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### Chemical and biological strategies for the mobilisation of metals/semi- metals in contaminated dredged sediments: experimental analysis and environmental impact assessment

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# Chemical and biological strategies for the mobilisation of metals/semi-metals in contaminated dredged sediments: experimental analysis and environmental impact assessment

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This study deals with laboratory-scale investigations to evaluate the efficiency of different chemical leaching agents (i.e. sulfuric, oxalic and citric acids) and bioleaching processes (based on different acidophilic bacterial strains) on the mobilisation of metals/semi-metals in contaminated harbour sediments. A simplified life-cycle assessment was also performed in order to compare the investigated strategies in terms of their main environmental impacts. The different chemical leaching agents provided different extraction efficiencies of toxic metals. Among the investigated chemical leaching agents, citric acid 0.5 M and sulfuric acid pH 2 were the most effective, with average mobilisation efficiencies of ~30% for Zn and Cr, ~40% for Ni, and 35 and 58% for As, under citric and sulfuric acid, respectively. Similar higher extraction efficiencies of metals were also observed in bioleaching experiments with the presence of ferrous iron. The life-cycle assessment revealed that treatments based on diluted sulfuric acid are a better option considering both resource requirements and emissions, leading to lower environmental impacts compared with the other treatment strategies. Overall results from this study provide new insights for the definition of the most efficient and environmentally friendly strategies to be used for dredged sediments contaminated with metals.

**Keywords:** marine sediments; metal contaminants; leaching; bioleaching; life-cycle assessment

## 1. Introduction

Metal contamination of dredged sediments in harbour sites is a widespread problem. Unlike organic pollutants, metals cannot be degraded and so techniques for the remediation of metal-contaminated sediments can be aimed at metal removal or metal chemical transformation into their less toxic/mobile forms [1–3]. Sediment washing, electro-dialytic remediation and phyto-extraction are examples of strategies able to extract/separate metals from solid matrices [4–6], whereas phyto-stabilisation, cation exchange and sorption are stabilisation processes able to minimise metal migration potential [4,7,8]. Compared with the latter, a significant advantage of extraction/separation methods is that metal concentrations can be reduced below regulatory limits, and sediment reuse may be allowed. Different physical–chemical treatments can be potentially

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used to achieve this goal, but the application of environmentally friendly techniques should be preferred [9]. Chelating agents such as citric, oxalic, gluconic and ascorbic acids are naturally produced by living organisms (e.g. bacteria and fungi) [10,11] and can form soluble metal complexes leading to metal removal from contaminated sediments. Some studies have investigated their potential for sediment and soil remediation as low environmental impact alternatives to conventional techniques and results seem to suggest that organic acids could be potentially applied with high efficiency [6,12–14].

Another biological strategy that could be successfully applied on metal-contaminated sediments is the biological solubilisation of metals based on the ability of Fe/S-oxidising bacteria to produce leaching agents (i.e. mainly ferric ions and sulfuric acid) by their metabolism (i.e. bioleaching) [15]. In fact, bioleaching is gaining increasing prominence as biological technique for metal removal from environmental matrices and several papers have been aimed at evaluating bioleaching performance in sediment bioremediation [16–21]. Such investigations have increased our knowledge on the main mechanisms involved during bioleaching processes [21–24] and have often suggested that bioleaching may be a promising environmentally friendly technique for sediments contaminated with high concentrations of metals [17–19,25], however, comparative analyses of the efficiency of chemical vs. biological strategies on metal mobilisation in contaminated marine sediments are still missing. This information is crucial to identify the most efficient strategies to be used for the remediation of dredged sediments contaminated by metals. Furthermore, treatment options of dredged sediments should be defined on the basis of not only their efficiency, but also their environmental sustainability. In this regards, life-cycle assessment (LCA) may be an important tool in defining technologies with the lowest environmental impact [26–29]. No single environmental assessment tool can cover all relevant aspects of the sediment treatment chains [30], but a life-cycle-oriented approach may identify hidden impacts, which are generally neglected, especially in treatment processes applied to contaminated sediments [26,31].

