Chemical extraction of trace elements from dredged sediments into a circular economy perspective: Case study on Malmfjärden Bay, south-eastern Sweden

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A B S T R A C T

Worldwide, sediments are dredged from water bodies to guarantee proper water levels and remediate aquatic ecosystems. As a consequence, large volumes of sediments reach the land and need proper disposal management (Akcil et al., 2015). According to SedNet (European Sediment Network), Europe alone produces around 100 to 200 million m³ of dredged material per year (SedNet, 2004). Dredged sediments are commonly disposed of in open oceans or landfill (Ali et al., 2014). However, the traditional methods are restricted by legal and environmental concerns. On the one hand, open ocean disposal is banned in several countries due to its potential contamination to the surrounding environment (Akcil et al., 2015). On the other hand, landfilling is associated with a high demand for space and the production of risky by-products (Pellenz et al., 2020). The potential emission of methane (contributor to global warming) and polluted leachate could likely contaminate soil and water environments (Pellenz et al., 2020).

The beneficial use of dredged sediments represents an alternative for the conventional disposal methods and contributes to ceasing the mining of raw resources. Sediments can potentially be employed in several uses, such as a plant-growing substrate in agriculture and forestry, as material in the construction sector or as coverage for landfill (Sheehan and Harrington, 2012; CEDA, 2019; PIANC, 2009).

However, several environmental, economic, social and technological factors determine the viability of implementing the practices. Social aspects require attention, particularly the end-user acceptance of using sediments (Laboryie et al., 2018). Investment and operational costs are also one of the barriers since using sediments in industries could require new inputs of money for the development of technologies, adjustments and upgrades of existing practices, and implementation of cleaning up technologies, among others (CEDA, 2019). Assessments of the costs are required to facilitate the decision-making of sediment management options (Laboryie et al., 2018).

The composition of the dredged material is a decisive factor to determine the viability to use sediments for beneficial purposes. Typically, sediments contain organic matter, sulphides, chlorides, nutrients, organic compounds and trace elements (Yoo et al., 2013). When the concentration of risky compounds (such as metals/metalloids) overpasses the legal maximum permissible concentrations, it is necessary to reduce their levels to be able to use the sediments. Furthermore, compounds with a high value on the market could potentially be recovered to be commercialised (Beolchini et al., 2013). Hence, technologies to extract sediment components are highly required to enhance and promote beneficial uses.

Metals are elements that, opposite to organic compounds, are non-biodegradable, persistent and accumulate in nature (Akcil et al., 2015).

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In aquatic ecosystems, metals come from natural and anthropogenic origins. Industrial pollution sources include shipping and harbour facilities, agriculture, metallurgical, mining and paint and chemical factories (Polettini et al., 2006). Metal pollution on sediments represents a worldwide environmental issue since the toxic nature of certain elements denotes a threat to public health and natural ecosystems (Zhang et al., 2019). Investigating metal extraction technologies for sediments is crucial to decrease the released metal pollution to the environment (Yoo et al., 2013). Additionally, the obtained elements could potentially be recycled in metallurgical industries, contributing to reintroducing the material to production cycles instead of landflling valuable resources (Hasegawa et al., 2019).

Techniques used for soils are also employed to release trace elements in sediments (Di Palma and Mecozzi, 2007). Previous studies have researched methods including phytoremediation (Wu et al., 2014; Doni et al., 2015), bio-leaching (Gan et al., 2015; Zeng et al., 2015), soil/sediment washing (Polettini et al., 2009; Tsang and Hartley, 2014) and electro-kinetic extraction (Pazos et al., 2013; Colaccio et al., 2010). Among all, the chemical leaching of metals is a prosed and flexible technique that offers efficient results even to extract elements linked to fine particles (Peters, 1999). The method releases the elements by transferring them from the solid matrix to an aquatic solution by adding dissolving agents such as oxidants, chelating agents or inorganic acids (Wang et al., 2017a). The selection of the washing agent is crucial to guarantee proper dissolution rates (Yoo et al., 2013). Although strong acids offer efficient extraction rates, the nature and structure of sediments can be destroyed, affecting, for example, the ability to use the material as a plant-growing substrate (Dermont et al., 2008).

Chelating agents are ligands with the capacity to link with central metal ions to create chelate complexes (Song et al., 2016). They are an alternative for strong acids that keep the structure of sediments, efficiently extract metals, create stable complexes and present a high complexation ability (Hasegawa et al., 2019). Different chelating agents are available in the market. The selection process should consider effectiveness according to the chemical speciation of metals, regulatory perception, costs, biodegradability, toxicity to the environment and capacity to be recycled (Di Palma et al., 2011).

