This is the published version of a paper published in *Chemosphere*.

Citation for the original published paper (version of record):

Chemical speciation of metals from marine sediments: assessment of potential pollution risk while dredging, a case study in southern Sweden
*Chemosphere*, 263(January): 1-9
https://doi.org/10.1016/j.chemosphere.2020.128105

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

Permanent link to this version:
http://urn.kb.se/resolve?urn=urn:nbn:se:lnu:diva-98002
Chemical speciation of metals from marine sediments: Assessment of potential pollution risk while dredging, a case study in southern Sweden

Laura Ferransa,*, Yahya Jania, Juris Burlakovsb, Maris Klavinsc, William Hoglanda

a Department of Biology and Environmental Science, Linnaeus University, Norrakajplan 6, 39231, Kalmar, Sweden
b Chair of Rural Building and Water Management, Estonian University of Life Sciences, Kreutzwaldi 5, 51014, Tartu, Estonia
c Department of Environmental Science, University of Latvia, Raina Blvd 19, LV, 1586, Riga, Latvia

HIGHLIGHTS

- Metals were highly linked to the residual fraction showing a lower risk of pollution.
- While dredging, Pb and Zn could be potentially released with the intrusion of oxygen.
- There is a low risk of metal pollution while using dredged sediments on in-land uses.

ABSTRACT

Contamination associated with metals is a critical concern related to their toxicity, persistence, and bio-accumulation. Trace elements are partitioned into several chemical forms, which some are more labile during fluctuations in the environment. Studying the distribution of metals between the different chemical fractions contributes to assess their bioavailability and to identify their potential risk of contamination to surrounding environments. This study concerns the speciation of metals (Pb, Cr, Ni, Zn and Fe) from sediments coming out from Malmöfjärden bay, Sweden. The aim was to assess the potential risk of metal pollution during present and future dredging as well as while using dredged sediments in beneficial uses. The Tessier speciation procedure was chosen, and the results showed that low concentrations of metals were associated with the exchangeable fraction. In contrast, the major concentrations were linked to the residual part. The risk indexes (contamination factor and risk assessment code) showed that, during dredging activities, there is a low concern of pollution for Cr, Ni and Fe and a medium risk for Pb and Zn. Additionally, in all elements, the sum of non-residual concentrations was below the Swedish limits for using dredged sediments in sensitive lands. The findings suggested that the investigated metals in Malmöfjärden sediments are related to low risks of spreading during using in beneficial uses.

© 2020 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Metals have received high importance due to the environmental pollution caused by their toxicity, abundance, non-biodegradable characteristics, persistence and accumulation (Bastani et al., 2017). In marine environments, trace elements frequently affect aquatic ecosystems impacting animals, plants and benthic communities. Trace elements can also cause ecological problems while accumulating in the food chain, creating risks for humans and inland organisms (Thinh et al., 2018).

Lead, copper and nickel are highly studied metals due to their toxicity. Additionally, zinc and iron also receive significant attention due to their wide distribution in nature. More specifically, lead is a toxic metal with no nutritional value, which is associated with adverse effects on animals and human health. This element is abundant in nature and can accumulate in the food chain (Zhang et al., 2016). Leaded fuels, industrial discharges, paints and batteries are potential sources of this metal (Romieu et al., 1997). Copper is an essential element required by organisms, but, in high
concentration, it can potentially be toxic (Mackie et al., 2012). This metal exists in nature, and its emissions to the environment are highly related to antifouling paints (Srinivasan and Swain, 2007) and corrosion from metal structures and electrical devices and cables (Barceloux, 1999). Iron is one of the most common elements on the Earth’s crust (Pytianos and Lourantou, 2004) and is essential for organisms since it is a component of haemoglobin that is related to the transport of oxygen in bodies (Camuschella et al., 2020). The mobilisation of the metal is mainly linked to human activities such as removal of ores, combustion of fuel fossils and metallurgical production (Wang et al., 2007).