Here, chemical and biological strategies have been applied to contaminated marine sediments with the aim of comparing their efficiency in chromium (Cr), nickel (Ni), zinc (Zn) and arsenic (As) mobilisation and their environmental impact, through LCA. Different chemical leaching agents (i.e. sulfuric, oxalic and citric acids) and bioleaching processes (based on different acidophilic bacterial strains) have been investigated in laboratory-scale experiments. This work presents a new methodological approach, based on integration of the experimental results, dealing with metal-extraction efficiencies, with the environmental impact assessed by means of a LCA. Both these aspects are considered fundamental tools in assessing the sustainability of a strategy for the management of contaminated marine sediments.

## 2. Materials and methods

### 2.1. Sediment samples

Sediment samples were collected in the port of Ancona (43.62495°N, 13.49915°E, Adriatic Sea, Mediterranean Sea, Italy), by means of a Van Veen grab sampler. After collection, sediments were sieved to <2 mm to remove gravel, homogenised and then stored at 4 °C until further use. Sediment subsamples were collected to establish bioleaching experiments and for characterisation analyses.

Sediment grain-size analysis, determined using a sieving technique [32], revealed that the sediment was largely dominated by the silt–clay fraction (i.e. <63 μm, ~80%). X-Ray diffraction analysis (Siemens D-500 diffractometer) revealed that ~90% of the sediment was composed of silicates and carbonates, ~5% by iron and manganese oxides, and <5% by sulfides.

## 2.2. Sediment characterisation

For water and total organic matter (TOM) determination, sediment aliquots were dried at 60 °C for 48 h and then treated for 16 h with an excess of 10% HCl to remove carbonates [33]. The sediment was then washed with water and dried at 60 °C for 48 h. Finally, the sample was calcinated for 2 h at 450 °C. TOM was estimated as the difference between the dry weight without carbonates and the weight of the residue after combustion [34]. Carbonates were also estimated as the difference between dry weight and the weight after acid digestion. Water content was calculated as the difference between dry weight and wet weight.

As, Cr, Zn and Ni contents in the sediment were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES), after acid digestion [35]. Metal distribution in sediment was estimated using a sequential extraction procedure, according to the European Union protocol [36]. Four different fractions were considered: (1) exchangeable and carbonate fraction, extracted by incubating sediment with 0.11 M acetic acid; (2) iron and manganese oxide fraction (reducible), extracted with 0.1 M hydroxylamine hydrochloride at pH 2; (3) organic and sulfide fraction (oxidisable), extracted by a first step with 30% hydrogen peroxide and a subsequent passage with ammonium acetate at pH 2; and (4) residual fraction, which remains in the residual solid, determined by ICP-AES, after acid digestion [35].

## 2.3. Experiment set-up

### 2.3.1. Chemical leaching experiments

Before conducting leaching experiments, sediments were twice washed with MilliQ water to remove inorganic salts. Experiments were performed in 250 mL microcosms containing 20% of sediment (dry weight) using solutions of oxalic (0.5 M), citric (0.5 M) or sulfuric acid (pH 2) as leaching agents. Further microcosms without the addition of acid solutions (i.e. untreated samples) were utilised as controls. Microcosms were incubated at room temperature for 4 h under continuous mixing (250 rpm).

### 2.3.2. Bioleaching experiments

Pure cultures of three different autotrophic Fe/S-oxidising bacterial strains (i.e., *Acidithiobacillus ferrooxidans* DSMZ 14882T, *A. thiooxidans* DSMZ 14887T and *Leptospirillum ferrooxidans* DSMZ 2705T) and a heterotrophic Fe-reducing bacterial strain (i.e. *Acidiphilium cryptum* DSMZ 2389T) were provided by the German Resource Centre for Biological Material. Bacterial strains were grown in their specific media according to the provider's instructions (www.dsmz.de) and aliquots of cell cultures collected during the exponential growth phase were inoculated into replicate microcosms according to the experimental plan described below.

For bioleaching experiments, sediment samples, previously washed by MilliQ water to remove inorganic salts, were added in 9 K medium, modified by removing FeSO<sub>4</sub> [16], unless otherwise specified.

Details on the experimental design are reported in Table 1. The investigated factors included the presence/absence of elemental sulfur, the presence/absence of ferrous iron, and the presence/absence of the different bacterial strains. Microcosms inoculated with *Acidiphilium cryptum* were also added with yeast extract (0.03 g · L<sup>-1</sup>; i.e., 10% of the ideal concentration).

To investigate the role of glucose in microcosms where heterotrophic bacterial strains were present two additional treatments were carried out. In particular, glucose 0.1 g · L<sup>-1</sup> (i.e. 10% of the ideal concentration) was added to microcosms with either S<sup>0</sup> or Fe<sup>2+</sup>.