Ethylenediamine-tetraacetic acid (EDTA) is a well-known chelating agent used widely to extract metals due to its high efficiency to dissolve a wide range of elements (Yoo et al., 2013). The agent acts with two mechanisms. The first step is characterised by a fast thermodynamically favourable complexation with cation metals, which are linked to the most labile chemical fractions. The second process, or EDTA-promote dissolution, partially disrupts the sediment and indirectly mobilises metals bound to oxides as well to organic matter (Zhang et al., 2010). However, EDTA is recognised for its potential impacts on the environment. It is rather persistent and could cause eutrophication in waters (caused by ferric phosphate dissolution), influence on photosynthetic organisms (inhibiting cellular division and chlorophyll production) and resistance to bacterial degradation (Polettini et al., 2006). EDTA is relatively expensive, but it potentially could be recycled due to its low degradability, reducing the treatment costs and the environmental impacts (Deng et al., 2017). Ethylenediamine-disuccinic acid (EDDS) is an agent that is biodegradable and therefore offers an alternative solution to the use of EDTA. Both chelators offer efficient leaching rates for several metals, creating stable element complexes (Zhang et al., 2008).

The chemical extraction of metals depends on the interaction of several factors. Recognised influencing parameters are the chemical speciation of the metals and sediment characteristics such as particle size, organic matter content, type of mineral oxides and metal concentrations. Sediment properties are invariable; however, they contribute to determining the operational conditions during the sediment washing process. Other parameters influencing the chemical extraction are the operational aspects, including the time, pH, temperature, liquid-to-solid ratio and chelating type and concentration (Beiyan et al., 2018). The pH affects the dissolution of metals and re-adsorption mechanisms of the newly formed element-chelating complexes (Begum et al., 2012). The chelating agents could offer a variable range of selection to dissolve metals as well as different capacities to extract and create stable complexes with the elements. The concentration of the agents also plays an essential role in the leaching efficiency since the right level of chelate must be dosed to enhance the extractions (Di Palma and Mecozzi, 2007).

The technique has been widely researched for soil samples; however, for sediments, the studies are limited (Wang et al., 2017b). Sediments compared to soils highly differ in their chemical composition (Song et al., 2016). Since the matrix components play a vital role in the chemical extraction, more studies are necessary to understand the application of the technique for this material. Additionally, testing the effect of operational factors contributes to enhancing and optimising the process. Therefore, the aim of the present study is to evaluate the influence of pH and concentration of EDTA and EDDS on the chemical extraction of several elements (Pb, As, Cu, Ni, Cr and Zn) from marine sediments. The study also aims to shed light on the decontamination of sediments to enhance the beneficial use of the material and the potential recovery of metals.

2. Materials and methods

2.1. Study site

Kalmar is a municipality located in south-eastern Sweden. The city possesses a long coastal area, where one important spot, due to its central location, is Malmfjärden bay. The water body is located in the city centre (560 66’ N, 160 36’ E) and belongs to the Western Gotland Basin of the Baltic Sea (see Fig. 1). The place provides habitat for birds and wildlife as well as recreational spaces for the population. The bay is semi-enclosed with limited connections to the open sea and currently presents eutrophication and slight metal pollution (Nilsson, 2013). The main water inlet is the runoff collected from the adjacent areas, lacking industrial or domestic sewage emissions. The neighbouring areas include commercial and residential zones as well as an old waste dumpsite.

Malmfjärden is currently very shallow, and extraction of sediments is necessary to reach a proper water level that allows activities such as boating, bathing, canoeing and other aquatic activities. In October 2019, the municipality started a dredging project aiming to improve the conditions on the bay. The project will use the dredged material for beneficial uses to avoid landfilling and loss of valuable resources. The complete planned dredging area is shown in Fig. 1. Previous studies suggested that sediments from Malmfjärden exposed a medium-high concentration of nitrogen and phosphorus and low-medium pollution with metals. Sediments were mainly constituted by silt (60%–70%). Clay (15%–20%) and sand (10%–20%) represented a smaller fraction of the particle size distribution (Ferrans et al., 2019).

2.2. Sample collection and processing

Sediment samples were directly taken from the bay using a manual core sampler. The samples were not removed from the dredging system since it only started in 2019, and the samples for this study were taken in 2018 to create a baseline for the project. Cores were extracted from 25 stations. The sampling points were distributed into four areas covering all the planning dredging area. Cores of approximately 60 cm were collected, and triplicates were taken at each sampling point. Before analysis, all samples were stored on pre-cleaned polythene bags at 4 °C to avoid organic matter degradation.