Sediments in the aquatic ecosystem act as a sink of pollutants by accumulating a major amount of metals, while a minor fraction remains in the water phase (Neyestani et al., 2016). The sediment column has a crucial role in the transportation, repository, and release of metals into the environment (Kang et al., 2017). Contaminants are not all fixed in the crystal structure of the sediment, and its mobilisation to the water phase can occur under physicochemical changes of the surroundings (Prabakaran et al., 2019). Metals are partitioned into several chemical forms, where some are more labile during physical and chemical fluctuations. Variations of the aquatic system are caused by natural and human activities like dredging and use of engines, or under environmental changes such as fluctuation of salinity, pH, redox potential and ionic strength (Fathollahzadeh et al., 2014). Studying the bioavailability of metals in aquatic environments is critical to identify their potential environmental risks. The total concentration of metals is a poor indicator to specify mobilisation risks, whereas the speciation of metals contributes to quantifying the amount of metals that can be released from the different chemical fractions during variations in environmental conditions (Prabakaran et al., 2019).

One of the most used methods for metal speciation in sediments is the Tessier et al. (1979), which includes five geochemical fractions. The exchangeable fraction (F1) is the most rapidly bioavailable due to its weak bonds (Islam et al., 2015). Metal migration can occur easily after a shift in salinity, alteration of the adsorption equilibrium of the system or a change of ionic concentration in water. The second fraction is related to trace elements bind to carbonates (F2), and it is readily available and mobile under changes of pH. The third fraction (or reducible fraction) counts trace elements bind to iron and manganese oxides (F3). Mobilisation of metals can occur under changes of redox potential specifically under the reduction of available oxygen in the environment (Prabakaran et al., 2019). The fourth fraction (or oxidisable fraction) includes metals bind to organic material and sulphides (F4). This fraction is also sensitive to redox potential, and elements can be mobilised under oxidising conditions or by decomposition of organic matter (Chen et al., 2015). Lastly, the metals in the fifth or residual fraction (F5) are part of the mineralogical structure of the sediment, where elements are unlikely to be released due to the strong bonds to alumino-silicate minerals (Zhang et al., 2016).

Dredging of sediments is a worldwide activity necessary for the restoration of water bodies and maintenance of harbours (Radenovic et al., 2019). Common disturbances while dredging cause physical, chemical and ecological changes related to the notorious intrusion of oxygen, resuspension of solids and perturbation of sediments as well as possible variations of pH and temperature (Fathollahzadeh et al., 2014). Traditional dredging techniques involve mechanical excavation of sediments with buckets causing large ecological fluctuations (Patmont et al., 2018). The variation in the environmental conditions can possibly affect the aquatic ecosystem by promoting the mobilisation of metals to the surroundings. Studying the speciation of metals contributes to evaluate the risk of pollution while dredging (Xia et al., 2018).

Moreover, when sediments are already on the land, a disposal solution is required. Frequently, dredged sediments are disposed of in open oceans (Chen et al., 2019) or landfills (Mymrin et al., 2017). However, these methods are restricted by environmental and legal concerns. Disposal in open oceans is banned in several countries since it could pollute marine ecosystems (Cesar et al., 2014). Landfills are related to large area requirements and may pose a threat due to the production of risky by-products such as methane (greenhouse gas) and polluted leachate (Depontis et al., 2009). Using dredged sediments in beneficial uses could be a response to eliminate traditional disposal methods and to develop a new source of resources such as nutrients or raw material for construction or industrial processes (Baxter et al., 2004). However, when sediments are exposed to surrounding conditions, the environment is more oxidising, and the pH can easily drop. Leaching of metals could potentially occur, affecting the final use of sediments (Fathollahzadeh et al., 2015). Studying the speciation of metals contributes to evaluate the risk of mobilising metals from sediments to the new in-land environment (Xia et al., 2018).

The aim of this study is to evaluate the speciation of metals in sediments from Malmöfjärden bay, Sweden to preliminary assess the potential ecological risk of releasing metals during dredging activities as well as input towards using the dredged sediments in beneficial uses.

2. Materials and methods

2.1. Study site

Malmöfjärden is a semi-enclosed bay located in Kalmar, south-eastern Sweden (56°36’ N, 16°30’ E) and belongs to the Western Gotland Basin from the Baltic Sea (Fig. 1-b). The water body is situated in the city centre and is a crucial place for the municipality since it provides habitat for wildlife development and recreational spaces for the population. Domestic or industrial sewage discharges are absent in the bay, and the only water inlet to the water body is the emission of runoff collected from surrounding areas. The neighbouring sector of Malmöfjärden includes residential and commercial zones and an old dumpsite.