Table 1. Experimental design for bioleaching experiments (25 °C, 100 g · L<sup>-1</sup> sediment, initial pH 2, 14 days of treatment, sediment pretreatment by washing with deionised water). pH values after 7 and 14 days are also reported.

S <sup>0</sup> (g · L <sup>-1</sup> )	Fe <sup>2+</sup> (g · L <sup>-1</sup> )	pH			
		Glucose	Inoculum	7 days	14 days
0	0	0	no	3.0	3.0
1	0	0	no	6.2	5.3
0	8.9	0	no	2.3	2.0
1	8.9	0	no	2.3	1.9
0	0	0	Auto	5.8	6.4
1	0	0	Auto	7.2	7.2
0	8.9	0	Auto	2.1	2.2
1	8.9	0	Auto	2.1	2.1
0	0	0	Mix	2.8	2.9
1	0	0	Mix	5.5	5.1
0	8.9	0	Mix	2.0	2.0
1	8.9	0	Mix	2.0	2.1
1	0	0.1	Mix	5.1	4.7
0	8.9	0.1	Mix	2.1	1.9

Notes: Auto, autotrophic strains (*A. ferrooxidans*, *A. thiooxidans* and *L. ferrooxidans*); Mix, autotrophic and heterotrophic strains together (*A. ferrooxidans*, *A. thiooxidans*, *L. ferrooxidans* and *Acidiphilium cryptum*).

In all the experimental systems the initial pH was adjusted to 2 using 5M H<sub>2</sub>SO<sub>4</sub> and the microcosms were then incubated at room temperature for 14 days under continuous mixing (250 rpm).

During incubation, pH and Eh measurements were carried out (Inolab Multi 720, WTW) and aliquots of sediment slurries were collected to determine prokaryotic abundances and metal concentrations.

#### 2.4. Analytical determinations

During bioleaching experiments, small slurry aliquots were periodically collected from each microcosm for prokaryotic abundance enumeration, which was performed by counting cells using epifluorescence microscopy, after staining with acridine orange. A standard procedure specifically developed for marine sediments was applied [37].

Oxidation reduction potential (ORP) and pH were measured throughout the experiment using Inolab Multi 720 precision measuring instrument by WTW; the ORP probe was a platinum electrode combined with a Ag/AgCl reference electrode in a 3 M KCl solution.

#### 2.5. Statistical analyses

To assess the statistical significance of investigated treatments an analysis of variance (ANOVA) was carried out using the GMAV 5.0 software (University of Sydney, Australia). Prior to analyses, the homogeneity of variance was tested by the Cochran test, and when necessary, the data were appropriately transformed.

#### 2.6. Environmental impact assessment

The environmental impact of the metal mobilisation strategies investigated was assessed by means of LCA, according to ISO guidance belonging to family 14040 [38–40]. LCA was conducted using GaBi 4.4 Professional software developed by the PE International, Stuttgart, integrated

with the EcoInvent database. The impacts of the processes used in this study were evaluated in the following categories: abiotic depletion, acidification potential, eutrophication potential, global warming potential, ozone layer depletion potential and photochemical ozone creation potential. The methodology chosen to evaluate the impacts was CML2001 – Nov. 09. Normalisation was carried out according to CML2001 – Dec. 07, EU25+3, and weighting (valuation) was referred to Southern Europe, the area where this study was carried out (CML2001 – Dec. 07, Experts IKP).