Sub-samples from all sampling stations were used to create one composite sample. Only one sample from all over the planning dredging area was used to increase the representativeness of the study. The
A composited sample was created using subsamples from the top (0–20 cm) and bottom (21–60 cm) layers of all cores (in total 75 top and 75 bottom sub-samples). All sub-samples were oven-dried at 40 °C until achieving a constant weight. Later, the samples were pulverised using a pestle and mortar and grinded using a 1 mm stainless-steel mesh. All dried-grinded samples were manually mixed to create the composite sample. The sample preparation procedure was adapted from other studies such as Zhang et al. (2009), Ianni et al. (2010) and Akcay et al. (2003).

2.3. Analyses

The total metal/metalloid concentrations of the composite sample were calculated at the commercial laboratory Synlab-Sweden. The samples were digested and processed according to EN-ISO-11885, and the element concentrations were measured using inductively coupled plasma mass spectroscopy (ICP-MS) (Perkin Elmer NexION 350D).

The organic content of the sediments was calculated following SS-EN 15169:2007 (loss on ignition test). First, a sample of 50 g from the composite sample was oven-dried at 105 °C until achieving a constant weight. When all the water was evaporated, the remaining sample was heated at 550 °C for 2 h. The organic content was calculated by finding the weight difference before and after drying at 550 °C. The analysis was performed in triplicates.

The pH of the sediment was measured in a 1:2.5 (w/v) ratio. Ten grams of the sediment was stirred with 25 ml of deionised water for 10 min. Later, the mix was allowed to settle for 30 min, and the pH was calculated from the supernatant using a pH-metre (HQD field case, Hach Lange — Germany). The analysis was performed in triplicates. The procedure was adapted from Di Palma and Mecozzi (2007).

2.4. Metal/metalloid extraction

The composited sediment sample was used to perform the metal extraction. Different experiments were carried out to study the influence of variables such as the type of chelating agent, chelating concentration and pH. Table 1 shows the conditions employed in all experiments. Batch leaching experiments were performed at room temperature on pre-acid washed glass flasks mounted on magnetic stirrers.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>pH</th>
<th>Chelator</th>
<th>Chelator concentration (M)</th>
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<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>EDTA</td>
<td>0.01</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>EDTA</td>
<td>0.05</td>
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<tr>
<td>3</td>
<td>4</td>
<td>EDDS</td>
<td>0.01</td>
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<tr>
<td>4</td>
<td>4</td>
<td>EDDS</td>
<td>0.05</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>EDTA</td>
<td>0.01</td>
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<td>6</td>
<td>6</td>
<td>EDTA</td>
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<tr>
<td>7</td>
<td>6</td>
<td>EDDS</td>
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<tr>
<td>8</td>
<td>6</td>
<td>EDDS</td>
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<tr>
<td>9</td>
<td>8</td>
<td>EDTA</td>
<td>0.01</td>
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<tr>
<td>10</td>
<td>8</td>
<td>EDTA</td>
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<td>11</td>
<td>8</td>
<td>EDDS</td>
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<tr>
<td>12</td>
<td>8</td>
<td>EDDS</td>
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DM: Dry matter.

Each experiment was performed in duplicates and, blank treatments (containing deionised water) were used to evaluate if the employed method incorporated any metals. The liquid to solid ratio was fixed for all extraction tests, and 2 g of sediments was mixed with 50 ml of the chelating agent (solid to liquid ratio of 25). The proportion was selected based on the range of similar studies such as Wen et al. (2019) and Polettini et al. (2009).

The experiments were carried out for 24 h at 200 RPM, and the conditions were selected according to other studies with successful extraction rates like Kim et al. (2003), Di Palma et al. (2011) and Lumia et al. (2020). In the experiment, pH values of 4, 6 and 8 were tested to find the effect on the metal extraction process. The range was chosen according to results from other studies like Begum et al. (2012) and Lumia et al. (2020). The pH was fixed using 1 M NaOH (Acros Organics — United States) or HNO₃ (Sigma-Aldrich — United States). Ethylenediamine-tetraacetic acid (EDTA) (Acros Organics — United States) and ethylenediamine-disuccinic acid ([S,S]-EDDS) (Sigma-Aldrich — United States) were used for the extraction experiments. The chelating agents were tested in a concentration of 0.01 M and 0.05 M. The range was selected according to previous studies such as Di Palma and Mecozzi (2007) and Lumia et al. (2020).
After 24 h, the slurry was centrifuged (Beckman Avanti J-25 — United States of America) at 4000 RPM for 15 min. The supernatant was filtered on a 0.45 μm membrane filters (Frisenette — Denmark). The filtrate was sent to the commercial laboratory Synlab — Sweden to analyse the total concentration of metals using an ICP-MS (Perkin Elmer NexION 350D). All experiments were conducted in dupli-cates, and the results were reported as averages. The pre-analysis procedure was adapted from other metal extraction experiments such as Tsang and Hartley (2014) and Beiyuan et al. (2018). The extraction rates were calculated using Eq. (1), where \( \frac{C_{\text{sup}} \times V}{M} \) is the concentration in the supernatant; \( V \) (L) is the washing solution volume; \( M \) (kg) is the mass of sediment in each sample and \( C_{\text{tot}} \) (mg kg\(^{-1}\)) is the initial concentration of the metal in the sediment.

