Geochemical and physical characteristics of contaminated sediment in a harbour area

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ABSTRACT

Heavy metals adsorbed by sediments are of particular concern due to their mobility and toxicity in the aquatic ecosystem. Harbour areas, particularly on the banks of large rivers, have been facing deposition of polluted sediment. Considering a technique for remediation of contaminated sediment needs a comprehensive understanding of the geochemical and physical characteristics of sediment. In this study, a set of surface sediment samples was taken from a harbour on the bank of the St. Lawrence River, Quebec, Canada. The harbour area was polluted by heavy metals and there was an urgent need to dredge the sediments. However, prior to managing the sediments, the toxicity and availability of metals in sediment should be evaluated. Determination of the particle size distribution was performed in addition to pH, loss on ignition (LOI) and oxidation-reduction potential (ORP). To examine the mobility and dynamics of heavy metals in sediments, a sequential extraction technique was used. Cr, Ni, Cu, Zn, As, Cd and Pb were the elements investigated in this study. Results showed that the sediment samples were highly organic and the textures were pretty fine. The results also indicated that the copper, zinc and chromium were the main elements that exceeded the occasional effect level based on the Environment Canada sediment quality guidelines. However, the risk of mobility due to the availability of cadmium and lead was significantly more than the other elements. For example, the concentration of cadmium in a location was around 60% in exchangeable and carbonate fractions of the total. The most contaminated location was near the dock area, where it usually receives the runoffs from the boat maintenance area. To conclude, the concentration and potential mobility of heavy metals in sediments near the dock area must be considered when determining the most appropriate management strategy.

Keywords: contaminated sediment, harbor areas, heavy metals, sequential extraction.

1 INTRODUCTION

Harbour areas, particularly on the bank of large rivers, have been facing deposition of sediments. During the decades, significant amounts of pollutants are received at these areas and most of them adsorbed by sediment. Among the various pollutants, heavy metals adsorbed by sediments are of particular concern due to their mobility and toxicity in the aquatic ecosystem.

Copper, zinc, lead and chromium are the most common heavy metals, which can be found at harbour areas. Those metals are the components of many antifouling paint formulations (Simpson et al. 2013). In order to prevent the growth and colonization of river microorganisms on the hulls of boats, antifouling paints are employed (Yebra et al. 2004; Braithwaite et al. 2007). Recently due to recognized environmental impacts of organotin compounds (i.e. tributyltin), which are considered as toxic chemicals, copper (I) oxide as a biocidal component and prithione or zinc oxide are used in antifouling paint formulations (Simpson et al. 2013). Moreover, lead is added to enhance drying and hexavalent chromium is still widely used in primer paint (U.S. Department of Labor 2013). Sanding the old paints prior to repainting boats on the maintenance area causes transport of a significant amount of heavy metals to the river by runoffs. Sediment can adsorb up to 99% of contamination in rivers (Salmons et al. 1995). Shallowness and contaminated sediments at harbour areas become the challenging issues since dredging the contaminated sediments without an appropriate management strategy can spread heavy metals in aquatic ecosystems and put public health in danger.

In this study, the geochemical and physical characteristics of sediment in a harbour area were evaluated in order to understand the key parameters for the best management strategy. Moreover, identifying the best remediation technique in these cases requires appropriate information about
physicochemical features of contaminated sediments.

2 STUDY AREA

A yacht club in the province of Quebec was selected for this study, which located on the bank of the St. Lawrence River. The area of the harbour is approximately 15,000 m². Nine stations along the passage way and dock area, which are the most potential places for dredging, were chosen for analysis (Figure 1).

There was an urgent need to remove the sediments from the selected area (around dock area and passageways) in order to facilitate the passage of the larger yachts. However, prior to dredging, the quality of sediments should be evaluated to prevent spreading of the contaminants. It has been almost 13 years since dredging was employed in this harbour. Quasi-steady water flow around dock area as well as receiving a significant amount of contamination from boat maintenance area causes contaminated sediment.