Kalmar is continuously expanding, and its development plan includes building a large household complex in the south-western part of Malmöfjärden bay. Since October 2019, the municipality started a minor pilot scale of a dredging project to reach a proper water level, which could recover the conditions of the bay and provides an improved environment for the new inhabitants. The full scale dredging project will start in autumn 2020 and finish in summer 2021. The complete future dredging area is shown in Fig. 1-c. Previous studies suggested that in this zone, the sediments exhibit a high concentration of nutrients and medium-low concentrations of metals (Nilsson, 2013). The dredged sediments will be employed on beneficial uses to avoid landfilling of valuable resources.

2.2. Sample collection and processing

On June 2018, sediment samples were directly extracted from
the bay since the dredging activities only started at the end of 2019 with minor operations. The sediment samples were taken from 4 different zones covering all the future dredging area. Each zone included 5–8 stations adding a total of 25 locations (see Fig. 1-C). Sediment cores of approximately 60 cm length and 10 cm of diameter were collected using a core manual sampler, and triplicates were taken in each station. Using a plastic spatula, each core was divided into top (0–20 cm) and bottom (21–60 cm) layers. All samples were stored at 4 °C in pre-cleaned polythene bags. One composited sample was created for the speciation analysis. Subsamples of 50 g from all top and bottom samples (in total, 75 top and 75 bottom samples) were oven-dried at 40 °C (until achieving a constant weight). The dry samples were ground using a pestle and mortar and then grinded through a 1 mm stainless-steel mesh. The composite sample was formed by manually mixing all ground subsamples. The procedure was adapted from several speciation studies such as Ianni et al. (2010) and Akcay et al. (2003).

2.3. Speciation method

A five-step speciation method developed by Tessier et al. (1979) was chosen to perform the speciation of metals (Pb, Cu, Cr, Ni, Zn and Fe). The experiment was carried out using 2 g from the composited sediment sample (the preparation procedure is illustrated in section 2.2.). The extraction procedure was performed as follows.

Step 1. The 2 g sediment sample was taken to a 250 ml wide-neck
flask, and the first fraction was extracted at room temperature with 16 ml of 1 M magnesium chloride (Enola - Latvia) for 1 h on a magnetic shaker.

**Step 2.** The sediment left from the 1st step was carefully transferred to a 250 ml wide-neck flask, and the fraction was extracted with 16 ml of 1 M sodium acetate (PeaChem - Russia) at room temperature for 16 h on a magnetic shaker.

**Step 3.** The sediment remaining from the 2nd step was taken to a 250 ml wide-neck flask, and the fraction was extracted with 40 ml of 0.04 M hydroxylamine hydrochloride (Enola - Latvia) for 16 h at 96 ± 1 °C on a magnetic shaker.

**Step 4.** The sediment left from the 3rd step was transferred to a 250 ml wide-neck flask, and the fraction was extracted with a three-step procedure on a magnetic shaker. First, the sample was mixed with 6 ml of 0.02 M nitric acid (Enola - Latvia) for 2 h at 85 ± 2 °C. Second, 6 ml of 30% hydrogen peroxide (Merck - Germany) was added and mixed for 3 h at 85 ± 2 °C. Lastly, 10 ml of 3.2 M ammonium acetate (Sigma Aldrich - United States) was added and mixed for 0.5 h at 25 ± 1 °C.

**Step 5.** The residual fraction was extracted through wet acid-based digestion with nitric acid and hydrogen peroxide. The original treatment with HF–HClO4 was exchanged due to internal laboratory restrictions. In the procedure, 100 ml of 65% (w/v) nitric acid (Enola - Latvia) along with 5 ml of 30% (w/v) hydrogen peroxide (Merck - Germany) was added. After 24 h, the solution was heated at 96 ± 1 °C until half of the volume was evaporated. Nitric acid was added until complete sample mineralisation. More details of the extraction procedure are shown in Table 1. At the end of each extraction step, the solution was centrifuged at 4500 RPM for 30 min (centrifuge WIFUG - United Kingdom). The obtained aliquot was collected separately from the solid phase by filtering using 0.45 μm filters (Frisenette - Denmark). Before analysis, samples were stored at 4 °C. Inductively coupled plasma - optical emission spectrometry (ICP-OES) (ThermoFisher Scientific - United States) was employed to analyse the metal concentrations from all extracted aliquots. The pre-analysis procedure was adapted from other speciation studies such as Bastami et al. (2017) and Medici et al. (2011).