\[
\% \text{ Removal} = \frac{C_{\text{sup}} \times V}{M} \times 100
\]

(1)

2.5. Statistics

Analysis of variance (ANOVA) test was used to determine the statistical significance \( (p < 0.05) \) of the conditions on the different experiments. Prior to analysis, the homogeneity of variance and normal distribution were tested. If requirements were violated, Wilcoxon and Kruskal tests were also run to verify the veracity of the parametric tests. The mean significance difference between groups for variables where ANOVA showed a significant effect was analysed using the Tukey test. The statistical analyses were calculated using the software R version 3.6.1.

3. Results and discussion

3.1. Sediment characteristics

The organic content of the sample was 12.9 ± 0.6%, expressing a medium value according to SS-EN ISO 14688e2:2018. The pH of the sediment was neutral, with a value of 6.7 ± 0.1. The total concentrations of trace elements (in mg kg\(^{-1}\) dry matter (DM)) in the sediments were 8.3 ± 1.6 for As, 44.9 ± 5.6 for Pb, 40 ± 6.0 for Cu, 24 ± 3.6 for Cr, 23 ± 3.5 for Ni and 120 ± 18 for Zn. Results from cadmium are not presented in the study due to its low concentration in the sediment. The obtained results are in agreement with previous characterisation studies from Malmfjärden sediments. Table 1 shows the concentration range for different elements reported by Ferrans et al. (2019) and Fathollahzadeh (2012).

The national Swedish Environmental Protection Agency (SEPA) regulates the maximum permissible concentrations of metals/metalloids for soils and dredged sediments (SEPA, 2009). The thresholds are determined according to the final usage of the sediments. The regulation determines more strict limits for very sensitive land uses and lower thresholds for non-sensitive uses. All concentrations of Pb, As, Cu, Cr, Ni and Zn in the composted sample from the studied sediments were below both threshold limits (see Table 2). However, due to previous studies, it is expected that certain areas and levels in the sediment column might have higher trace element concentrations that overpass the more sensitive limit, highlighting the need for using metal extraction technologies.

3.2. Extraction of metals by chemical leaching

The extraction percentages of metals at the different conditions of pH and concentration for EDTA and EDDS are shown in Fig. 2. EDTA was selected as a non-specific chelate (Kim et al., 2003) that presents high metal leaching rates (Lumia et al., 2020). Regarding EDTA, the extraction efficiencies followed the order of Pb (74.1 ± 5.9%) > Zn (66.4 ± 9.6%) > Cu (54.3 ± 3.1%) > As (47.1 ± 11.0%) > Ni (29.7 ± 1.5%) > Cr (3.1 ± 1.0%). EDDS presented similar results expressed as Zn (58.7 ± 3.2%) > Cu (52.9 ± 2.6%) > Pb (48.3 ± 25.3%) > As (30.3 ± 7.6%) > Ni (27.9 ± 1.5%) > Cr (2.1 ± 0.8%).

Chelating agents such as EDTA and EDDS offer a high affinity for divalent cationic metals (like Pb, Zn, Ni and Cu), facilitating their dissolution (Dermont et al., 2008). In this study, lead, zinc and copper showed the highest leaching rates. Other studies, such as Polettini et al. (2006), Beiyuan et al. (2018), Di Palma et al. (2011) and Lumia et al. (2020), reported similar extraction of lead from sediments in a range of 65%–85% using EDTA and 50%–80% employing EDDs. Polettini et al. (2006), Wang et al. (2017b) and Di Palma and Mecozzi (2007) introduced zinc dissolution rates of 40%–80% (using EDTA and EDDS), showing agreement with the presented results. Copper was extracted in a range of 30%–70% for EDTA and 20%–60% for EDDS in studies like Polettini et al. (2006), Lumia et al. (2020) and Tsang and Hartley (2014). Additionally, Begum et al. (2012), Lumia et al. (2020) and Zhang et al. (2009) reported comparable results for nickel extraction in a range of 15%–50%, employing EDTA and EDDS.

