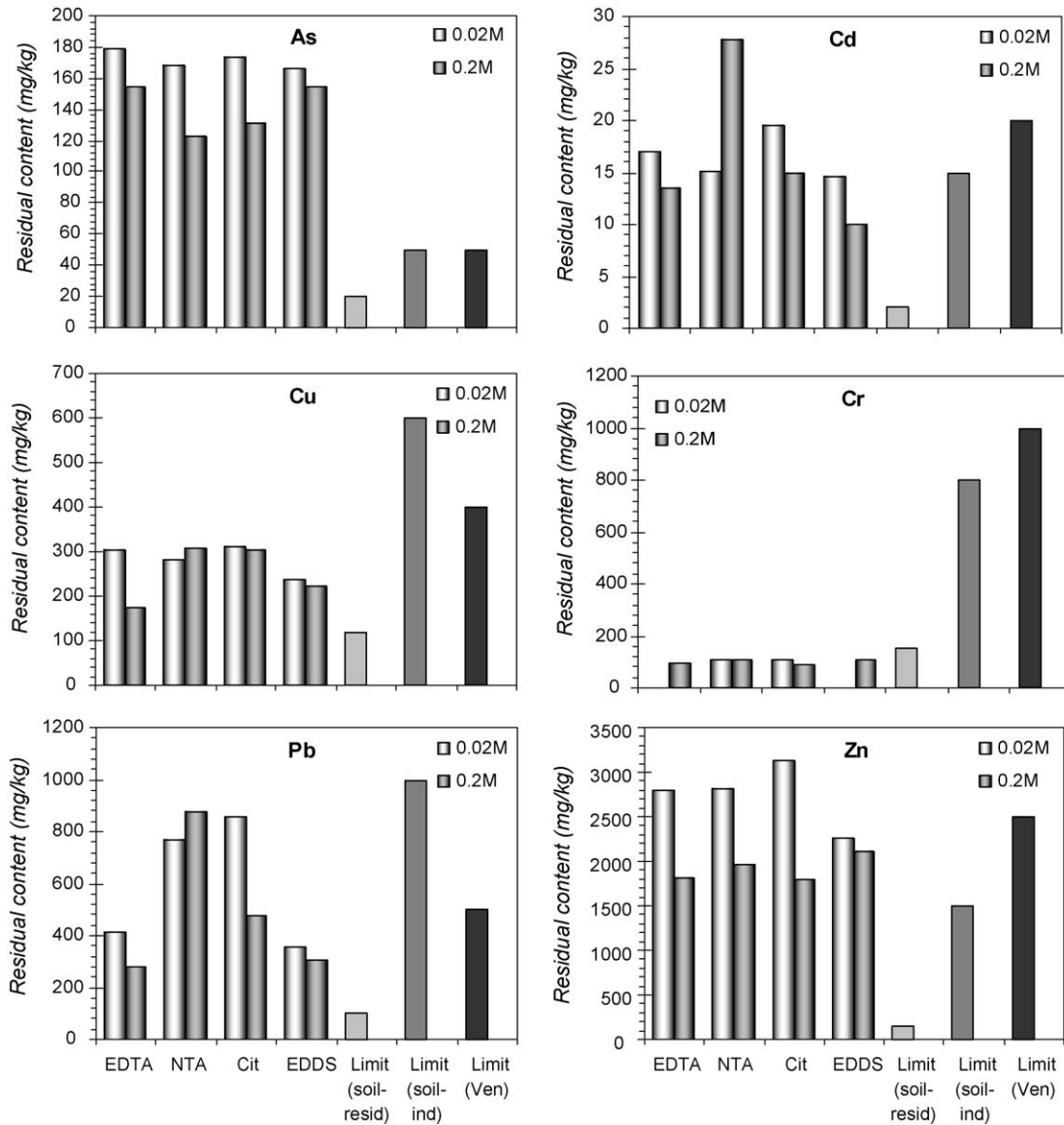


Fig. 5. Residual metal content in treated sediment (2-h washing).

fact that solid matrix alterations induced by washing are lower for EDDS than for the other investigated chelants. This may be a positive feature of EDDS in view of the final destination of treated sediment.

To derive general considerations on the overall washing efficiency of the investigated chelating agents in terms of compliance with regulatory values, the residual contaminant concentrations in 2-h treated sediment were evaluated (Fig. 5).

For the three heavy metals Cd, Pb and Zn, EDTA and EDDS were always found to be capable of reducing total content below the limit values established for sediment; only in the case of Zn, did not 0.02 M EDTA allow to meet the required quality level. Conversely, the efficiency of NTA and Cit appeared inadequate in most cases (particularly at the 0.02 M level). As emphasized above, an important issue still to be resolved is the inability of the selected chelating agents to produce appreciable As removal. Extraction of As from sediment would require an additional

treatment step using different washing agents than those investigated in the present study. On the basis of a number of studies on spiked soil [23,34,35], phosphate could be a possible candidate for As removal from the investigated sediment. Further study on As extraction is currently on the way.

