

Heavy metals mobilization from harbour sediments using EDTA and citric acid as chelating agents

L. Di Palma*, R. Mecozzi

*Dipartimento di Ingegneria Chimica, Materiali, Materie Prime, Metallurgia,
Università di Roma "La Sapienza", Via Eudossiana 18, 00184 Roma, Italy*

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Abstract

In this paper experimental tests of heavy metals mobilization from sediments collected from an Italian harbour are presented and discussed. Batch tests of washing with an aqueous solution of chelating agent were performed at selected liquid/solid (L/S) ratios and chelant concentration (0.01, 0.05 and 0.1 M). Two chelating agents were chosen: EDTA and citric acid. The objective of the tests was to investigate metal mobilization and soil mineral dissolution promoted by the washing treatment. The study was focused on the mobilization of Pb, Zn, and Cu: their concentrations in the contact solution, together with Fe and Ca concentration, were monitored along time for 144 h.

Results of experimental tests performed at different chelant concentration and L/S ratio show EDTA effectiveness in mobilizing metals bound to the sediment. The overall amount of the three selected metals (Cu, Pb and Zn) extracted in the tests with EDTA varied in a quite narrow range (from 2.262 to 2.724 mmol), while the higher was the EDTA concentration in the washing solution, the higher the dissolution of other competitive cations, such as Ca and Fe. In addition, a general difficulty in copper extraction from the organic fraction of the sediment was observed, due to the high stability of copper humate.

The mechanism of metals extraction was found to involve the initial metals salts dissolution, that was pH-dependant, followed by the development of exchange reactions between the metal–EDTA complexes previously formed. Depending upon the pH of the washing solution an initial high Ca dissolution was observed, followed by dramatic reduction in Ca^{2+} content, mainly determined by calcium carbonate precipitation, as a result of the increase of pH during mixing.

Metal mobilization was evaluated performing sequential extraction tests: the dissolution of Cu, Pb and Zn from the carbonate fraction of the sediment was almost total, as the mobilization of Pb and Zn from the Fe–Mn oxides and hydroxides fraction. On the contrary, as a consequence of the mobilization induced by washing treatment, about 17% of the remaining Cu and 10% of the remaining Zn resulted in the exchangeable fraction.

At the investigated operating conditions, citric acid was unable to extract Pb and Cu from the sediment, while at the strong acidic conditions maintained during the extractions with citric acid, a Zn mobilization up to the 80% of the initial amount was observed, depending upon the operating conditions in the extractions. In addition, because of the great affinity between citric acid and Fe, and the strong acidic conditions maintained during extraction, a high Fe dissolution was observed (up to about the 39% of the total Fe content in the sediment).

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1. Introduction

Heavy metals are continuously discharged into the environments from several industrial, civil and agricultural activities [1]: as a consequence, their spread in the aquatic systems and soil has been found to increase along time. Harbour sediments are often rich in heavy metals: since they are not subjected to

degradation phenomena, they can easily be suspended or dissolved by surface waters, thus becoming available to plankton, nekton and benthic filter and deposit feeders [2]. As a consequence they can enter the food chain and become concentrated in fish and other edible organisms [3].

The environmental impact of marine sediment contamination depend not only by the total metals amount, but mainly by their mobility and availability, that influence their leaching and interactions with the other components of the ecosystem, such as water and air.

* Corresponding author. Tel.: +39 06 44585571; fax: +39 06 44585622.
E-mail address: luca.dipalma@uniroma1.it (L. Di Palma).

Marine sediments are in fact constituted by a complex heterogeneous mix of geochemical phases, able to bind metals by means of precipitation, ionic exchange and absorption reactions [4,5]. As a result, heavy metals can be found in sediments in several forms, including exchangeable forms such as carbonates, iron or manganese hydroxides, organic matter and sulphides [6]. The higher heavy metal accumulation is generally observed onto the pelitic fraction, due to the higher specific surface of silt and clays.

In Italy it is estimated that about 10% of marine sediments are contaminated, and so the need exist to perform experimental tests to evaluate the possibility of contaminated sediment remediation.

The technologies used for sediments remediation are similar to those generally widely adopted for soil remediation including thermal treatment, physical separation, solidification/stabilization and washing treatments [7,8]. Since physical and chemical characteristics of sediments are generally quite different from that of soils, feasibility studies based upon preliminary lab scale experiments are necessary to assess the success of the technology and to evaluate the extent of remediation [9,10].

In the *ex situ* washing technology [11,12] undesirable contaminants in soils or sediments are removed by dissolving or suspending them in a washing solution. In the case of heavy metal contaminated soil or sediments, the washing solution is generally an aqueous solution of a chelating agent. In the remediation of copper contaminated soil and sediments, the effectiveness of EDTA has been widely demonstrated as a chelating agent in washing treatment [13–15].

In comparison with other chelating agents, EDTA presents the following advantages: a low degree of biodegradability in groundwater [16] and soil [17,18] and moreover a high level of complexing capacity with respect to heavy metals [19].

Conversely, the low selectivity of EDTA may cause a high consumption of this reagent due to the enhancement in the mobilization of all the exchangeable cations present in the solid matrix [20]. As a consequence, a substantial excess of EDTA is generally adopted in washing treatment, thus increasing the cost of the whole remediation process, and also inducing simultaneously a strong mineral dissolution, that may determine the modification of sediment structure and cause the presence in the extracted solution of a great number of metals, thus affecting the following treatment of the extracted liquid phase.