Certain ions of arsenic (As(III), As(V)) and chromium (Cr(VI)) create oxynions with oxygen. Chelating agents like EDTA and EDDS hardly develop complexes with oxynions, reducing the extraction efficiencies (Polettini et al., 2009), Polettini et al. (2006), Tsang and Hartley (2014) and Polettini et al. (2009) presented studies where arsenic from soils and sediments was extracted in a range of 15%–45% (using EDTA and EDDS), showing similar percentages to the ones reported by this study. Likewise, other authors like Polettini et al. (2006), Wang et al. (2017b) and Zhang et al. (2009) showed chromium dissolution with an efficiency of less than 10%.

The extraction efficiency is highly dominated by the distribution of metals into the different chemical fractions, where higher dissolution rates could be achieved when the element is less linked to the labile residual fraction (Tsang and Hartley, 2014). Ferrans et al. (2021) reported that lead and zinc in sediments from Malmfjärden are the elements with a higher link to the labile chemical fractions. Lead and zinc were bound to the exchangeable (Pb: 1 ± 0.5%, Zn: 4 ± 0.5%), carbonates (Pb: 14 ± 1%, Zn: 18 ± 1%), reducible (Pb: 24 ± 5%, Zn: 27 ± 4%), oxidative (Pb: 31 ± 8%, Zn: 14 ± 3%) and residual (Pb: 30 ± 4%, Zn: 37 ± 4%) parts. The extraction rates of the elements suggested that all the potential extractable fractions were leached out in the experiment, showing that the concentration of the chelating agents and the employed time were enough to support the dissolution of organic matter/sulphides and Fe-Mn oxides complexes (Wang et al., 2017b). Moreover, zinc and lead had higher initial concentrations than other metals, enhancing the extraction as high initial concentrations could improve the efficiencies (Yoo et al., 2013).

Copper and nickel were less labile than other cationic metals. According to Ferrans et al. (2021), in sediments from Malmfjärden, the elements showed a weak linkage to the exchangeable (Cu: 0%, Ni: 0%)}
Nickel had a bind to the reducible fraction (Cu: 0%, Ni: 12 ± 5%), and both metals were strongly linked to the oxidable (Cu: 45 ± 3%, Ni: 35 ± 5%) and residual (Cu: 54 ± 3%, Ni: 48 ± 1%) parts. The linkage to the mineral section of the sediment reduced the extraction rates of the elements. For copper, all the extractable part linked to the organic matter/sulphide fraction was dissolved by the chelating agents. The extraction from the oxidable fraction was due to the capacity of the chelates to dissolve organic matter, releasing the metal for complexation (Polettini et al., 2006). For nickel, all the potential extractable fraction was not successfully dissolved. The optimal extraction of copper was probably related to the strong affinity of EDTA and EDDS to create complex with the element, as well as to the high stability constants of Cu-EDDS and Cu-EDTA for all the tested pH range (Hasegawa et al., 2019).

Previous studies showed that, in sediments from Malmfjärden, arsenic and chromium were highly associated with the residual fraction (As: 56 ± 5%, Cr: 70 ± 1%). The elements presented no link to the exchangeable part (As and Cr: 0%) and a slight bind to carbonates (As: 4 ± 0.5%, Cr: 1 ± 0.5%). The reducible (As: 17 ± 7%, Cr: 6 ± 1%) and oxidable (As: 23 ± 8%, Cr: 23 ± 1%) fractions showed a higher presence on the sediments (Ferrans et al., 2021). On the one hand, chromium exists in nature in the forms of Cr(+VI) and Cr(+III) since Cr(+VI) can be reduced by organic matter and divalent ions. The extraction of the element in this study is likely associated with the fact that Cr(+III) is a cationic specie able to make complexes with the employed chelating agents. Its extraction is related to the dissolution of iron oxides (Zhang et al., 2010). However, the low extraction of the element could be explained by the high linkage to the mineral part of the sediment, which chelating agents hardly can dissolve. Additionally, the ion Cr(+VI) and the employed chelates hardly form complexes with the element (Abumaizar and Smith, 1999).

On the other hand, arsenic was better dissolved, and most of the extractable fraction was leached out. Arsenic presents two forms, As(+III) and As (+V), which both form unstable complexes with chelating agents such as EDTA and EDDS (Polettini et al., 2006). However, the metalloid is related to iron, and therefore it can be extracted by co-dissolution of iron oxides (Tsang and Hartley, 2014). Moreover, the element leach out is significantly increased by the co-precipitation with cationic metals, such as zinc, by forming Zn-As surface complexes (Von der Heyden and Roychoudhury, 2015) and copper (Tsang and Hartley, 2014). The residual part of the metalloid is not expected to be extracted (Shih et al., 2019). The high dissolution rates of arsenic, sometimes closely passing the percentage of the potentially extractable fraction, could be explained since the metalloid showed the lowest initial concentrations. This deteriorates the quantification for the speciation and the extraction since the concentrations are close to the detection limit (Akay et al., 2003). Additionally, the high concentration of iron in sediment samples could lead to spectral interference with other components, deviating the precision of quantifying other elements (Pillay, 2020). Also, the sediment samples are highly heterogeneous, explaining that the concentrations are not equal in a sample (Song et al., 2016).