### 3. Results and discussion

#### 3.1. Sediment characteristics

The sediment investigated was characterised by a water content of  $41 \pm 2\%$ , an estimated carbonate content of  $460 \pm 10 \text{ mg} \cdot \text{g}^{-1}$  and a high TOM content ( $28.2 \pm 0.6 \text{ mg} \cdot \text{g}^{-1}$ ), as typically observed in shallow benthic systems characterised by high primary productivity values and/or high anthropogenic inputs [41]. The total concentrations of the different metals analysed in the harbour sediments were  $85 \pm 9$ ,  $450 \pm 60$ ,  $12 \pm 2$  and  $73 \pm 7 \mu\text{g} \cdot \text{g}^{-1}$  for Zn, Ni, As and Cr, respectively. Considering Italian legal limits (Decree of the Ministry of the Environment, Land and Sea, 7 November 2008) for the management of dredged sediments in highly contaminated sediments, all metals were below the limits for their disposal in confined facilities; consequently, the tested sediment cannot be considered highly contaminated and could be disposed of in such facilities. Nevertheless, an evaluation of sediment quality aimed at assessing the potential reuse of the dredged sediment, showed that all were above the base chemical levels for marine sediments in Italy (reported in the national guidelines [42]), especially Ni, whose concentration in the sediment was 10-fold higher than threshold levels. Consequently, a treatment aimed at metal extraction would avoid disposal in confined facilities and would open up other possibilities for sediment reuse (e.g. as a raw material in the building sector). However, total metal concentrations do not provide information about metal mobility which is, in turn, controlled by their speciation and repartition in the different geochemical phases of the sediments. It is known that different sediment components can greatly affect the ability of sediments to adsorb metals. For instance, sulfides, iron and manganese (hydro)-oxides and organic matter are known to be important metal scavengers in marine sediments [23]; in particular, sulfides and Fe/Mn oxides affect several biogeochemical processes and, thus, the ability of bacteria to affect metal speciation [23]. The analysis of metal partitioning among the geochemical fractions of the sediment provides important insights on metal potential fate (i.e. mobilisation; Figure 1). Among the considered metals and semi-metals, Cr, Ni and Zn were mainly associated with the residual fraction of the sediment (accounting for 97, 85 and 65% of their total content, respectively), whereas As was quite homogeneously distributed in all four geochemical sediment fractions. On the basis of these results, the metals and semi-metals studied can be ordered in terms of decreasing mobility, as follows:  $\text{As} > \text{Zn} > \text{Ni} > \text{Cr}$ .

#### 3.2. Efficiency of chemical and biological leaching experiments

In this work, chemical and biological leaching experiments were set up to investigate the real potential of ex situ mobilisation strategies, which are expected to have a lower environmental impact than conventional strategies, for the clean-up of marine contaminated sediment. For this purpose, metal solubilisation efficiency by bioleaching and chemical leaching with organic acids (oxalic and citric acids) were compared with those by an inorganic acid (sulfuric acid). In fact, acidophilic strains used in bioleaching strategies can be considered as leaching agents because of

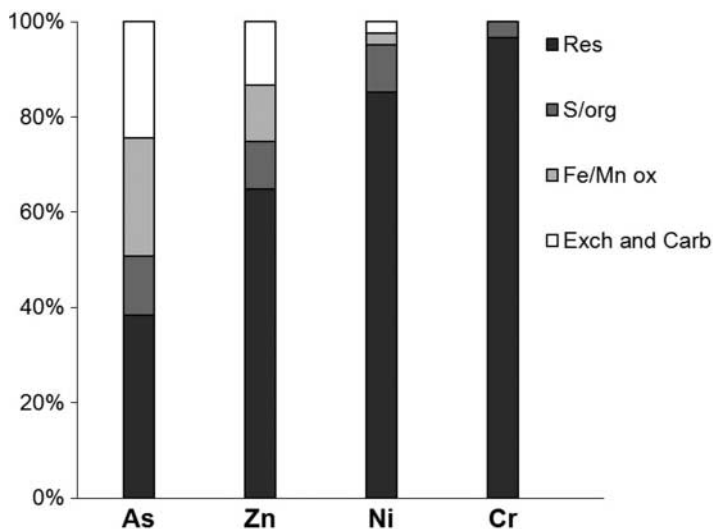


Figure 1. Metal partitioning in the sediment. Res, residual fraction; S/org, sulfide/organic fraction; Fe/Mn ox, iron and/or manganese oxide fraction; Exch and Carb, exchangeable and carbonate fractions.

their ability to produce and recirculate sulfuric acid and ferric ions [19]; by contrast, low molecular mass organic acids can complex metal cations leading to their mobilisation from contaminated solids [6,10–12].