### 2.4. Total metal concentrations in sediments

The total concentration of metals in the sediments was also analysed to evaluate the performance of the speciation procedure. A sample of 2 g from the composite sample was employed for the procedure. The metals were extracted through wet acid-based digestion with nitric acid and hydrogen peroxide. 50 ml of 65% (w/v) nitric acid (Enola - Latvia) along with 5 ml of 30% (w/v) hydrogen peroxide (Merck - Germany) was added per gram of dry sediment. The pH during the digestion was adjusted to 2. After holding for 24 h, the solution was heated at 96 ± 1 °C until half of the volume was evaporated. Nitric acid was added until complete sample mineralisation. The digestion procedure was adapted from Burlakovs et al. (2018), where the HF–HClO4 digestion were also present. After digestion, the solution was centrifuged at 4500 RPM for 30 min (centrifuge WIFUG - United Kingdom). The obtained aliquot was filtered using 0.45 μm filters (Frisenette - Denmark). The concentration of metals was analysed using an inductively coupled plasma – optical emission spectrometry (ICP-OES) (ThermoFisher Scientific - United States).

### 2.5. Quality control

Recovery rates were determined to compare the total concentration of each metal and the sum of concentration from the five fractions. Eq. (1) was employed to calculate the recovery rates, where CF1-5 represents the sum of concentrations from all fractions, and Ctot indicates the total concentration calculated in the experimental procedure. Recovery rates between 100 ± 15% were classified as satisfactory, showing accuracy in the speciation procedure.

\[
\%\text{Recovery} = \frac{\sum \text{CF1-5}}{\text{Ctot}} \times 100 \quad [\text{Eq.1}]
\]

Besides calculating the recovery rates, other measures were taken to ensure reliable results. The speciation experiment was run in triplicates, and each extraction step included blank samples. Additionally, all glassware used during the experiment was previously soaked with 10% HCl solution for at least 12 h.

### 2.6. Risk indexes

The contamination factor (CF) and the risk assessment code (RAC) were chosen to measure the risk to release metals from the sediments to the surrounding environment. The CF was selected to compare the non-residual fraction over the residual portion, while the RAC was chosen to contrast the concentration of the most labile fractions (F1–F2) over the total concentration. The CF was calculated using the Eq. (2), where \(\text{CF}_{1-4}\) represents the sum of the concentration of the first four fractions, and \(\text{CF}_{5}\) denotes the concentration in the residual part. CF with values < 1 stands for no contamination; 1 < CF < 3 shows moderate pollution; 3 < CF < 6 denotes considerable contamination and CF > 6 states very high pollution (Håkanson, 1980). The RAC was calculated using Eq. (3), where \(\text{CF}_{1-2}\) represents the sum of the concentration of F1 and F2, and \(\text{CF}_{2}\) the total concentration calculated as the sum of concentrations from all the fractions. The criteria to interpret the risk assessment code is taken from Perin et al. (1985), and it is shown in Table 2.

\[
\text{CF} = \frac{\text{CF}_{1-4}}{\text{CF}_{5}} \quad [\text{Eq.2}]
\]