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1 SD: Standard Deviation.
3.2.1. Effect on type of chelating agent

Considering all the studied cases, EDTA (45.74 ± 24.74%) presented a significantly higher mean extraction rate than EDDS (35.60 ± 21.33%) (ANOVA, $F_{1,142} = 5.55, P = 0.02$). EDTA could potentially dissolve a larger amount of metals since it presents a higher capacity to dissolve iron and manganese oxides–metal complexes (Polettini et al., 2006). Additionally, in general terms, the metal-EDDS complexes present lower stability constants than the corresponding metal-EDTA complexes (Chen et al., 2010).

EDTA showed a significantly higher mean efficiency compared to EDDS for lead (ANOVA, $F_{1,22} = 11.85, P = 0.002$), zinc (ANOVA, $F_{1,22} = 9.47, P = 0.006$), nickel (ANOVA, $F_{1,22} = 6.26, P = 0.02$), arsenic (ANOVA, $F_{1,22} = 19.15, P = 0.0002$) and chromium (ANOVA, $F_{1,22} = 7.63, P = 0.01$). The higher efficiency of EDTA than EDDS could be explained by the chemical distribution of the metals/metalloid. The elements presented a high link with the reducible fraction, and as previously mentioned, EDDS has a low capacity to dissolve Fe-Mn oxides complexes. Contrarily, EDTA could break Fe-Mn oxides when the proper concentration has been employed in the extraction (Beiyuan et al., 2018). Additionally, according to Tsang and Hartley (2014), EDTA presents a higher mineral dissolution than EDDS. For copper, both chelating agents had considerably similar mean extraction rates (ANOVA, $F_{1,22} = 1.54, P = 0.23$). Results could be explained by the lack of linkages of copper with Fe-Mn oxides.

3.2.2. Effect of pH

For EDTA and EDDS, pH caused no significant difference accounting all the experiments of the study (EDTA: ANOVA, $F_{2,141} = 0.147, P = 0.86$) (EDDS: ANOVA, $F_{2,56} = 0.536, P = 0.59$). More specifically, the variation of pH presented a similar effect on the leaching of some cationic metals. Zinc (EDTA: ANOVA, $F_{2,9} = 3.02, P = 0.10$; EDDS: ANOVA, $F_{2,9} = 3.17, P = 0.09$), copper (EDTA: ANOVA, $F_{2,9} = 0.62, P = 0.56$; EDDS: ANOVA, $F_{2,9} = 0.50, P = 0.62$), chromium (EDTA: ANOVA, $F_{2,9} = 0.53, P = 0.60$; EDDS: ANOVA, $F_{2,9} = 0.81, P = 0.47$) and nickel (EDTA: ANOVA, $F_{2,9} = 1.35, P = 0.31$; EDDS: ANOVA, $F_{2,9} = 2.45, P = 0.14$) presented no significantly different in the mean extraction of the different pH values using EDTA and EDDS. Results could be explained since the stability constants of the elements with the chelating agents are similar in the tested pH range (Begum et al., 2012). Moreover, the metals were slightly linked to carbonates. Since this fraction is more affected by pH changes, potentially, the extraction of the elements was not affected by variations in pH (Prabakaran et al., 2019).

The mean extraction rates for lead presented a significant difference for the three pH values for the case of EDTA (ANOVA, $F_{2,10} = 5.63, P = 0.026$). A higher mean was achieved for pH 4, followed by pH 6 and finally pH 8. A Tukey-test ($a = 0.05$) showed that the mean extraction rate of the more acidic conditions (pH 4) was significantly higher than the mean leaching rates for pH 6 and 8. Additionally, the mean extractions for pH 6 and 8 were significantly similar. The dissolution rates of chelating agents at the acidic media could be explained by the effect of H+, which react with the sediment surface sites and enhance the desorption of metals (Dermont et al., 2008).