4. Conclusions

The results from a study on sediment washing using the four chelating agents EDTA, NTA, citric acid and [S,S]-EDDS were reported in the present paper. The study was mainly aimed at investigating the kinetics of the extraction process and possible interfering mechanisms including competition for complex formation as well as re-adsorption of chelated metals onto the solid matrix. Despite the lower stability constant values of the corresponding complexes, major cations including Ca and Mg above all were found to be strong competitors with trace metals

for metal–ligand complexes formation. Among the target contaminants, Cd, Cu, Pb and Zn were found to be removed with high efficiencies under a number of treatment conditions.

In particular, on the basis of the experimental results, the use of 0.2 M EDDS was found to yield good extraction efficiencies for Cd, Cu, Pb and Zn, at the same time reducing solubilization of the main constituents of the sediment matrix including Ca, Mg, Fe and Mn. However, the need to meet stringent regulatory limits for such metals would also require an additional washing step, as also suggested by previous studies [29].

The study also showed that none of the chelating agents investigated was capable of producing residual As concentrations below the corresponding limit values. Such results claim for further investigation of suitable remediation processes for this metal.

References

- [1] R.W. Peters, Chelant extraction of heavy metals from contaminated soils, *J. Hazard. Mater.* 66 (1999) 151–210.
- [2] T.-T. Lim, J.-H. Tay, J.-Y. Wang, Chelating-agent-enhanced heavy metal extraction from a contaminated acidic soil, *J. Environ. Eng. ASCE* 130 (2004) 59–66.
- [3] H.A. Elliott, G.A. Brown, Comparative evaluation of NTA and EDTA for extractive decontamination of Pb-polluted soils, *Water Air Soil Pollut.* 45 (1989) 361–369.
- [4] G.A. Brown, H.A. Elliott, Influence of electrolytes on EDTA extraction of Pb from polluted soils, *Water Air Soil Pollut.* 62 (1992) 157–165.
- [5] S.R. Cline, B.E. Reed, Lead removal from soils via bench-scale soil washing techniques, *J. Environ. Eng. ASCE* 121 (1995) 700–705.
- [6] I.M.C. Lo, X.Y. Yang, EDTA extraction of heavy metals from different soil fractions and synthetic soils, *Water Air Soil Pollut.* 109 (1999) 219–236.
- [7] C.N. Neale, R.M. Bricka, A.C. Chao, Evaluating acids and chelating agents for removing heavy metals from contaminated soils, *Environ. Prog.* 16 (1997) 274–280.
- [8] N. Papassiopi, S. Tambouris, A. Kontopoulos, Removal of heavy metals from calcareous contaminated soils by EDTA leaching, *Water Air Soil Pollut.* 109 (1999) 1–15.
- [9] J.E. van Benschoten, M.R. Matsumoto, W.H. Young, Evaluation of soil washing for seven lead contaminated soils, *J. Environ. Eng.* 123 (1997) 217–224.
- [10] M.C. Steele, J. Pichel, Ex-situ Remediation of a metal-contaminated superfund soil using selective extractants, *J. Environ. Eng.* 124 (1998) 639–645.
- [11] C. Kim, Y. Lee, S.K. Ong, Factors affecting EDTA extraction of lead from lead-contaminated soils, *Chemosphere* 51 (2003) 845–853.
- [12] S. Tandy, K. Bossart, R. Mueller, J. Ritschel, L. Hauser, R. Schulin, B. Nowack, Extraction of heavy metals from soils using biodegradable chelating agents, *Environ. Sci. Technol.* 38 (2004) 937–944.
- [13] C. Oviedo, J. Rodríguez, EDTA: the chelating agent under scrutiny, *Quim. Nova* 26 (2003) 901–905.
- [14] R. Bahnemann, E. Leibold, B. Kittel, W. Mellert, R. Jäckh, Different patterns of kidney toxicity after subacute administration of Na-nitrilotriacetic acid and Fe-nitrilotriacetic acid to Wistar rats, *Toxicol. Sci.* 46 (1998) 166–175.
- [15] J.S. Jaworska, D. Schowanek, T.C.J. Feijtel, Environmental risk assessment for trisodium[S,S]-ethylene diamine disuccinate, a biodegradable chelator used in detergent applications, *Chemosphere* 38 (1999) 3597–3625.