### Table 1

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable (F1)</td>
<td>1 M magnesium chloride (MgCl2), 8 ml g⁻¹ DM, pH 7, 25 ± 1 °C, 1 h, continuous mixing</td>
</tr>
<tr>
<td>Carbonates (F2)</td>
<td>1 M sodium acetate (C₂H₃NaO₂), 8 ml g⁻¹ DM, pH 5, 25 ± 1 °C, 1 h, continuous mixing</td>
</tr>
<tr>
<td>Fe–Mn oxides (F3)</td>
<td>0.04 M hydroxyamine hydrochloride (NH₂OH-HCl), 20 ml g⁻¹ DM, pH 3, 96 ± 1 °C, 16 h, occasional mixing</td>
</tr>
<tr>
<td>Organic matter-Sulphide (F4)</td>
<td>a) 0.02 M nitric acid (HNO₃), 3 ml g⁻¹ DM + 30% hydrogen peroxide (H₂O₂), 5 ml g⁻¹ DM, pH 2, 85 ± 2 °C, 2h, occasional mixing</td>
</tr>
<tr>
<td></td>
<td>b) 30% hydrogen peroxide (H₂O₂), 3 ml g⁻¹ DM, pH 2, 85 ± 2 °C, 3h, intermediate mixing</td>
</tr>
<tr>
<td></td>
<td>c) 3.2 M ammonium acetate (NH₄OAC), 5 ml g⁻¹ DM, pH 2, 25 ± 1 °C, 0.5 h, continuous mixing</td>
</tr>
<tr>
<td>Residual (F5)</td>
<td>65% (w/v) nitric acid (HNO₃), 50 ml g⁻¹ DM + 30% (w/v) hydrogen peroxide (H₂O₂), 5 ml g⁻¹ DM, pH 2, 96 ± 1 °C, 24 h, occasional mixing</td>
</tr>
</tbody>
</table>

* DM: Dry Matter.
3. Results and discussion

3.1. Sediment characteristics

The results revealed that the organic content of the sediments had an average value of 12.9 ± 0.6%, highlighting a medium value according to SS-EN ISO 14688–2:2018. Table 3 shows the total concentration of metals. Lead had an average concentration of 37.2 mg kg⁻¹, copper 51.1 mg kg⁻¹, chromium 37.9 mg kg⁻¹, nickel 27.9 mg kg⁻¹, zinc 138.5 mg kg⁻¹ and iron 23,855 mg kg⁻¹. Fathollahzadeh (2012) analysed the total concentration of metals in sediments from Malmfjärden, and most of the results are in agreement with the current work. The Fathollahzadeh (2012) study reported a concentration of Pb 74.6 mg kg⁻¹, Cr 40.7 mg kg⁻¹, Cu 53.2 mg kg⁻¹, Ni 16.7 mg kg⁻¹, Zn 150 mg kg⁻¹ and Fe 29,000 mg kg⁻¹. Zinc, iron, copper and chromium had a variance under 15% comparing the previous and the current studies, while lead and nickel had larger differences in concentrations. Discrepancies between the results could be explained by the difference in the age of samples. The studies were separated eight years apart, and therefore the distribution of metals could change since the discharges might vary over time.

3.2. Recovery rates

The recovery rates are shown in Table 3. All the results were between 95 and 122%. Rates between 100 ± 15% were considered satisfactory. Spectral interferences with other components of the sediments are common for soils or sediment samples with a high level of iron (Pillay, 2020). Since the sample from the study present high levels of this elements, the spectral interference could be a reason to explain the deviation of the recovery rates away from the range. For the case of Cu several samples had concentrations close to the detection limit of the equipment producing less accurate results (Akçay et al., 2003).

3.3. Metal speciation

Fig. 2 illustrates the distribution (in percentage) of metals in the five chemical fractions, while the risk factors values for all the studied elements are shown in Table 4. More details concerning each metal are in the following sections.

3.3.1. Lead

Lead was mainly bound to F4 (31 ± 8%), F5 (30 ± 4%), F3 (24 ± 6%). F2 also had a considerable presence with 14 ± 1%, while the amount in the exchangeable fraction was low (<1%). The link of the metal to the residual fraction can be explained by the fact that, over time, lead can be incorporated in the alumina-silicate minerals of sediments (Lasheen and Ammar, 2008). Moreover, Fe–Mn oxides are important scavengers, and the metal is also likely to form compounds with organic material and carbonates (Islam et al., 2015). The results are in agreement with Fytianos and Lourantou (2004) and Islam et al. (2015). Both described sediments, which lead was linked with the oxidisable (20–35%), reducible (10–20%), residual (10–30%) and carbonate (15–25%) fractions.