For EDDS, the pH also presented a major impact in the dissolution of lead (ANOVA, $F_{2,56} = 321, P = 4.3 \times 10^{-19}$). The pH 6 and 8 presented a significantly higher extraction rate than pH 4 (Tukey-test, $a = 0.05$). The mean extraction rate at pH 4 was affected by the low efficiency of the chelating agent to remove lead at acid conditions. The chelator forms very unstable complexes with lead at this pH (LogK of 3 for Pb-EDDS (Begum et al., 2012)), explaining the low efficiency.

Similarly to lead, the mean leaching rate for the different pH values presented a significant difference for arsenic in both cases of EDTA and EDDS (EDTA: ANOVA, $F_{2,9} = 11.47, P = 0.003$; EDDS: ANOVA, $F_{2,9} = 33.06, P = 0.0007$). A Tukey-test ($a = 0.05$) showed that, for EDDS, pH 4 had significantly higher efficiency than pH 6 and 8, and between the last, there was no considerable difference in the mean extraction rate. In the case of EDTA, the leaching rate for pH 4 was significantly similar to pH 6, and both pH 4 and 6 were considerably higher than pH 8. Acid conditions enhance the dissolution of iron, increasing the extraction of the element (Kim et al., 2003) and the one from arsenic since its extraction is closely associated with iron dissolution (Tsang and Hartley, 2014).

3.2.3. Effect of chelating concentration

Considering all experiments, the concentration of the chelating agents presented no considerable effect on the mean extraction rates for EDTA (ANOVA, $F_{1,142} = 1.01, P = 0.32$) and EDDS (ANOVA, $F_{1,70} = 0.28, P = 0.60$). The concentration of the chelating agents presented a different impact on the dissolution of the elements. For EDDS and EDTA, no significant effect on the mean extraction was reported for lead (EDTA: ANOVA, $F_{1,10} = 2.22, P = 0.17$; EDDS: ANOVA, $F_{1,10} = 0.06, P = 0.81$), zinc (EDTA: ANOVA, $F_{1,10} = 2.75, P = 0.13$; EDDS: ANOVA, $F_{1,10} = 4.28, P = 0.07$) and arsenic (EDTA: ANOVA, $F_{1,10} = 2.99, P = 0.11$; EDDS: ANOVA, $F_{1,10} = 0.55, P = 0.48$). The results suggest that, for both concentration conditions, most of the labile fractions of the elements were already removed by the chelating agents; hence, a higher concentration did not contribute to increasing the leaching rates.

On the opposite, for both chelating agents, the concentration had significantly different mean efficiencies for copper (EDTA: ANOVA, $F_{1,10} = 11.52, P = 0.007$; EDDS: ANOVA, $F_{1,10} = 17.01, P = 0.002$), nickel (EDTA: ANOVA, $F_{1,10} = 22.34, P = 0.0008$; EDDS: ANOVA, $F_{1,10} = 6.55, P = 0.03$) and chromium (EDTA: ANOVA, $F_{1,10} = 11.20, P = 0.007$; EDDS: ANOVA, $F_{1,10} = 27.23, P = 0.0004$), where 0.05 M presented higher dissolution than 0.01 M. Larger extractions by the higher concentration could be explained since the metals from the reducible and oxidative fractions were probably not fully released. A major dissolution could be achieved when a higher concentration of chelating agent is used, presenting significantly higher leaching rates (Kim et al., 2003).

3.2.4. Potential of metal recovery from the chelating-metal solution

The chemical leaching from dredged material could also offer a new alternative to mine trace elements for industrial purposes. The depletion of resources is an increasing environmental issue, where sustainable sources of metals are required to guarantee the supply of the demand of economic activities (Ali et al., 2021). Recovering EDTA is a potential step to complement the environmental-friendly management of the chelating-metal solution, and it can be achieved along with recovering the dissolved metals. The complete recovery procedure counts with a series of chemical processes. Preliminary, the solution needs to be evaporated (to reduce the volume of the solution). Second, EDTA could be precipitated by acidification and later filtrated from the liquid solution (DiPalma et al., 2005). The final extraction of metals could be achieved by several technologies depending on the targeted elements. Three important techniques that could be applied are chemical precipitation, ion exchange and membranes (Krishnan et al., 2021; Peng et al., 2020). All are well-researched and have been implemented in large scale applications for industrial-process and drinking water treatment (Qasem et al., 2021), increasing the possibilities to use them for the recovery of metals from chelating-metal solutions.