3 MATERIAL AND METHODS

3.1 Sampling

A set of surface sediment samples was obtained at the selected stations (Figure 1) based on the sediment-sampling guide for dredging and marine engineering projects in the St. Lawrence River (Environment Canada 2002).

The surface samples were taken with an Ekman-Birge grab from the surface of the sediments to a vertical distance of a maximum of 10 centimeters below. During the sampling at the site, all samples were kept in the airtight plastic bottles and placed in an ice-cooled box. They were transferred to the freezer (-18°C) at the Environmental Engineering laboratory at Concordia University and were analyzed later.

3.2 Analytical parameters

All measurements were carried out at the Environmental Laboratory of Concordia University. Among physical characteristics of sediments, information about their texture and the size distribution are most useful. Analysis of the particle size distribution of sediment samples was done by the laser scattering analyzer (HORIBA, LA-950V2). D_{50} (50% of particles are less than this size) and the percentages of clay, silt and sand for each sample were determined. Table 1 shows some physicochemical features of the surface samples.

\[ \text{LOI} \% = \left( \frac{W_{105^\circ C} - W_{550^\circ C}}{W_{105^\circ C}} \right) \]

The concentrations of heavy metals and metalloids were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7700x). In order to use the ICP-MS for solid samples (e.g. sediment), acid digestion was required. EPA 3050B was the protocol used to digest the solid samples and prepare them for ICP-MS analysis. For digestion, 1 or 2 grams of wet sample were digested with repeated additions of nitric acid (HNO₃, 70%, trace metal grade) and hydrogen peroxide (H₂O₂, 30%). The digested samples were kept in the fridge around 4°C and were analyzed later.

A sequential extraction (SSE) was employed on the basis of the method of Yong et al. (1993). Heavy metal ions in sediments are partitioned between the different fractions. Determination of the concentration of metals in each fraction can provide detailed information about their origin, mode of occurrence, physicochemical availability and mobilization (Filgueiras et al. 2002). The most available metals were found in the water soluble and exchangeable fraction by adding 8 ml of 1 M MgCl₂, pH 7 to 2 g dried sediment sample with shaking for 1 hour at room temperature (23°C). Metals associated with carbonates were extracted by adding 8 ml of sodium acetate, pH adjusted to 5 with acetic acid, 5 hours shaking at room temperature. Metals bound to Fe-Mn oxides and hydroxides were removed by adding 20 ml of 0.04 M NH₄OH.HCl in 25% (v/v) acetic acid at 96°C in a water bath for 6 hours. To extract metals from organic and sulphide matter, 3 ml of 0.02 M HNO₃ and 5 ml of 30% H₂O₂ (pH 2) were added at 85°C for 2 hours, followed by 3 ml of 30% H₂O₂ (pH 2) at 85°C for 3 hours. Finally 5 ml of 3.2 M ammonium acetate in 20% (v/v) HNO₃ were added and then diluted to 20 ml at room temperature (23°C).
for 30 minutes. The last fraction is called the residual fraction and sediment samples were digested in order to remove heavy metals in this fraction by applying a diluted aqua regia (50 ml HCl + 200 ml HNO₃ + 750 ml deionized water) for 3 hours at 96°C. The liquid phase was extracted at the end of each fraction by centrifuging at 3500 rpm for 20 minutes and analyzed by ICP-MS.

All plasticware and glassware for analyses were cleaned by soaking in 5% (v/v) HNO₃ at the beginning and end of each measurement for a minimum of 8 hours, followed by rinsing with deionized water (Milli-Q 18 μΩ cm and 2 ppb TOC). Moreover, all chemicals (e.g. acids) were trace metal grade. For quality control, all sediment samples were analyzed using a blank and duplicates.

3.3 Sediment quality guidelines

According to the guidelines (Environment Canada and Ministère du Développement Durable, 2007), the level of contamination for the management of dredged sediment is evaluated based on the Occasional Effect Level (OEL) and Frequent effect Level (FEL). For substance above the OEL, adverse effects are anticipated in many benthic species. Therefore, open-water disposal is prohibited unless the toxicity test shows there is no threat to aquatic biota (i.e. those organisms living in or near sediment and depend upon it for their existence). However, those sediments need to be managed properly. For heavy metals equal or exceeding the FEL, open-water disposal is banned without any further tests. Sediments containing elements exceeding FEL are highly contaminated and the site must be treated before any action. Adverse effects are expected for the majority of benthic species (Environment Canada 2007).