Among all metals (see Fig. 2), lead was one with a higher amount linked to the non-residual fractions, suggesting a probable anthropogenic origin. In the Malmfjärden case, the inlet of runoff could be related to the source of origin of this element due to the lack of sewage discharges. Additionally, the link of Pb to labile fractions can enhance the leaching potential due to changes in the redox conditions and fluctuations of pH. Considering all the mobile fractions, the contamination factor of 2.33 represented a moderate risk of pollution. The RAC of 14.7% indicated a medium risk of mobilisation of F1 and F2.

Dredging could induce substantial environmental changes in the aquatic ecosystem (such as the intrusion of oxygen and variations of pH). With fluctuations in the surroundings, the labile fractions of lead could potentially be released. Therefore, it is recommended to employ more environmental dredging methods, which could cause less resuspension of particles and variations in ecological conditions.

3.3.2. Copper

The residual fraction had the highest proportion of copper (54 ± 3%), followed by the organic matter-sulphides fraction (45 ± 3%). Fe–Mn oxides, carbonate and exchangeable fractions had a low amount of the metal (<1%). Results are explained by the high

| Table 2 |
|-----------------|------------------|------------------|-----------------|
| Evaluation | RAC (%) |
| No risk | <1 |
| Low risk | 1–10 |
| Medium risk | 11–30 |
| High risk | 31–50 |
| Very high risk | >50 |

RAC = C_F1–2/C_F |

2.7. Determination of organic matter content

Following the standard SS-EN 15169:2007, the organic matter content was calculated using 50 g of the composited sample, which was first extra dried at 105 ± 5 °C until achieving a constant weight. The remaining material was taken to an oven for 1 h at 550 °C. The organic content was calculated using the weight difference before and after heating at 550 °C. The sample was analysed in triplicates.

3.3.3. Nickel

Nickel had an average value of 12.9 ± 0.6%, highlighting a medium value according to SS-EN ISO 14688–2:2018. Table 3 shows the total concentration of metals along with the sum of concentrations in all fractions and recovery rates (mean ± SD; n = 3).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Total concentration (mg kg⁻¹ DMa)</th>
<th>Sum concentration F1–F5 (mg kg⁻¹ DMb)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>37.2 ± 0.8</td>
<td>42.5 ± 2.4</td>
<td>114.2 ± 6.5</td>
</tr>
<tr>
<td>Cu</td>
<td>51.1 ± 1.2</td>
<td>62.1 ± 4.9</td>
<td>121.6 ± 9.8</td>
</tr>
<tr>
<td>Cr</td>
<td>37.9 ± 1.2</td>
<td>36.4 ± 0.6</td>
<td>96.1 ± 1.6</td>
</tr>
<tr>
<td>Ni</td>
<td>27.9 ± 0.1</td>
<td>27.8 ± 0.8</td>
<td>99.4 ± 2.9</td>
</tr>
<tr>
<td>Zn</td>
<td>138.5 ± 0.4</td>
<td>167.1 ± 10.4</td>
<td>120.7 ± 7.5</td>
</tr>
<tr>
<td>Fe</td>
<td>23,855 ± 651</td>
<td>26,338 ± 1034</td>
<td>110.4 ± 4.3</td>
</tr>
</tbody>
</table>

a DM: Dry Matter.

b F1–F5: F1 + F2 + F3 + F4 + F5.
affinity of the element to form compounds with organic matter (Chen et al., 2013). Similar distributions of sediments with a high amount of copper linked to the oxidisable (30–50%) and residual (20–50%) fractions were described by Tokalioglu et al. (2000), Fytianos and Lourantou (2004) and Lasheen and Ammar (2008).

The distribution of copper suggests that the metal has anthropogenic and non-anthropogenic origins. Copper presented the highest amount linked to the organic matter-sulphide fraction (see Fig. 2). Due to strong binding to F4, copper can principally be released to the surroundings under oxidisable conditions or while degradation of organic matter. The metal also exhibited a high presence in the residual fraction, reducing its bioavailability. The RAC value of 1.1% represented a low risk of pollution of copper associated with F1 and F2. The contamination factor of 0.87 expressed no risk of contamination by this metal in the bay during dredging activities.