In this paper experimental tests of metal extraction from contaminated sediments are presented and discussed. Sediments were collected from an Italian harbour, where a significant heavy metal content has been observed. In particular, Cu, Pb and Zn were chosen as target pollutant in this study.

Fangueiro et al. [21] first verified that the main factors that induce metal mobilization are chelating agent concentration, pH of the washing solution, and liquid/solid (L/S) ratio.

In our study the extraction from five different sediment fractions (exchangeable, bound to carbonate, bound to Fe–Mn oxides, bound to organic matter and residual) was investigated.

In addition, the extent of competitive ions extractions was also evaluated and a comparison with citric acid as extractant agent was also performed.

Preliminary sequential extraction test were performed to evaluate metal distribution in the sediment, and to assess metal availability to leaching.

One hundred and forty-four hours of extraction tests were then carried out by washing 100 g samples of sediment with aqueous solution 0.05 or 0.1 M of EDTA and 0.05 or 0.1 M of citric acid, at selected liquid/solid ratios (5, 8 or 12.5).

The aim of the experimentation was to evaluate the metal mobilization induced by washing treatment, and to assess the possibility of reducing heavy metals content in the sediment, limiting the dissolution of sediments minerals, in the view of the optimisation of the washing technique for sediment remediation.

2. Materials and methods

2.1. Sediment characterization

Twenty-four samples were collected at different sites and at selected depth from an Italian harbour in the Tirrenian Sea. The samples were stored in glass container, and then air dried at room temperature and weighed prior to the analytical determination of their physical and chemical characteristics. The experimental tests were performed on an average sample, prepared by mixing in a Hobart type mixer for 16 h an equal amount of each of the 24 former collected samples.

Table 1 shows the main characteristics of this average sample.

Twenty-five milliliters of double deionised water were added to 10 g of the sediment. The mixture was stirred for 10 min and allowed to settle for 30 min, pH and conductivity measurements were performed in the supernatant. pH was determined using a Crison GLP21 pH-meter; electric conductivity was measured using a Delta-Ohm HD9213-R1 conductimeter.

To determine metal content, an acid digestion was performed on 1 g of sediment, according to EPA3050B method [22]: the suspension was then centrifuged at 3000 rpm for 15 min in a ALC 4226 centrifuge, the supernatant was filtered through Whatman filter paper (0.45 μm) and then analysed by flame atomic absorption spectrophotometry (FAAS),

Table 1
Composite samples characteristics

Fraction >2 mm (wt%)	6.89
Fraction 2 > x > 0.063 mm (wt%)	14.14
Fraction < 0.063 mm (wt%)	78.97
Organic carbon (g/kg)	20.03
CaCO ₃ (g/kg)	81.60
pH	7.73 \pm 0.3
Metals, mg/kg (mmol/kg)	
Al ^a	32306.25 (1197.41)
As ^a	9.88 (0.132)
Cd ^a	1.08 (0.009)
Cu ^b	79.38 (1.25)
Fe ^b	47710.30 (854.41)
Pb ^b	87.22 (0.42)
Zn ^b	175.70 (2.687)

^a As determined by acid digestion.

^b As calculated after sequential extractions.

using a Philips PU9200 apparatus, after acidification with HNO₃ (detection limits: Al = 0.38 mg/l; As = 0.69 mg/l; Cd = 0.010 mg/l; Cu = 0.035 mg/l; Fe = 0.06 mg/l; Pb = 0.10 mg/l; Zn = 0.01 mg/l).

Hydraulic conductivity was determined according to Falling Head Method described by the ASTM standard test D 2434 [23].

Sediment organic carbon content was determined by the Walkley–Black method [24].

2.2. Sequential extraction tests

On the basis of the data reported in Table 1, the study was focused on three selected metals: Cu, Pb and Zn. Since metal extraction effectiveness depends on the binding form of the element of interest, preliminary sequential extraction using the Tessier's method [25–28] were performed to investigate their distribution into five fractions: exchangeable, bound to carbonate, bound to Fe–Mn oxides and hydroxides, bound to organic matter and residual.

The exchangeable fraction was determined through extraction with 8 mL of 1 M MgCl₂ at pH 7 for 1 h. The fraction bound to carbonates was determined after extraction with 8 mL of 1 M NaOAc adjusted to pH 5 with acetic acid for 5 h. The fraction bound to oxides and hydroxides was determined after extraction with 20 mL of 0.04 M NH₂OH·HCl in 25 vol.% acetic acid (pH 2) for 6 h at 96 °C. The fraction bound to sediment organic matter was determined after extraction with 3 mL of 0.02 M HNO₃ and 5 mL of 30% H₂O₂ (pH 2) for 2 h at 85 °C, followed by 3 mL of 30% H₂O₂ (pH 2) for 3 h at 85 °C and then 5 mL of 3.2 M NH₄OAc in 20 vol.% HNO₃ diluted to 20 mL at room temperature for 30 min.

The residual fraction was determined after digestion at 90 °C with 25 mL of dilute aqua regia (50 mL HCl, 200 mL HNO₃ and 750 mL water) for 3 h.

At the end of the washing tests, the same procedure was used to perform sequential extraction on the treated sediment.

2.3. Extraction tests

The aim of the washing tests was to determine the optimal conditions for metal extraction: the main operating parameter in the tests were the nature and concentration of the extractant solution, and the liquid versus solid ratio.

Experimental tests were performed at room temperature (20 ± 2 °C), in 21 glass beaker on 100 g samples: in each test the suspension was kept in agitation for up to 144 h at 175 rpm by a magnetic stirrer (ARE, Velp Scientifica).

