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Selection of an appropriate management strategy for contaminated sediment: A case study at a shallow contaminated harbour in Quebec, Canada

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ABSTRACT

Harbours, as strategic places in tourism and transportation, are exposed to many sources of contamination. Assessing the quality of harbours sediment by guidelines and regulations does not reflect the actual level of contamination and the risk posed to aquatic ecosystems. Selection of an appropriate management technique for contaminated sediments in those strategic locations is crucial for the aquatic environment. The purpose of this study is to show that insufficient information, provided by sediment quality guidelines (SQGs) to identify the actual contaminants, could lead to a destructive or potentially ineffective decision for risk reduction in contaminated harbours. A comprehensive evaluation on physicochemical characteristics of sediment and water samples of a shallow harbour in St. Lawrence River was performed. Results of trace metal fractionation and risk assessment indicated that Cd and Pb were the contaminants that could pose a threat to aquatic ecosystem, although the SQG outcomes implied that Cu and Zn may cause an adverse effect on the benthic organisms. The results of multivariate statistical analysis demonstrated that the locations in the vicinity of the maintenance area contained the most contaminated sediment samples and require appropriate management. Antifouling paint particles and probably the runoff entering the harbour were the main sources of pollution. Among the diverse range of management strategies, the resuspension technique is suggested as a viable alternative in this specific case for shallow locations with contaminated sediments. A suitable management strategy could reduce the cost of remediation process by identifying the actual contaminated spots and also reduce the risk of remobilization of trace metals.

1. Introduction

Harbours have a vital role in the economy through the transport of traded goods and tourism. However, the anthropogenic activities in harbours raise concern about the adverse effects on marine and coastal environments (Buruaem et al., 2012). A wide range of contaminants derived from commercial, industrial and leisure activities can be transported to the sediments in riverbeds (Iannelli et al., 2012). Sewage, industrial and domestic wastewater, petroleum and its derivatives from motorboats and the residues of boat painting and surface treatment from maintenance areas are major sources of pollution entering the rivers (NRC, 1997). Among the various activities, repairing and repainting of the boats and yachts in the vicinity of harbours have been recognized to be harmful.

For many years antifouling paints have been applied to the hulls of boats and to many static submerged structures (Turner, 2010). Widespread applications of antifouling paints have introduced a high level of pollution into the aquatic ecosystem. Antifouling paint particles (APP), generated through the boat repainting and repairing process, are transported into the rivers through runoff and eventually settle in the sediments at the bottom of the harbours. APP is the main source of the inorganic and non-degradable biocidal elements in harbour sediment. Traditionally antifouling paints have incorporated some toxicants such as copper and tributyltin, TBT (Dafforn et al., 2011). By ultimately banning triorganotin (e.g., TBT) formulations, a Cu (I)-based biocidal pigment in combination with zinc oxide (mainly as a booster) has been used in marine antifouling paints (Turner, 2010). New formulations of antifouling paints also contain some additives and non-biocidal pigment made by lead antimonates [$Pb(SbO_3)_2$], lead chromates

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and cadmium yellow (Abel, 1999). Nevertheless, leaching of biocides from APP in marine systems (e.g. harbours) has been previously reported (Turner, 2010).

Besides the contamination as an issue in harbours, construction of breakwaters causes changes in the sediment transport, and leads to deposition of significant amounts of sediments annually. In the quasi-stationary water situation around the dock areas, suspended sediments in the river gradually settle. The sizes of the settled sediments are usually fine, since they are mainly suspended load. Suspended loads are the particulate sediments, which are carried in the body of the flow river. They are small particles with relatively large surface area and electrostatic attraction. Subsequently, they have a great tendency to adsorb and sink the contaminations that have entered into the water (Mulligan et al., 2009). Accordingly, shallowness and contaminated sediment become challenges for managing the sediments in harbours.

Identifying suitable management strategies for contaminated sediments has been previously discussed (Walker et al., 2013; Ghosh et al., 2011; Kiker et al., 2008; Birch and Taylor, 2002). Sediment quality guidelines (SQGs), developed in different countries, are normally used for assessment of the level of contamination and estimating possible biological adverse effects on the benthic biota (Birch and Taylor, 2002). A management strategy is typically designed based on the assessment information derived from SQGs. Sediment risk management (according to the SQGs) is often based on the total concentration of contaminants (Cornelissen et al., 2005; Ehlers and Luthy, 2003). Therefore, for numerous cases, the risk of availability of trace metals, for instance, is often overlooked. Additionally, the predictive ability of SQGs to recognize the actual threat to environments and some other associated issues such as inability to identify bioavailability of contaminants in sediment, lack of information to plan a more cost effective strategy and even absence of some elements' standard level has been previously discussed (Walker et al., 2013, 2015).