3.3.3. Chromium

The results exhibited that chromium was mainly linked to F5 (70 ± 1%) followed by F4 (22.8 ± 1%) and F3 (6 ± 1%). The metal had no considered amount related to F1 and F2 (<1%). The findings are explained by the fact that the element is prevalent on the Earth’s crust (Baraud et al., 2017), and that organic matter has a high affinity for it (Radenovic et al., 2019). Results are in agreement with Morillo et al. (2004), who described marine sediments with a high amount of chromium linked to the residual fraction (80%) followed by the organic matter-sulphide portion (10%).

As observed in Fig. 2, chromium is the metal with less amount linked to the labile fractions, implying a considerable natural origin. The presence of this element in F4 may pose a threat of release under oxidising conditions or by the degradation of organic matter. Nevertheless, the low proportion of chromium in the labile fractions suggested a reduced risk of pollution. Findings are supported by the contamination factor of 0.42 and a RAC of 0.8%. These results suggested that dredging activities would be likely not connected to the release of chromium.

3.3.4. Nickel

Nickel was mainly linked to F5 (49 ± 1%) followed by F4 (35 ± 5%), F3 (12 ± 5%) and F2 (4 ± 1%). The amount connected to F1 was low (<1%). The high presence of this element in F5 and F4 is explained by the natural sources of the element (Duda-Chodak and Blaszczyk, 2008) and its affinity to bind with sulphur (Kang et al., 2017). Chen et al. (2013), Lasheen and Ammar (2008) and Yuan et al. (2004) reported similar findings of nickel from sediments associated with the oxidisable (20–40%) and residual (40–50%) fractions.

The distribution of nickel along all fractions suggested both anthropogenic and natural origins. This metal can potentially be leached out by changes in the redox potential, and either oxidisable or reducible conditions can affect its mobility. Nevertheless, the high amount of nickel linked to the residual fraction leads to less risk of contamination presented by the contamination factor of 1.05. The RAC of 4.9% indicated a low risk of pollution by mobilisation of the most labile fractions. Consequently, during dredging, it is not expected to generate contamination with nickel in the aquatic environment.

3.3.5. Zinc

In the sediments from Malmfjärden, zinc had one of the highest total concentration. The residual part (37 ± 4%) was the highest followed by the Fe–Mn oxide fraction (27 ± 4%). The metal was also bound to F2 (17 ± 1%) and F4 (14 ± 3%), while F1 had a low proportion (4 ± 0.5%). The results are explained by the fact that Fe and Mn are great carriers of zinc. Organic matter also exhibits a pronounced affinity, forming metal-organic complexes (Prabakaran et al., 2019), and carbonates can also bind to this element (Chen et al., 2019). Additionally, the presence of this metal in the
residual fraction is explained by its widespread in the Earth’s crust (Plum et al., 2010). Results are in agreement with Chen et al. (2013), who reported zinc from sediments mainly linked to the carbonate (30%), Fe–Mn oxide (30%), organic matter - sulphide (10%) and residual (30%) fractions.

Similar to lead, zinc is highly associated with the non-residual fractions suggesting an anthropogenic origin. In Malmfjärden, this element is probably associated with the runoff discharges since the bay lacks sewage inputs. Possible changes affecting the mobility of this metal are the decomposition of organic matter and fluctuations of pH and redox conditions. Medium risk of pollution of zinc to the surroundings was determined by the CF of 1.71. The RAC of 21.6% showed a medium risk of mobilisation of F1 and F2. Zinc can potentially be released into the aquatic ecosystem during the implementation of dredging activities. As a preventive measurement, it is recommended to employ more environmental dredging techniques, which are less associated with substantial variations on the bay conditions reducing the possibility to release this metal.

3.3.6. Iron

Iron was the metal with the highest total concentration. Nevertheless, most of its amount was linked to the residual fraction (58 ± 1%) followed by F4 (36 ± 4%) and F3 (7 ± 3%). F2 and F1 had no main linkage. Findings are explained by the broad presence of the metal in nature and its high affinity to bind to organic matter (Pytianos and Lourantou, 2004). Tokalioglu et al. (2000) reported similar results, where iron in sediments was mainly linked to the residual (60%) and oxidisable (30%) fractions.