More specifically, chemical precipitation is a technically mature technology widely employed due to its relatively inexpensive costs. The technique relies on the extraction of soluble metals by changing the solution composition and forming insoluble metal complexes. Later, the pH must be adjusted to alkaline conditions to convert the dissolved elements into an insoluble solid phase. The precipitates can be recovered employing sedimentation or another physical process (Krishnan et al., 2021). In the case of ion exchange, ions from the solution are exchanged by similarly charged ones contained in resins (Krishnan et al., 2021). The material could later be employed as a source of metals. The technology is less implemented than chemical
precipitation since the costs are higher and more research is necessary to polish the method (Qasem et al., 2021). Lastly, membranes are able to filtrate a wide range of contaminants, including metals. Different sizes of membranes (such as ultrafiltration, nanofiltration and reverse osmosis) can be employed depending on the particle size of the element that is wished to be recovered (Krishnan et al., 2021). The technology has been highly researched, increasing its technical maturity. However, the investment and operational costs are the highest compared to the other two methods (Qasem et al., 2021).

In all cases, the amount of recovered metals is related to the initial concentration of the elements in the dredged material, the efficiency of extracting the metals from the sediments and the performance recovering them from the washing liquid. As shown by the current study, the efficiency of leaching the elements from the sediments highly depends on the correct selection of operational parameters, such as the chelating agent and its concentration, pH of the solution and others like liquid to solid ratio and retention time. Additionally, higher initial concentrations of metals guarantee more recovery of elements, helping to redeem the costs. Today, in the market, metals have a price (in euro ton\(^{-1}\)) of 2500 for Zn, 7850 for Cu, 16 200 for Ni, 2200 for Pb, 6500 for Cr and 1000 for As. Elements with higher revenue (such as Cu and Ni or rare-earth elements) are preferable for recovery. It is expected that metals will raise their value while their limited reservoirs are fully exhausted. Therefore, the economic feasibility to implement the recovery of metals from sediments will increase in the future (Kumar et al., 2021). Marketing studies could contribute to finding the exact industries where the extracted elements could be commercialised. Additionally, further investigation on the recovery of metals will contribute to implementing the recycling concept in full-scale projects.

3.3. Cost assessment and future implementation of the technology

The extraction of metals represents a safe path to implement the beneficial use of polluted dredged sediments by reducing the concentration of elements to permissible regulatory concentrations. The clean material could potentially be employed in beneficial uses. The cost to implement the technology depends on local conditions. However, as an approximation Lumia et al. (2020) reports that a treatment plant to perform chemical leaching of sediments (including separation of coarse-fine particles, chemical washing process and separation process between sediment–chelating solution) could cost around 1 to 5 million euros for a capacity of 10–15 t h\(^{-1}\); 1.75 to 2.5 million euros for 25–30 t h\(^{-1}\); and 5 to 8 million euros for 60 t h\(^{-1}\). The operational cost is also an important factor for the decision making process. The chelating price is a differentiating parameter. In the case study (southern Sweden), EDTA has a cost of approximately 75 €kg\(^{-1}\) and EDDS of 1000 €kg\(^{-1}\), both from the brand Sigma-Aldrich (United States). EDTA shows a clear advantage due to its lower cost. Since the chelating agent is more toxic and persistent, it is recommended to include its recycling, decreasing the cost of operation and the environmental impacts related to its discharge.

4. Conclusions

A batch chemical extraction of As, Pb, Zn, Cu, Ni and Cr from sediments from Malmfjärden Bay, Sweden, was performed to assess the viability to reduce the element concentrations before beneficial uses. Key operational parameters, such as pH (4, 6 and 8), type of chelating agent (EDTA and EDS) and concentration (0.01 M and 0.05 M), were studied to find their impact on the extraction of the elements. The current study suggests that the selection of operational parameters is a crucial factor in achieving efficient extraction rates. For both chelating agents, lead, zinc and copper were the metals with higher mean extraction percentages, followed by arsenic and nickel. Chromium was poorly extracted. EDTA is highly cheaper than EDDS and is a potential optimal chelating to leach out cationic metals. This was more efficient than EDDS to leach out the elements. The difference is especially considerable when the elements are linked to the reducible fraction (since EDDS presents a low capacity to dissolve iron oxides). For Cu, Ni and Cr, the concentration of 0.05 M presented higher extraction rates for both EDTA and EDDTA; however, for As, Pb and Zn, both concentrations showed no significant difference in the mean extraction rates for EDDS and EDTA. Moreover, an acidic pH value was optimal to extract As using EDTA and EDDS. Similarly, lead presented a significant higher extraction rate at acidic conditions employing EDTA. Other metals showed significantly no difference in the mean dissolution rates from the different tested pH values. Finally, it was seen that the clean-up process of dredged sediments contributes to obtaining a material that is allowed to use for beneficial purposes. At the same time, the recovery of metals from the washing solution could be implemented to obtain a new source of elements in the future (helping to pause the depletion of natural raw mines). More studies are required to promote the implementation of full-scale metal-recovery projects.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared the work reported in this paper.

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