A preliminary extraction with distilled water (pH 6.8) was carried out, to evaluate the extent of metal leaching in the absence of any extractant agent.

Two different extractant agents were tested: EDTA and citric acid (CA), both used as aqueous solution 0.05 M (pH equal to 4.40 and 2.02, respectively) or 0.1 M (pH equal to 4.37 and 1.92, respectively).

Three selected liquid/solid ratio were tested: 5, 8 and 12.5, in the range successfully investigated in other experimentation of metal extraction from soils [29].

Table 2
Washing tests: summary of the operating conditions

Test	Extractant solution	L/S ratio	Chelant (mmol)	pH ₀
P1	EDTA 0.05 M	12.5	62.5	4.59
P2	EDTA 0.1 M	12.5	125	4.43
P3	EDTA 0.05 M	5	25	7.05
P4	EDTA 0.05 M	8	40	6.51
P5	EDTA 0.1 M	8	80	5.93
P6	Citric acid 0.1 M	12.5	125	2.87
P7	Citric acid 0.1 M	8	80	3.57

In Table 2 the experimental conditions of washing tests are summarized: each tests was performed in triplicate. In all tests, with the exception of test P4, the chelant amount used was always in excess with respect to the overall metals amount in the sediment as reported in Table 1, without considering calcium amount.

The pH measured in each test in the contact solution after 10 min of stirring (pH₀) are also reported in the table. The pH values were found to be strongly dependant upon the liquid/solid ratio, due to the high buffer power of the solid.

Since the objective of the experimentation was to maximize the amount of Cu, Pb and Zn extracted, but limiting the mobilization of other undesirable cations, the tests were performed evaluating two possible factors influencing the possibility to achieve this goal: reduce the pH value, to increase metal mobilization, and/or increase the excess of EDTA with respect to metal availability (this latter corresponded to about 20.58 mmol in each test). Tests P1 and P2 were performed in strongly acidic initial conditions, due to the very large excess of EDTA together with the high L/S ratio. In the following tests the L/S ratio was reduced, and, as a consequence, due to the buffer effect of the sediment, the pH measured during the tests was only slight acidic (test P4 and P5) or at least neutral (test P3).

In tests P6 and P7 the same consideration were made, but using citric acid as chelating agent.

At selected time interval, agitation was stopped to allow sedimentation and 2 mL samples of liquid were drawn and, after dilution with distilled water, subjected to analyses.

3. Results and discussion

3.1. Speciation of heavy metals in the sediment before washing

The results of preliminary sequential extraction tests performed to assess Cu, Pb and Zn distribution in the sediment are reported in Table 3.

Practically all copper was found in the organic fraction of the sediment; zinc was present mainly in the residual fraction, with lower and almost equal amount in the carbonate, Fe–Mn oxides and organic fractions, and lead was mainly accumulated in the carbonate fraction, the Fe–Mn oxides, and the residual fraction. Iron was present almost totally in the residual fraction.

Table 3
Results of sequential extraction tests performed before the treatment

Fraction	Cu	Pb	Zn
Exchangeable (%)	n.d.	n.d.	n.d.
Carbonate (%)	8.42 ± 0.07	49.07 ± 0.02	12.97 ± 0.04
Fe and Mn oxides and hydroxides (%)	n.d.	31.07 ± 7.94	29.11 ± 1.27
Organic matter (%)	88.32 ± 1.24	n.d.	14.69 ± 0.44
Residual (%)	3.26 ± 0.83	19.86 ± 7.94	43.23 ± 1.75

Only traces for all the four investigated metals were detected in the exchangeable fraction: this is consistent with the pH of the sediment, since other studies have already assessed that when sediment pH is higher than 5.6 the exchangeable amount of metals become negligible [18].

3.2. Sediment washing tests with EDTA

Sediment washing tests were performed to investigate the mobilization of the three considered contaminants (Cu, Pb and Zn). As and Cd were not considered, due to their very low amount in the sediments (as shown in Table 1).

As competitive cations, only Fe^{3+} , because of its great amount in the investigated sediments and since trivalent iron forms a very stable complex with EDTA ($\log K_{\text{EDTA-Fe}} = 25.1$), and Ca^{2+} were considered. Several studies have in fact already assessed that under acidic conditions the dissolution of carbonates resulted in a huge Ca^{2+} release in solution [30,31].

This was also confirmed by the results of preliminary tests performed by using tap water as extractant solution (series P, data not shown): only a slight dissolution of calcium was in fact observed.

Test P also confirmed that metals were adsorbed onto sediment particles in stable form: the extent of metals other than calcium dissolved in the absence of the chelant was negligible, and only traces of iron were found.

Fig. 1 shows the percentage of calcium, iron, lead and zinc with respect to their initial content in the sediment as determined by the total digestion of the samples, mobilized during time in the tests performed with EDTA. The mean values of three replicate tests are reported. The standard deviation calculated for the replicate tests was about 6% of the average value. Results generally confirm EDTA effectiveness in removing metals weakly bond to carbonate, oxide and hydroxide fractions. It was observed that increasing the L/S ratio both mixing and settling were favoured: the settling time of the solution necessary to