All of the acid solutions tested in this study significantly enhanced the extraction efficiencies of metals when compared with the controls (i.e. microcosms containing only water; Table 2). The chemical leaching agents provided different extraction efficiencies of metals/semi-metals, ranging from 21% for Cr with oxalic acid 0.5 M to 58% for As with sulfuric acid pH 2. Cr and Zn showed extraction efficiencies of ~22, 29 and 34% with oxalic, citric and sulfuric acid, respectively. The highest mobilisation of Ni was ~40% with sulfuric acid and citric acid. In the case of As, the performances of the leaching agents were, in ascending order of efficiency, citric acid (33%), oxalic acid (42%) and sulfuric acid (58%). In general, the observed mobilisation performance was consistent with metal/semi-metal partitioning in the sediment fractions: those mainly associated with the residual phase (such as Cr), which are supposed to be largely immobile, were only slightly mobilised [43]; however, As, that was homogeneously distributed among the four geochemical sediment fractions, showed the highest mobilisation. Among the investigated chemical leaching agents, citric acid 0.5 M and sulfuric acid pH 2 were the most effective, with average mobilisation efficiencies of ~30% for Zn and Cr, ~40% for Ni, 35 (citric) and 58% (sulfuric) for As. Such performance can be considered satisfactory, even if did not result in complete mobilisation; indeed, the contamination level of the sediment can be considered moderate rather than severe, and the

Table 2. Metal/semi-metal mobilisation efficiencies after chemical treatment with inorganic and organic acids (20% w/v sediment, room temperature, 4 h treatment, mixing 250 rpm).

	Zn (%)	Cr (%)	Ni (%)	As (%)
Control (deionised water)	n.r.	n.r.	n.r.	n.r.
Sulfur acid pH 2	29 ± 3	29 ± 3	38 ± 2	58 ± 6
Oxalic acid 0.5 M	23 ± 2	21 ± 2	24 ± 2	42 ± 4
Citric acid 0.5 M	34 ± 4	32 ± 3	40 ± 4	33 ± 4

Note: n.r., not relevant.



observed mobilisation efficiencies may meet regulatory levels for reuse options, which depend strictly on single country specificities [44].

In this study, we also investigated the efficiency of biologically mediated solubilisation of metals from contaminated dredged sediments using different substrata (i.e. elemental sulfur and ferrous ion) and bacterial strains. Sulfur was added to the sediments because it can efficiently promote the growth of autotrophic Fe/S oxidising bacteria and the subsequent sulfuric acid production [20,25,45]. Iron was added to stimulate the growth of autotrophic Fe/S-oxidising bacteria (as ferrous iron), and also to promote oxidation processes, when bio-oxidised in its ferric form. In this study, the role of heterotrophic Fe-reducing bacterial strains and of glucose as amendment, which have been previously reported to support and enhance the metabolism of Fe/S-oxidising bacterial strains [16] has been also investigated. Results of bioleaching experiments indicated that iron addition increased the solubilisation of zinc and nickel up to >40%, whereas the mobilisation of As and Cr was rather low in all the investigated conditions (Figure 2). The addition of ferrous iron had an important effect not only on metal mobilisation, but also on bacterial growth rates and the maintenance of acidic conditions. After 7 days of incubation, microcosms containing ferrous iron showed values of total prokaryotic abundance significantly higher than those without iron (range:  $1.2\text{--}2.0 \times 10^9$  and  $0.5\text{--}1.1 \times 10^9$  cells  $\cdot$  g<sup>-1</sup>, respectively). At the same time, the presence of ferrous iron allowed the maintenance of acidic conditions over time (see Table 1), which is required for maintaining mobilised metals in soluble phase and for the metabolism of acidophilic bacterial strains [46,47]. In any case, microcosms without inoculated bacterial strains (i.e. controls: microbial abundances determined over time were not relevant) did not show significant differences in metal mobilisation when compared with those amended with autotrophic and/or heterotrophic bacterial strains, suggesting a minor role of these biological components