- [16] P.C. Vandevivere, H. Saveyn, W. Verstraete, T.C.J. Feijtel, D.R. Schowanek, Biodegradation of metal–[S,S]-EDDS complexes, *Env. Sci. Technol.* 35 (2001) 1765–1770.
- [17] P. Vandevivere, F. Hammes, W. Verstraete, T. Feijtel, D. Schowanek, Metal decontamination of soil, sediment, and sewage sludge by means of transition metal chelant [S,S]-EDDS, *J. Environ. Eng.* 127 (2001) 802–811.
- [18] Poletini, A., Pomi, R., Rolle, E., The effect of operating variables on chelant-assisted remediation of contaminated dredged sediment, submitted to *Chemosphere*, 2006.
- [19] Ministero delle Politiche Agricole e Forestali (Ministry for Agriculture and Forests). Metodi ufficiali di analisi chimica del suolo (Standard methods for chemical analysis of soil), D.M. 13/9/1999, Suppl. Ord. n. 185 G.U. n. 248 21/10/1999, 1999 (in Italian).
- [20] Consiglio Nazionale delle Ricerche (National Research Council), Istituto di Ricerca sulle Acque (Water Research Institute). Metodiche analitiche per i fanghi: Parametri chimico-fisici, biochimici e biologici (Methods for the analysis of sludge: Physico-chemical, biochemical and biological parameters), Quaderni n. 64, 1985 (in Italian).
- [21] L. Campanella, D. D’Orazio, B.M. Petronio, E. Pietrantonio, Proposal for a metal speciation study in sediments, *Anal. Chim. Acta* 309 (1995) 387–393.
- [22] H.A. Elliott, N.L. Shastri, Extractive decontamination of metal-polluted soils using oxalate, *Water Air Soil Pollut.* 110 (1999) 335–346.
- [23] S. Tokunaga, T. Hakuta, Acid washing and stabilization of an artificial arsenic-contaminated soil, *Chemosphere* 46 (2002) 31–38.
- [24] S. Goldberg, Competitive adsorption of arsenate and arsenite on oxides and clay minerals, *Soil Sci. Soc. Am. J.* 66 (2002) 413–421.
- [25] F. Bordas, A.C.M. Bourg, Effect of complexing agents (EDTA and ATMP) on the remobilization of heavy metals from a polluted river sediment, *Aquat. Geochem.* 4 (1998) 201–214.
- [26] K. Güçlü, R. Apak, Modelling of copper(II), cadmium(II), and lead(II) adsorption on red mud from metal–EDTA mixture solutions, *J. Colloid Interface Sci.* 228 (2000) 238–252.
- [27] H. Xue, L. Sigg, F.G. Kari, Speciation of EDTA in natural waters: exchange kinetics of Fe–EDTA in river water, *Environ. Sci. Technol.* 29 (1995) 59–68.
- [28] B. Nowack, F.G. Kari, H.G. Krüger, The remobilization of metals from iron oxides and sediments by metal–EDTA complexes, *Water Air Soil Pollut.* 125 (2001) 243–257.
- [29] D. Ceremigna, A. Poletini, R. Pomi, E. Rolle, L. De Propris, M. Gabellini, A. Tornato, Comparing sediment washing yields using traditional and innovative biodegradable chelating agents., in: Proceedings of Third International Conference on Remediation of Contaminated Sediments, New Orleans, LA, USA, 2005 (January 24–27).
- [30] Ritschel, J., Extraction of heavy metals from soil with selected biodegradable complexing agents, Diploma Thesis, ETH Zürich, 2003.
- [31] H.A. Elliott, J.H. Linn, G.A. Shields, Role of Fe in extractive decontamination of Pb-polluted soils, *Hazard. Waste Hazard. Mater.* 6 (1989) 223–229.
- [32] B. Sun, F.J. Zhao, E. Lombi, S.P. McGrath, Leaching of heavy metals from contaminated soil using EDTA, *Environ. Pollut.* 113 (2001) 111–120.
- [33] D.-J. Whitworth, E.P. Achterberg, V. Herzl, N. Mimmo, M. Gledhill, P.J. Worsfold, Development of a simple extraction procedure using ligand competition for biogeochemically available metals of estuarine suspended particulate matter, *Anal. Chim. Acta* 392 (1999) 3–17.
- [34] M.G.M. Alam, S. Tokunaga, T. Maekawa, Extraction of arsenic in a synthetic arsenic-contaminated soil using phosphate, *Chemosphere* 43 (2001) 1035–1041.
- [35] S.A. Wasay, W. Parker, P.J. Van Geel, S. Barrington, S. Tokunaga, Arsenic pollution of a loam soil: retention form and decontamination, *J. Soil Contam.* 9 (2000) 51–64.