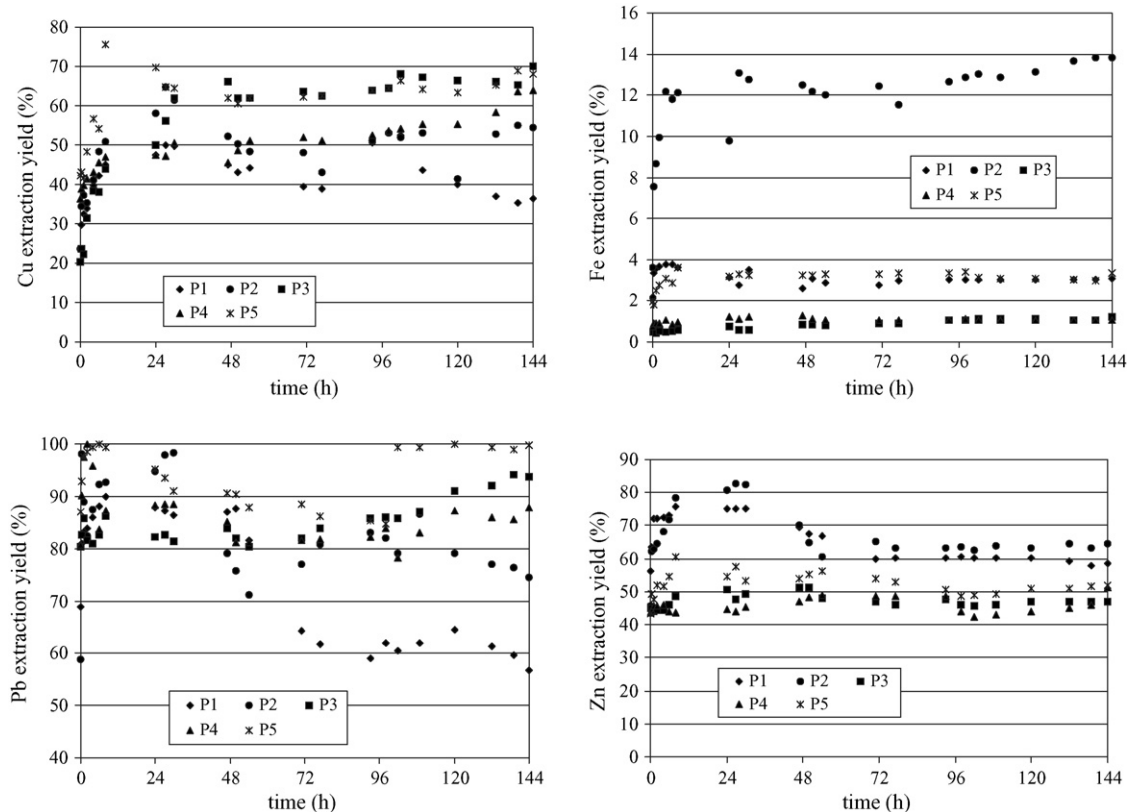


Fig. 1. Results of sediment washing tests with EDTA.

Table 4
Washing tests: summary of the experimental results

Test	pH _f	Cu (mmol)	Pb (mmol)	Zn (mmol)	Ca (mmol)	Fe (mmol)	η _{Cu} (%)	η _{Pb} (%)	η _{Zn} (%)
P1	8.15	0.454	0.238	1.570	19.75	2.61	36.33	56.68	58.62
P2	8.00	0.681	0.313	1.730	17.41	11.82	54.50	74.39	64.49
P3	7.82	0.876	0.394	1.260	10.46	1.04	70.09	93.72	47.01
P4	8.09	0.797	0.383	1.382	17.54	0.91	63.84	91.07	51.45
P5	7.76	0.852	0.419	1.393	19.30	2.88	68.15	99.71	51.84
P6	4.20	0.129	0.109	2.205	24.70	33.60	10.38	25.98	82.07
P7	4.65	0.140	n.d.	1.141	7.84	15.04	11.22	n.d.	42.48

allow sampling at L/S = 12.5 was about 10 min, while at lower L/S the settling time was considerably higher (up to a maximum of about 2 h for test P7).

The trend of Cu and Zn dissolution followed the same general behavior: after an initial quick increase of metal extraction, a plateau was reached after about 72 h of mixing. The initial Cu availability is quite lower, with respect to Zn and Pb: copper was mostly present in the organic fraction of the sediment, the difficulty in copper extraction shown by the results, can be attributed to the fact that humus organic substances associate strongly with copper in sediment [32], because they may form water insoluble metal complexes [29]. Most metal cation form “outer sphere” complexes with humus functional groups (amino, carboxyl and hydroxyl): then they remain fully hydrated and there is not a direct binding with the ligand. Conversely, copper forms “inner sphere” complexes: functional groups on the humate replace some of the hydration water molecules, and, as a result, these complexes are very stable [33]. In addition, other studies have already assessed that copper extraction from the organic matter is not pH-dependant in the presence of a large excess of EDTA [6,34,35].

Table 4 reports the amount of each metal in the contact solution and the calculated extraction yield, together with the measured pH (pH_f), at the end of each test. The mean values of three replicate tests are reported, together with the calculated standard deviation. The very close values measured for pH_f in the five tests performed with EDTA confirm again the high buffer power of the sediment [36].

According to Kim et al. [37], in the pH range between 4 and 6, the order of complex stability is: Fe³⁺-EDTA > Cu²⁺-EDTA > Pb²⁺-EDTA > Zn²⁺-EDTA > Ca²⁺-EDTA, while under less acidic or alkaline conditions, Fe³⁺-EDTA stability is dramatically reduced, and at pH 8 is similar to that of Zn²⁺-EDTA [38]. As a consequence at the end of all the tests performed, Cu²⁺-EDTA should be the preferred EDTA complex. On the contrary, the data reported in Fig. 1 and Table 4 show a general difficulty in copper extraction: this difficulty in copper extraction, confirmed by the lower extraction efficiencies with respect to Pb and Zn, was due to the above mentioned high stability of copper humate.