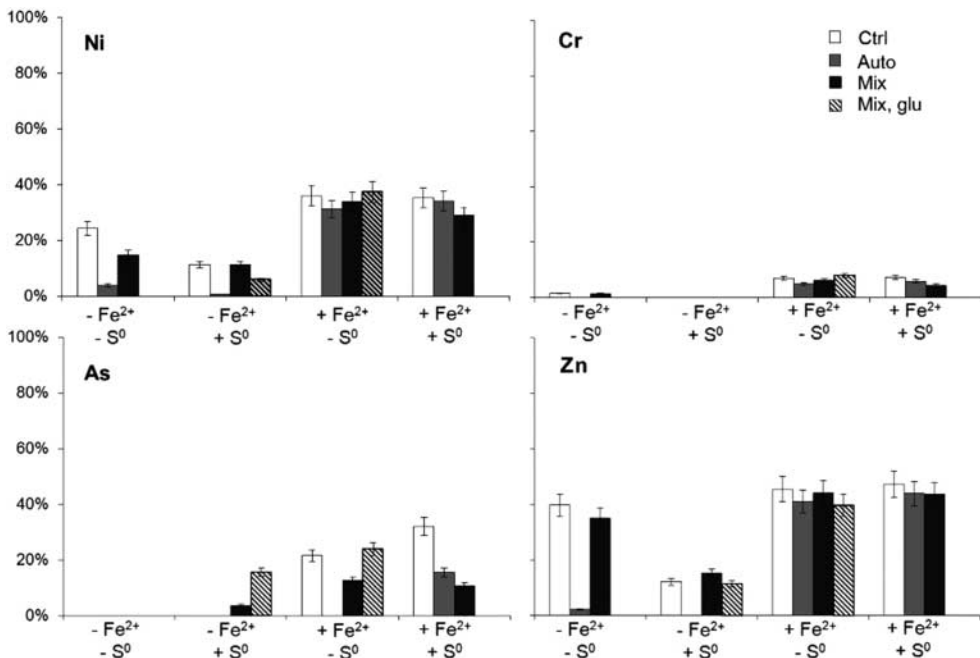


Figure 2. Metal-extraction efficiencies at the end of the bioleaching experiments. Ctrl, abiotic controls; Auto, bioleaching treatments with autotrophic bacterial strains (only Fe/S-oxidising bacteria); Mix, bioleaching treatments with both autotrophic (Fe/S-oxidising bacteria) and heterotrophic bacterial strains (Fe-reducing bacteria); Mix, glu, bioleaching treatments carried out using both autotrophic (Fe/S-oxidising bacteria) and heterotrophic bacterial strains (Fe-reducing bacteria) in the presence of glucose.

in the metal leaching processes, when sediment concentration is relatively high (10% in this work vs. 2% in Beolchini et al. [16]). To provide insights into the main factors influencing metal mobilisation during bioleaching experiments we carried out statistical analyses based on ANOVA, together with assessment of the components explaining the observed variance (Table S1, available online). ANOVA indicated that the presence of iron had a statistically significant effect for all of the metals investigated ( $p < 0.01$ ). Moreover, a large fraction of the variance in the different metals analysed (up to 88% for Cr) was explained by the presence of iron. These results, together with the significant inverse relationships we observed between iron and pH values ( $r = -0.751$ ;  $p < 0.01$ ), confirm that metal mobilisation efficiency depends strictly on the system pH, which can be maintained under acidic conditions either by chemical or biological strategies.

### 3.3. Environmental impact assessment

On the basis of the different strategies applied here, we carried out an analysis of the potential environmental impact of such treatments for metal mobilisation in dredged sediments. This analysis was performed using a simplified LCA. The functional unit selected for LCA was 100 000 m<sup>3</sup> of sediment containing 50% sand (as an average of material dredged annually from an Italian port of medium dimensions) to be treated. Figure 3 shows the system boundaries. The following three scenarios were compared: (1) treatment with citric acid (0.1 M), for 4 h, (2) treatment with diluted sulfuric acid (0.05 M) for 4 h and (3) biological treatment for 3 days in 9 K medium. It was assumed that all treatments were applied on 25% sediment concentration (dry weight/volume) and all of the processes which are common to the three scenarios were not included in the inventory (i.e. for the upstream: dredging operations, sand separation, sediment conditioning; for the downstream: sediment reconditioning and reuse, wastewater treatment and water reuse). Therefore, according to this simplified approach, the three different treatment options included only production processes for the requested raw materials (i.e. citric acid, sulfuric acid and reagents of the 9 K medium)