If the total concentration of heavy metals exceeds the Threshold Effect Level (TEL) but were less than the OEL, the site should be monitored. However open-water disposal is allowed. It is worth noting that the presence of a single heavy metal in sediment samples that exceeds the quality criterion is sufficient to categorize sediments as contaminated. Table 1 presents the criteria for assessing the quality of sediment samples for heavy metals.

Table 1. Environment Canada criteria for the assessment of sediment quality (mg/kg).

| Level  | Cr | Ni | Cu | Zn | As | Cd | Pb |
|--------|----|----|----|----|----|----|----|
| TEL    | 37 | 36 | 120| 6  | 0.6| 35 |
| OEL    | 57 | 47 | 63 | 170| 8  | 1.7| 52 |
| FEL    | 120| 700| 770| 23 | 12 | 150|

4 RESULTS AND DISCUSSION

4.1 Physicochemical characteristics of sediment samples

Physical characteristics (e.g. D₅₀, particle size distribution) and some chemical features of sediment samples (e.g. pH, DO and ORP) are presented in Table 2.

The results indicate that the sediment samples were highly organic (high LOI) and cohesive since the clay content was substantial. With D₅₀ about 1 micron, sediments were fine in texture. At station 1 (the entrance of maintenance boat area to harbour) the texture of sediment was significantly coarser than the other stations. The condition of sediments at the harbour was aerobic since the ORP was positive (except for S5) and pH was neutral.

4.2 Total concentration of heavy metals

At the first step, the total concentration of heavy metals was determined by acid digestion followed by using the ICP-MS to compare the results with the sediment quality guidelines. Table 3 shows the total concentration of heavy metals in the samples.

In Table 3, the bolded numbers are the concentrations of elements exceeding the OEL. All of the concentrations were below the FEL. Therefore the sediment samples can be categorized as contaminated sediment, which need to be managed. Open-water disposal in that case is prohibited unless the toxicity test indicates that there is no threat to benthic organisms.

Zn, Cu and Cr were the main sources of contamination. However Pb and As also had high
enough concentrations in some locations to be of concern.

Total concentrations of heavy metals in sediments at stations 1 to 4 were significantly higher than the rest of samples, particularly for Cu and Pb. These stations were the main locations received contaminations from the boat maintenance area. Normally, at the end of boating season, the boats are hauled out of the water to the maintenance area and the hulls of the boats are sanded and repainted each year. Significant amounts of pollutants (i.e. heavy metals) have been carried by runoffs and gradually entered into the river, which was mostly adsorbed by sediments. Cu and Pb are the common elements in antifouling paints as well as Zn and Cr. High concentrations of the previously mentioned metals in the sediment samples around dock area and passageway were expected.

4.3 Background and availability of heavy metals

According to the definition of contamination, sediments are considered contaminated when 1) the concentration of an element is high enough to have an adverse effect on benthic organisms, and 2) the concentration of an element exceeds the background level observed prior to industrialization (Environment Canada 1993). Therefore, comparing the concentration of heavy metals with their background level is necessary. Table 4 shows the background levels of selected heavy metals in this study from the fluvial section and fluvial estuary of the St. Lawrence River (Environment Canada 2007).