Since Pb was mostly bound to carbonates, the initial mobilization was easier. In particular Pb initial mobilization was strongly dependant upon the initial pH of the contact solution: under stronger acidic conditions carbonates dissolution was favoured. After this initial increase, a continuous decrease was observed in all the tests, in correspondence of the increase of

pH, because of the precipitation of PbCO₃, that is a competitive reaction even in the presence of EDTA at almost neutral conditions [39]. In all the tests, however, this decrease stopped, due to the cationic exchange between Fe²⁺ and Pb²⁺ in the EDTA complexes. As a consequence, Pb²⁺ concentration in the contact solution began progressively to increase. In the tests P3 and P5 this process continued until the end of the experiment, while, in the tests P1, P2 and P4, the effect of the subtraction of lead ions caused by the PbCO₃ precipitation was enhanced by the more alkaline conditions attained. This determined a successive progressive decrease of Pb²⁺ concentration until the end of the tests.

Zinc mobilization also appeared to be strongly influenced by pH, since zinc was almost equally distributed among the different fractions and the dissolution of several zinc minerals was involved during the extraction.

Fig. 1 also shows that in our tests, steady state conditions were not generally achieved, since even slight fluctuations in metal content and pH in the contact solution were observed until the end of the experiments. Kinetic studies of metals extraction performed on soil or sediments, showed that few hours [29,31], are required to reach steady state conditions. However, as already observed by Kim et al. [37] in a study regarding lead extraction from contaminated soils, the extraction period needs to be extended in the presence of more than one extractable metal and, as a consequence, when competitive effects are expected. In addition, in the present study, it must be taken into account that each metal was bound to different sediment fractions, and this strongly influenced the mobilization kinetic.

From a remediation point of view, the results reported in Table 4 and Fig. 2 show that the overall final amount of the three

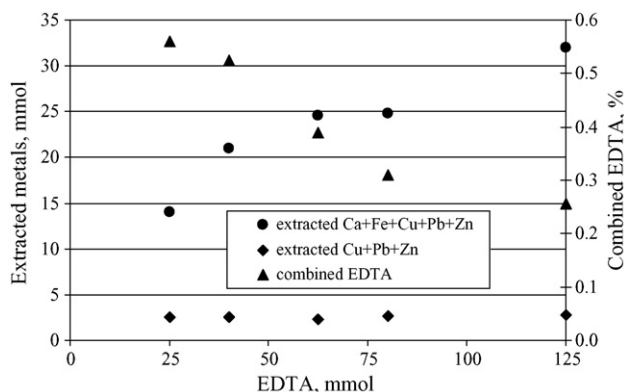


Fig. 2. Mass balance for the washing tests with EDTA.

selected metals (Cu, Pb and Zn) was in a quite narrow range (from 2.262 mmol in test P1 to 2.724 mmol in test P2), while it was different the distribution among the three metals: lead extraction yield was always higher, followed by copper in the less acidic tests (P3, P4 and P5) and by zinc in the more acidic tests (P1 and P2). The copper extraction yield values were more dispersed with respect to zinc, even considering the quite narrow range of pH_f observed, thus confirming that copper extraction was less influenced by pH.

Fig. 2 also shows the results of the mass balance performed at the end of the tests. The presence of an higher initial available amount of EDTA in the washing solution, determined an almost linear increase in the total amount of the five metals extracted ($R^2 = 0.9092$), essentially due to the enhancement in calcium and iron dissolution.

At the same time, this increase also corresponded to an increase in the contact solution of the amount of EDTA not complexed with the five considered metals, as shown in Fig. 2, where the percentage of EDTA combined with all the five metals in each test, with respect to the available EDTA in the contact solution is reported.

3.3. Leaching mechanisms

To evaluate the mechanism of metals mobilization, Fig. 3 reports the amount of Cu, Pb, Zn, Fe and Ca measured in the contact solution along time during the test P2. Also in this case the mean values of three replicate tests are reported. The standard deviation calculated for the replicate tests was about 5% of the average value.

An initial great availability of Ca^{2+} in solution was observed: since the tests were performed by dissolving EDTA- Na_2 in distilled water, the Ca^{2+} in solution was only due to calcium carbonate dissolution.

Simultaneously a lower immediate mobilization of the other metals in solution was observed.

The first step of the extraction mechanism was therefore dependant upon the pH of the extractant solution. The same trend was in fact observed in all the other washing tests, when

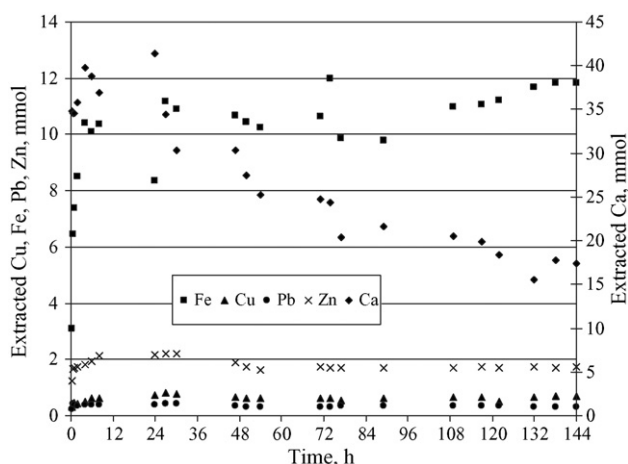
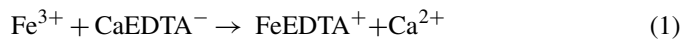


Fig. 3. Competitive effects in metal extraction: test P2.

a lower or higher initial dissolution of both calcium occurred, according to the pH of the extractant solution, determined by both the EDTA content and the L/S ratio, as shown in Table 2.