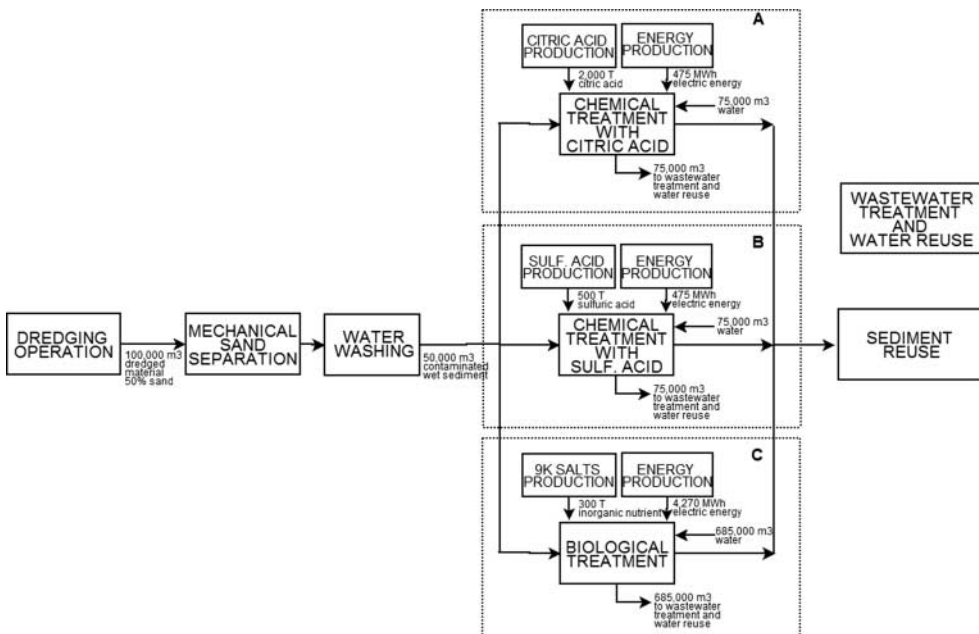


Figure 3. System boundaries of the three scenarios investigated for dredged sediment treatment: chemical treatment with citric acid (A), chemical treatment with diluted sulfuric acid (B), biological treatment with acidophilic strains (C).

and electric power for sediment stirring. In particular, for citric acid, the biological production route was taken into account due to the high impact of the chemical route, in terms of emissions and a 50% mass allocation was hypothesised, considering that the biological process produces both citric and oxalic acid [48]. For sulfuric acid, conventional production from the oxidation of primary sulfur was considered, even though its production as a co-product during clean-up of off-gas containing  $\text{SO}_2$  would significantly reduce the requirement of primary sources. Ferrrous iron is considered to be a chemical reagent, even though in this case its production by bioleaching of pyrite minerals is expected to reduce its contribution to the environmental impact of the treatment. Eventual energy requirements due to temperature control in the leaching/bioleaching reactors were not included in the analysis because we are following a simplified approach and all considered treatments are carried out at the same temperature (room temperature). The output of the life-cycle inventory analysis, in terms of the consumption of energy and material resources, and emissions to air, water and soil (Table S2, available online) showed that the treatment based on bioleaching requires the highest consumption of material and energy resources and gives the highest emissions. Conversely, treatment with diluted sulfuric acid appears a better option in terms of both resource requirements and emissions.

We also estimated the impact of the three different treatments on the global warming potential, together with the relative contributions of the raw material and energy requirements (Figure 4). As observed by life-cycle inventory analysis, the treatment based on diluted sulfuric acid exhibits the lowest impact in terms of carbon dioxide emissions when compared with the other two scenarios. Data, normalised on an annual basis with respect to the average European loads and weighted according to the environmental problems of Southern Europe, were then used to assess the overall environmental impact of each treatment. In addition to global warming potential, three other impact categories were considered including photochemical ozone creation potential, acidification potential and abiotic depletion (Figure 5). Our analyses support the conclusion that, conversely to what may be expected, treatments based on diluted sulfuric acid have the lowest environmental impact for all of the considered categories. The highest potential environmental impact of the chemical treatment with citric acid, thought to be more environmental friendly, is associated with the production of the required raw materials, which is usually neglected outside a life-cycle-oriented approach. In parallel, the highest impact for the biological strategy is mainly