New developments in managing the contaminated sediment are not always sustainable or suitable for this particular case. *In situ* management could be beneficial over dredging due to a reduction in costs and reduced solid disposal requirements. However, they are not applicable in shallow harbour areas. *Ex situ* remediation strategies, on the other hand, are costly and require dredging operations (Peng et al., 2009), which can have some serious environmental impacts. For instance, dredging the sediment increased turbidity levels, which ultimately leads to decreased numbers of invertebrate species (Crowe et al., 2010; De Leeuw et al., 2010). Additionally, costs, public perception, socio-economic and managerial aspects are the other conflicting issues that should be taken into consideration in the dredging process (Manap and Voulvoulis, 2015). An appropriate management scheme must be sustainable in order to minimize the waste, conserve the natural resources, minimize the landfill deposition and protect benthic habitats.

The main objective of this study is to show that information, provided by SQGs to identify the actual contaminants, could lead to the selection of a destructive or potentially ineffective method for risk reduction in contaminated sediment. This paper aims to determine the crucial factors, which actually affect the selection of an appropriate and balanced management strategy for contaminated sediments. Therefore, through a case study in a harbour in the province of Quebec, Canada and by analyzing the different physicochemical characteristics of contaminated sediment, the influential parameters for a proper management strategy were identified. After evaluating available management approaches, a viable and suitable strategy was suggested to manage the contaminated sediment for shallow aquatic environments.

2. Materials and methods

2.1. Site details and relevant information

The study area is located on the north bank of the St. Lawrence River in the province of Quebec, Canada. The site was a harbour for leisure boats with an area of approximately 15,000 m^2 (Fig. 1-a). Two floating and one solid breakwater have protected the harbour from the waves. Arial photos in the wintertime clearly show a quasi-stationary flow in the harbour especially around the passageways and dock area, which causes deposition of sediment in the harbour (Fig. 1-b).

There was an urgent need to remove the sediments from areas around the dock and passageways, in order to facilitate the passage of the larger yachts. It has been almost 15 years since dredging was employed at this harbour. However, prior to dredging or any method of management of the sediment, the quality must be assessed to evaluate the viable management options.

The water depth varied between 0.6 m (around the dock area) and 3 m (around the floating breakwater). The boat maintenance area was located at the northwestern part of the harbour and was mainly used for repairing and repainting in the summer and storing the boats in the winter. Fifteen different stations along the passageways and the dock area, which are the most potential places for dredging, were chosen for analysis. These stations are shown on the map in Fig. 1-a.

2.2. Sampling operation

Two sets of sediment samples were obtained at the selected stations (Fig. 1-a) based on the sediment-sampling guide for dredging and marine engineering projects in the St. Lawrence River (Environment Canada, 2002). The first set was surface samples, which was taken with a Birge-Ekman sampler from the surface of the sediments to a maximum depth of 10 cm. Each sample was about 1 $\pm$ 0.2 kg (wet). The second set was core samples, which were obtained from the surface of sediment at the bottom of the river to a depth of a maximum of 50 cm. The core sediments were compacted and trapped in a stainless steel cylinder with a diameter of 6.3 cm and a height of 17.8 cm. Sediment samples (i.e. surface and core samples) were transferred and kept in the airtight polyethylene bottles and placed in an ice-cooled box. In total, 15 surface and 12 core sediment samples were obtained from selected stations (Fig. 1). They were transferred to a freezer and were homogenized before analysis.

The river water samples were obtained from up to 20 cm depth from the water surface at five different locations (stations 1, 5, 6, 8 and 10) and were stored in the pre-cleaned polypropylene bottles. For dissolved metal analyses, they were also passed through a 0.45 μm filter and then acidified with 0.5 M HNO_3 and 0.3 M HCl (USEPA, 1992).

All plastic- and glass-ware used during the experiment process was soaked in 5% (v/v) nitric acid and 2.5% (v/v) hydrochloric acid (trace metal grade) for at least 8 h followed by two rinses with deionized water (prepared using a Milli-Q 18 $\mu\Omega$ cm). For quality control, all sediment samples were analyzed using a blank, control and duplicates.

2.3. Trace metal analysis

The concentrations of trace metals and metalloids were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7700x). Seven metals and metalloids including Cr, Ni, Cu, Zn, As, Cd and Pb were selected for analysis. In order to use the ICP-MS for solid samples (i.e. sediment), acid digestion was required.