Fig. 3 shows that the initial high Ca mobilization was followed by a dramatic reduction in Ca^{2+} content, mainly determined by calcium carbonate precipitation, as a result of the increase of pH of the contact solution during mixing, and the development of exchange reactions between the metal-EDTA complexes previously formed.

Due to the lower EDTA affinity for Ca^{2+} with respect to Fe^{3+} ($\log K_{\text{Fe-EDTA}} = 25.10$; $\log K_{\text{Ca-EDTA}} = 10.59$ [26]), an exchange reaction in fact occurred between Ca-EDTA and Fe-EDTA in the contact solution, according to the:



that show how an equimolar exchange between Ca^{2+} and Fe^{3+} occurred. Iron content in solution, however, did not dramatically arise, because of the simultaneous precipitation of iron hydroxides [21].

The extent of carbonates precipitation was also confirmed by the decrease shown in inorganic carbon content and electric conductivity of the contact solution (data not shown).

The same consideration can be made for the other three metals ($\log K_{\text{Pb-EDTA}} = 18.04$; $\log K_{\text{Cu-EDTA}} = 18.80$; $\log K_{\text{Zn-EDTA}} = 16.50$ [29]): it must be considered, however, that, due to their very low concentration and their lower affinity to EDTA with respect to iron, their extracted amount along time, after an initial increase, quickly achieve a practically constant value.

3.4. Sediment washing tests with citric acid

Figs. 4 and 5 illustrate the trend of Cu, Fe, Pb and Zn extraction yield, calculated with respect to the total initial amount, along time for tests P6 and P7. The standard deviation calculated for three replicate tests was about 6%.

The results show that citric acid was not as effective as EDTA, mainly with respect to Cu and Pb extraction, as it would be

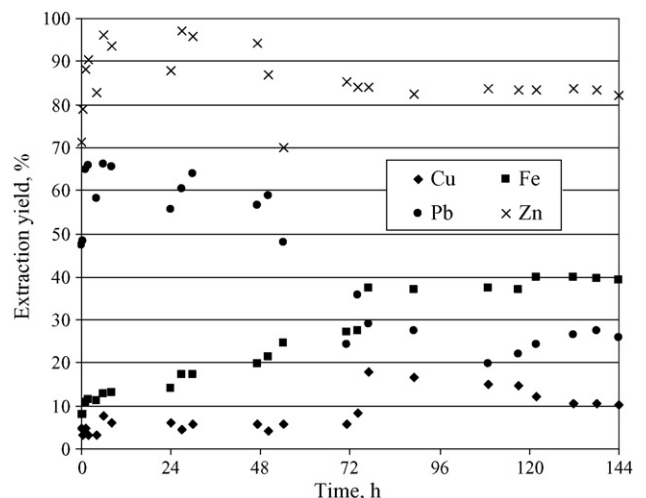


Fig. 4. Metal extraction with 0.1 M citric acid (test P6).

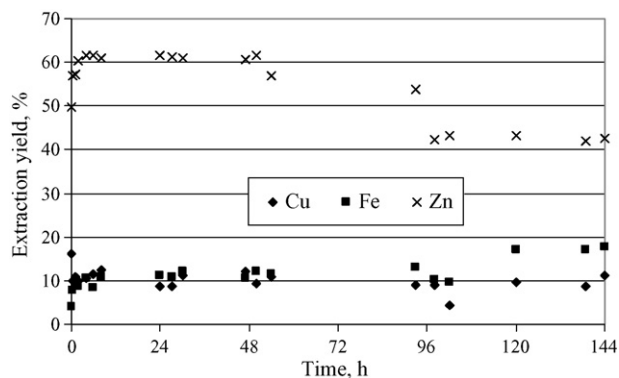


Fig. 5. Metal extraction with 0.1 M citric acid (test P7).

expected according to the complexation constant of the considered metal with citric acid ($K_{\text{Cu-CA}} = 6.1$; $K_{\text{Pb-CA}} = 4.1$). The stronger acidic conditions at the beginning and during all the tests (as shown by the data reported in Tables 2 and 4) determined a huge Ca dissolution, and the absence of carbonate precipitation (excluded at the measured pH values) contributed to maintain an high Ca concentration in the contact solution until the end of the tests.

In addition, the great affinity between citric acid and Fe ($K_{\text{Fe-CA}} = 11.85$) determined the exchange between iron and the other dissolved ions during the tests: Fe amount in the contact solution in fact increased simultaneously to a decrease of the concentration of the other metals, whose concentration, however, did not dramatically decay, with the only exception of Pb, due to the precipitation of PbCO_3 even under acidic conditions [39]. In addition, since acidic conditions were maintained along both the tests, the precipitation of iron hydroxides did not occur.

As regards the extraction efficiencies of the three investigated metals, results show that the preferred ion for citrate was Zn^{2+} . The calculated extraction efficiency for zinc in both tests P6 and P7 was higher to those calculated for the tests performed with EDTA, accordingly with the fact that strong acidic conditions were maintained during the tests (as reported in Tables 2 and 4 where the initial and final pH values are shown), thus favouring zinc extraction even from the residual fraction of the sediment.

Table 5 shows the results of the sequential extraction tests performed after the washing treatment P5. The remaining lead in the sediments (about 0.25 mg/kg) was found to be almost equally distributed between the exchangeable and residual fractions (data not shown).