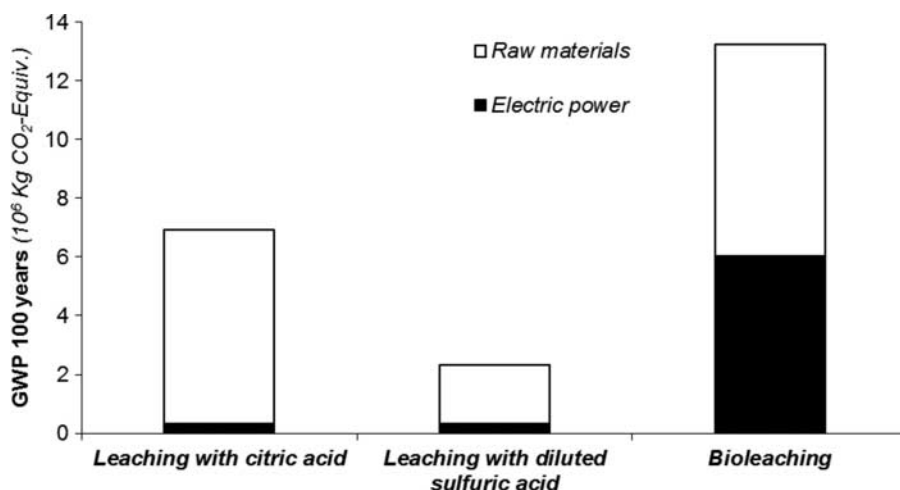


Figure 4. Environmental impact category global warming potential (kg  $\text{CO}_2$  equiv.) of the three scenarios (functional unit:  $100\,000\text{ m}^3$  dredged sediments).

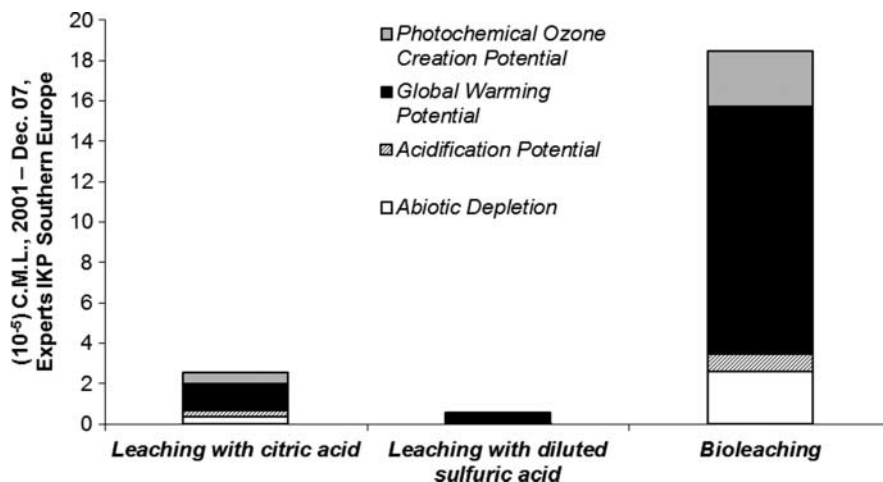


Figure 5. Overall environmental impact of the three scenarios, weighted according to environmental problems in Southern Europe (functional unit: 100 000 m<sup>3</sup> dredged sediments).

due to the high energy requirement for a relatively long treatment in slurry bioreactors, and consequently to energy production, according to life-cycle thinking [26].

#### 4. Conclusions

The above results show that all the investigated treatments gave a mobilisation of ~50% of the metal content. Considering that the initial contamination level was moderate, all these treatments may be adequate to solve the problem of dredged sediment disposal, but with efficiencies strongly dependent upon the metal partitioning in the solid matrix. Indeed, the definition of a proper reuse option can be performed only after assessment of the risk associated with the management of such sediment [49]. Nevertheless, analysis of the potential environmental impacts in a real application indicates that, conversely to what may be expected, treatment options based on organic acids or bioleaching processes can be less environmentally friendly than treatment with diluted sulfuric acid. Obviously, this also depends on the sediment geochemical characteristics that, in some cases, may improve the requirement of sulfuric acid for the acidification of the reaction medium. Overall, the results from this study provide new insights into the definition of the most efficient and environmentally friendly strategies to be used for the remediation of dredged sediments contaminated by heavy metals. The high environmental impact is associated with the production processes of requested raw materials, which is not usually taken into consideration outside the life-cycle approach.

Our results provide new insights into sediment remediation and definition of the best strategies for dredged sediment contaminated with metals and semi-metals. New investigations should focus on understanding how the characteristics of the sediment and of the metal contamination affect the efficiency of mobilisation strategies; furthermore, analysis of the environmental impact should not be overlooked, also for the strategies widely considered as environmentally friendly by the scientific community.

#### Supplementary material

Figures S1 and S2 are available as supplementary material at <http://www.tandfonline.com/doi/full/10.1080/02757540.2013.776547>.

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