Compared to other metals (see Fig. 2), iron had one of the highest association with the residual fraction, proposing a natural source of origin. The main risk of mobilisation of this element is connected to the decomposition of organic matter or changes to an oxidising environment. Nonetheless, the pollution risk of iron is low since most of its amount is found in the residual fraction. The contamination factor of 0.74 indicated no pollution with this metal, and the RAC of 0.1% showed no risk of mobilisation of the most labile fractions. During dredging activities, due to the low risk of
pollution, it is not expected to generate contamination by iron into the surroundings.

3.3.7. Potential metal risk pollution while using dredged sediments in beneficial uses

In Sweden, SEPA (2009) provides the national maximum permissible concentrations of metals in soils/dredged sediments in order to be employed in different land uses. The regulation determines separate limits for less sensitive and more sensitive land uses. Fig. 3 compares the concentration of metals in each chemical fraction with the maximum permissible thresholds for more sensitive uses. The figure also illustrates the sum of the concentrations of the non-residual part for each metal. Iron is not included in the figure since the Swedish regulation absences a maximum permissible concentration for this element.

The results showed that, in each fraction, the concentrations of the metals did not exceed the maximum permissible limits of the sum of concentrations of the non-residual part. Even if metals from the non-residual fractions are potentially leached out due to changes in the environment, the released concentrations are always below the permissible limits. Hence, it is concluded that, for the case of Malmöfjärden, using dredged sediments in beneficial uses is associated with a low risk of spreading of Pb, Cu, Cr, Ni and Zn.

4. Conclusions

The speciation of lead, copper, nickel, cadmium, zinc and iron in sediments from Malmöfjärden bay, Sweden was carried out to assess the potential risk of pollution in the aquatic ecosystem during future dredging activities and while using the material in beneficial uses. All metals, besides Pb, had their largest amounts associated with the residual fraction. The organic matter-sulphide, Fe–Mn oxides and carbonate fractions also presented an important association with the studied metals. Fewer amounts of metals were linked to the exchangeable phase. The risk indexes (contamination factor and risk assessment code) showed a slight concern of pollution for Cr, Ni and Fe. The risk increased for Pb and Zn, where the CF was between 2 and 3 and the RAC between 10 and 30%, expressing a medium risk of pollution to the surroundings. During dredging, it is not expected to have contamination associated with Cr, Ni ad Fe. However, it is recommended to decrease the risk of pollution of Pb and Zn into the aquatic ecosystem. Potential solutions include employing more environmental extraction methods, which could be associated with reduced particle resuspension and less fluctuations at the bay.

For all metals, the sum of the non-residual concentrations was below the Swedish limits to determine pollution in soil/dredged sediments. The results suggested that, while using the dredged sediments in beneficial uses, there is a low risk of metal pollution with Pb, Cu, Cr, Ni and Zn. Further metal speciation and leaching tests from the future dredged sediments will contribute to determining the potential metal spread pollution while using the sediments in land uses.

Credit author statement

Laura Ferrans, Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing-Original Draft, Writing - review & editing, Visualization Funding acquisition. Yahya Jani, Conceptualization, Methodology, Validation, Writing - review & editing and Supervision. Juris Burlakovs, Methodology, Writing - review & editing. Maris Klavins, Resources, Writing - review & editing. William Hogland, Conceptualization, Resources, Writing - review & editing, Supervision Funding acquisition.

Declaration of competing interest

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

Acknowledgement

The authors would like to acknowledge the team from the Environmental Science laboratory from Latvia University for all their support provided during the running of the experiments. Additional thanks to Stefan Tobiasson, David Silfversvård and Ling Gao for their contribution during the sampling campaign.

We greatly acknowledge Estonian scientific mobility support of ARCHIMEDES and ASTRA project ‘Value-chain based bioeconomy’ (Vaärtusalhelapõhine biomajandus). This research has also been supported by the Life program (grant no. LIFE15 ENV/SE/000279) and Erasmus + for mobility funds.

References


Fathollahzadeh, H., Kaczala, F., Bhatnagar, A., Hogland, W., 2015. Significance of environmental dredging on metal mobility from contaminated sediments in the...