Table 5
Results of sequential extraction tests performed after washing treatment P5

Fraction	Cu	Zn
Exchangeable (%)	16.93 ± 1.38	9.81 ± 0.60
Carbonate (%)	n.d.	13.71 ± 1.24
Fe and Mn oxides and hydroxides (%)	n.d.	20.38 ± 1.42
Organic matter (%)	75.55 ± 3.76	8.86 ± 0.77
Residual (%)	6.92 ± 0.24	46.32 ± 1.42

3.5. Speciation of heavy metals in the sediment after washing

The speciation of the investigated metals in the sediment after the washing treatment, is in accordance with the mobilization mechanisms observed and the results discussed in the previous sections.

The mobilization of the three metals from the carbonate fraction of the sediment was almost total, as the mobilization of Pb and Zn from the Fe–Mn oxides and hydroxides fraction. On the contrary, as a consequence of the mobilization induced by washing treatment, a significant amount of Cu and Zn metal resulted shifted to the exchangeable fraction.

As regards to the metals initially bound to the residue fraction of the sediment, the high values of pH_f measured at the end of the tests, did not allow Zn mobilization from this fraction, but, at the same time, an almost complete Pb mobilization was ensured.

4. Conclusions

The mobilization of Cu, Pb and Zn from an Italian harbour sediment induced by washing the sediment with EDTA or citric acid solutions was investigated. The aim of the experimentation was to determine the optimal conditions for the extraction of the three metals, and, at the same time, to investigate the extent of sediment minerals dissolution.

Results of experimental tests performed at different chelant concentration and L/S ratio show that EDTA resulted to be more effective with respect to citric acid in mobilizing metals bond to carbonate, oxide and hydroxide and organic matter fractions: in particular citric acid was unable to extract lead and copper from the sediment.

On the contrary, at the strong acidic conditions maintained during citric acid extractions, zinc mobilization from the residual fraction of the sediment was higher. In addition because of the great affinity between citric acid and iron, and the strong acidic conditions maintained during extraction, an higher iron dissolution was observed (up to about the 39% of the total iron content in the sediment).

However, a general difficulty in copper extraction was observed in both cases, due to the high stability of copper humate.

The mechanism of extraction with EDTA was found to involve an initial high Ca mobilization, depending upon the pH reached by the contact solution after mixing with the sediment, followed by a dramatic reduction in Ca^{2+} content, mainly determined by calcium carbonate precipitation, as a result of the increase of pH of the contact solution during mixing, and the development of exchange reactions between the metal–EDTA complexes previously formed.

The mobilization of Cu, Pb and Zn from the carbonate fraction of the sediment was almost total, as the mobilization of Pb and Zn from the Fe–Mn oxides and hydroxides fraction. On the contrary, as a consequence of the mobilization induced by washing treatment, a significant amount of Cu and Zn metal resulted shifted to the exchangeable fraction.

In the view of the field application of the washing technology for sediment remediation, the overall results suggest that the use of a 0.05 M EDTA washing solution would be preferred with respect to a more concentrated one, and, in any case, increasing the excess of chelating agent with respect to the metal availability, may enhance EDTA consumption through undesired mineral dissolution, rather than to increase toxic metals extraction.