Table 4. Natural levels of selected heavy metals and metalloids in pre-industrial sediment in the St. Lawrence River (mg/kg).

|     | Cr  | Ni  | Cu  | Zn  | As  | Cd  | Pb  |
|-----|-----|-----|-----|-----|-----|-----|-----|
| NL  | 60  | 29  | 19  | 86  | 7   | 0.2 | 13  |

In order to compare the concentration of heavy metals with their background, the following equation was employed:

\[
\text{Exceeding Level} \% = \left( \frac{M_{ML} - M_{NL}}{M_{NL}} \right) \times 100
\]

Where, \( M_{ML} \) is the measured concentration of the heavy metals and \( M_{NL} \) is the natural level of the heavy metals in pre-industrial sediment. Therefore, if the exceeding level (EL) was significant, it means that the concentration of that metal exceeds a natural level. Figure 2 shows the EL for selected heavy metals in all stations. Cu, Zn, Cd and Pb are the heavy metals exceed even more than 60% of their natural levels (NL). Previously, the roles of Cu, Zn and Pb have been recognized based on the sediment quality guideline, but now Cd also is the major pollutant in samples. Moreover, Cr is no longer considered as a major contaminant since in most of the stations it did not exceed 20% of its NL.

As it is widely recognized, the total concentration cannot provide comprehensive information about the availability and potential mobility of heavy metals. Consequently the sequential extraction method was applied to determine more information about the source and history of heavy metals.

Metal ions in sediments are partitioned between the different fractions, i.e., exchangeable, acid soluble, reducible, oxidizable and residual fractions. Heavy metals in the exchangeable and acid soluble (i.e. metals associated with carbonate) fractions are considered potentially bioavailable. However the reducible (i.e. metals associated with Mn & Fe hydrous oxides) and oxidizable (i.e. organic matter) fractions are relatively stable under normal conditions (Filgueiras et al. 2002). The most unavailable metals (stable bonds to the sediment matrix) are classified as in the residual fraction, which can be extracted by strong acids.

The results of selective sequential extraction (SSE) are presented in Figure 3 and indicate that the most available metals in sediments samples are Cd and Pb. On average over 9 stations, the concentrations of Cd and Pb in the exchangeable and acid soluble fractions were 32.7% and 23.5% of the total, respectively. It means that almost one third of Cd and one fourth of Pb, which exist in the sediment, are environmentally available. The availability of other elements is significantly lower than Cd and Pb. Moreover, Cu, which was the main contaminant, is the least available metal. By considering the SSE results, Cr cannot be classified as a contaminant since not only its concentration was not significantly higher than NL, but also it is not an available metal in this case study.
Station 2 was the most critical location in terms of availability of metals. More than 64% of total concentration of Cd and around 40% of Pb in S2 was found in the two first fractions; Part of them was recently added to the environment since aged pollutants usually were found in the more stable fractions (Liang et al. 2014).
In general, availability of heavy metals (i.e. sum of metal concentrations in F1 and F2) over 9 stations follows the order:

Cd > Pb >> As > Zn > Ni > Cr > Cu

Copper, the least available metal, mostly can be found in organic fraction (F4), which is in agreement with other studies (Sundaray et al. 2011, Vicente-Martorell et al. 2009). Moreover, at stations 2 and 3 with a high LOI, the organic fraction had a dominant role.

Although the results show that Cd, Pb, Cu and Zn are the inorganic contaminants in this case study, the toxicity test should be done to determine whether open-water disposal of those sediments is allowed or not. Moreover, SSE can be quite helpful beside the sediment quality guidelines for detecting the contaminants. Mobility and availability of heavy metals are more crucial than their total concentration.

5 CONCLUSIONS

Geochemical and physical characteristics of sediments at a harbour were determined in order to investigate about the safe dredging of sediment at a harbour in Quebec province. According to the sediment quality guideline by Environment Canada, the sediment samples were determined as contaminated sediments since some heavy metals (e.g. Cr, Cu and Zn) in each sample exceeded the OEL. Comparing the total concentration of heavy metals with their natural level (in pre-industrial sediment) implied that Cr is not a contaminant. However, Cu, Zn, Cd and Pb are introduced as the elements exceeding more than 60% of their natural levels. More information about availability of heavy metals in the aquatic ecosystem was obtained by performing sequential extraction technique. As a result, Cd and Pb were found to be significantly available in all sediment samples. Cu was the least available metal and was mostly found in the organic fraction.

Since none of the elements passed the FEL, the toxicity test should be done to clarify whether open-water disposal is prohibited or not.

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