References

- [1] B. Dahrazma, C.N. Mulligan, Evaluation of the removal of heavy metals from contaminated sediment in continuous flow tests with selective sequential extraction, *J. ASTM Int.* 3 (2006) 1–10.
- [2] R.N. Jackson, D. Baird, S. Els, The effect of the heavy metals lead (Pb^{2+}) and zinc (Zn^{2+}) on the brood and larval development of the burrowing crustacean, *Callinassa kraussi*, *Water SA* 31 (2005) 107–116.
- [3] E. His, R. Beiras, M.N.L. Seaman, The assessment of marine pollution—bioassays with bivalve embryos and larvae, *Adv. Mar. Biol.* 38 (1999) 178–371.
- [4] G. Birch, S. Taylor, Possible biological significance of contaminated sediments in Port Jackson, Sydney, Australia, *Environ. Monit. Assess.* 77 (2002) 179–190.
- [5] G. Dave, E. Nilsson, Sediment toxicity and contaminants in the Kattogatt and Skagerrak aquatic ecosystem, *Health Manage.* 2 (1999) 347–360.
- [6] A. Barona, I. Aranguiz, A. Elias, Metal associations in soils before and after EDTA extractive decontamination: implications for the effectiveness of further clean-up procedure, *Environ. Pollut.* 113 (2001) 79–85.
- [7] S. McCready, G.F. Birch, S.E. Taylor, Extraction of heavy metals Harbour sediments using 1 M HCl and 0.05 m EDTA and implications for sediments—quality guidelines, *Aust. J. Earth Sci.* 50 (2003) 249–255.
- [8] H.D. Detzner, W. Schramm, U. Doring, W. Bode, New Technology of mechanical treatment of dredged material from Hamburg harbour, *Water Sci. Technol.* 37 (1998) 337–343.
- [9] J.D. Coates, R.T. Anderson, Emerging techniques for anaerobic bioremediation of contaminated environments, *Trends Biotechnol.* 18 (2000) 408–412.
- [10] C.N. Mulligan, R.N. Yong, B.F. Gibbs, Remediation technologies for metal-contaminated soils and groundwater: an evaluation, *Eng. Geol.* 60 (2001) 193–201.
- [11] H.M. Freeman, E.F. Harris, *Hazardous Waste Materials: Innovative Treatment*, Technomic Publishing, Lancaster, Basel, 1995.
- [12] A. Moutsatsou, M. Gregou, D. Matsas, V. Protonotarios, Washing as a remediation technology applicable in soils heavily polluted by mining-metallurgical activities, *Chemosphere* 63 (2006) 1632–1640.
- [13] R.S. Tejowulan, W.H. Hendershot, Removal of trace metals from contaminated soils using EDTA incorporating resin trapping techniques, *Environ. Pollut.* 103 (1998) 135–142.
- [14] P.H.T. Beckett, The use of extractants in studies on trace metals in soils, sewage sludges, and sludge-treated soils *Advances in Soil Science*, vol. 9, Springer-Verlag, New York Inc., 1989, pp. 143–179.
- [15] B. Sun, F.J. Zhao, E. Lombi, S.P. McGrath, Leaching of heavy metals from contaminated soils using EDTA, *Environ. Pollut.* 113 (2001) 111–120.
- [16] B.E. Reed, P.C. Carriere, R. Moore, Flushing of a Pb(II) contaminated soil using HCl, EDTA and $CaCl_2$, *J. Environ. Eng. ASCE* 122 (1996) 48–50.
- [17] R.J. Abumaizar, E.H. Smith, Heavy metal contaminants removal by soil washing, *J. Hazard. Mater.* B70 (1999) 71–85.
- [18] R.W. Peters, Chelant extraction of heavy metals from contaminated soils, *J. Hazard. Mater.* 66 (1999) 151–210.
- [19] C.E. Martinez, Solubility of lead, zinc and copper added to mineral soils, *Environ. Pollut.* 107 (2000) 153–158.
- [20] M.A.M. Kedziorek, A.C.M. Bourg, Solubilization of lead and cadmium during the percolation of EDTA through a soil polluted by smelting activities, *J. Contam. Hydrol.* 40 (2000) 381–392.
- [21] D. Fangueiro, A. Bermond, E. Santos, H. Carapuça, A. Duarte, Heavy metal mobility assessment in sediments based on a kinetic approach of the EDTA condition: search for optimal experimental conditions, *Anal. Chim. Acta* 459 (2002) 245–256.
- [22] U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 1996, SW 846 On line Manual: <http://www.epa.gov/epaoswer/hazwaste/test/main.htm>.
- [23] C. Liu, J.B. Evett, *Soil Properties, Testing, Measurement, and Evaluation*, 5th ed., Prentice-Hall, New York, 2002.
- [24] A. Walkley, I.A. Black, An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method, *Soil Sci.* 37 (1934) 29–38.
- [25] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, *Anal. Chem.* 51 (1979) 844–851.
- [26] S. Vilar, A. Gutierrez, J. Antezana, P. Carral, A. Alvarez, A comparative study of three different methods for the sequential extraction of heavy metals in soil, *Toxicol. Environ. Chem.* 87 (2005) 1–10.
- [27] O. Abollino, A. Giacomino, M. Malandrino, E. Mentasti, The use of sequential extraction procedures for the characterization and management of contaminated soils, *Ann. Chim. Rome* 95 (2005) 525–538.
- [28] V. Cappuyens, R. Swennen, J. Verhulst, Assessment of heavy metal mobility in dredged sediments: porewater analysis, single and sequential extractions, *Soil Sediment Contam.* 15 (2006) 169–186.
- [29] R. Abumaizar, L.I. Khan, Laboratory investigation of heavy metal removal by soil washing, *J. Air Waste Manage. Assoc.* 46 (1996) 765–768.
- [30] N. Papassiopi, S. Tambouris, A. Kontopoulos, Removal of heavy metals from calcareous contaminated soil by EDTA leaching, water, air, *Soil Pollut.* 109 (1999) 1–15.
- [31] L. Di Palma, P. Ferrantelli, Cooper leaching from a sandy soil: mechanisms and parameters affecting EDTA extraction, *J. Hazard. Mater.* 122 (2005) 85–90.
- [32] G.H. Bolt, W.H. Van Riemsdijk, Surface chemical process in soil, in: W. Stumm (Ed.), *Aquatic Surface Chemistry*, Wiley-Interscience, New York, NY, USA, 1987, pp. 127–161.
- [33] J. Wu, L.J. West, D.I. Stewart, Copper(II) humate mobility in kaolinite soil, *Eng. Geol.* 60 (2001) 275–284.
- [34] J.P. Ghestem, A. Bermond, EDTA extractability of trace metals in polluted soils: a chemical–physical study, *Environ. Technol.* 19 (1998) 409–416.
- [35] C. Caplat, H. Texier, D. Barillier, C. Lelievre, Heavy metals mobility in harbour contaminated sediments: the case of Port-en-Bessin, *Mar. Pollut. Bull.* 50 (2005) 504–511.
- [36] W. Calmano, J. Hong, U. Foerstner, Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential, *Water Sci. Technol.* 28 (1993) 223–235.
- [37] C. Kim, Y. Lee, S.K. Ong, Factors affecting EDTA extraction of lead from lead-contaminated soils, *Chemosphere* 51 (2003) 845–853.
- [38] I.M.C. Lo, X.Y. Yang, EDTA extraction of heavy metals from different soil fraction and synthetic soil, water, air, *Soil Pollut.* 109 (1999) 219–236.
- [39] B. Nowack, F.G. Kari, H.G. Kruger, The remobilization of metals from iron oxides and sediments by metal–EDTA complexes, water, air, *Soil Pollut.* 125 (2001) 243–257.