Resuspension of Sediment, a New Technique For Remediation of Contaminated Sediment in Shallow Harbours

Mehdi Pourabadehei

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By: Mehdi Pourabadehei

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Dr. S. Bergler	Chair
Dr. A. Mucci	External Examiner
Dr. G. Vatistas	External to Program
Dr. L. Yerushalmi	Examiner
Dr. S. Li	Examiner
Dr. C. Mulligan	Thesis Supervisor

Approved by

Chair of Department or Graduate Program Director

January 2017

Dean of Faculty

ABSTRACT

Resuspension of sediment, a new technique for remediation of contaminated sediment in shallow harbours

Mehdi Pourabadehei, Ph.D.
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Shallow harbours with contaminated sediments are subjected to the risk of uncontrolled resuspension of sediment, which could remobilize weakly bound heavy metals into overlying water and pose a potential risk to aquatic ecosystem. Remediation of sediments in these areas cannot be performed by conventional *in situ* and *ex situ* remediation methods. Alternatively, the resuspension technique was introduced to address these issues. The concept of the resuspension method is that finer sediments have a greater tendency to adsorb the contamination due to their specific surface area and ionic attraction. Therefore, finer particles were targeted for removal from the aquatic environment by a suspension mechanism in a confined water column. The main objective of this study was to evaluate the feasibility of the resuspension technique as a new approach for remediation of contaminated sediment and a viable option to reduce the risk of remobilization of pollutants in harbours. The results indicated that the resuspension technique could successfully reduce the total concentration of contaminants (i.e. Cr, Co, Ni, Cu, Zn, As, Cd and Pb) in almost all samples below the probable effect level with no significant change in the overlying water quality. Precisely, by removing just 4% of contaminated sediment in this method, the contamination intensity of Cd and Pb (as the main pollutants) was reduced by 26 and 28 percent and for the rest of the contaminants returned to the non-polluted level. Removal efficiency of heavy metals was positive with a minimum 17.6% for Co and a maximum for 25.9% for Zn. The results of the sequential extraction test (SET) also illustrated that the contaminant removal efficiency could be drastically enhanced for metals in sediment with a higher enrichment factor. Principal component analysis, performed on the data sets from the SET results, implied the significance of the anthropogenic factor in contaminating the sediments in the study area. Removal of contaminants from sediment through this method could also reduce the risk of mobility and availability of metals under changing environmental conditions. No chemical substances were employed in the resuspension method. Subsequently, less destruction can be caused in the aquatic ecosystem.

Dedicated to

My Dear Wife Shaghayegh

And

My Amazing Parents, Farah & Ali

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Contribution of Authors

The thesis contains three manuscripts, which have been accepted for publication. The list of the manuscripts has been provided as follows:

Chapter 3

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Chapter 4

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Chapter 5

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All manuscripts presented in this thesis have been reviewed and approved by my supervisor Dr. Catherine Mulligan (the co-author of the articles), prior to submission.

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List of Abbreviations

AP: Antifouling Paint

APP: Antifouling Paint Particle

AVS: Acid Volatile Sulfide

CA: Cluster Analysis

CCC: Criterion Continuous Concentration

CCME: Canadian Council of Ministers of the Environment

CMC: Criterion Maximum Concentration

COD: Chemical Oxygen Demand

CTC: Chronic Toxicity Criterion

CWQG: Canadian Water Quality Guidelines

DO: Dissolved Oxygen

EC: Electric Conductivity

EDTA: Ethylenediaminetetraacetic Acid

EF: Enrichment Factor

EI: Exceeding index

EPA: Environmental Protection Agency

FEL: Frequent Effect Level

GPD: Gross Domestic Product

HCA: Hierarchical Cluster Analysis

ICP-MS: Inductively Coupled Plasma Mass Spectrometry

I_{geo}: Geoaccumulation Index

LOI: Loss on Ignition

MDDEP: Ministère du Développement durable, de l’Environnement et des Parcs mV: millivolt

NL: Natural Level

NOM: Natural Organic Material

NRC: National Research Council

NTU: Nephelometric Turbidity Unit

OEL: Occasional Effect Level

OM: Organic Matter

ORP: Oxidation-Reduction Potential

PC: Principal Component

PCA: Principal Component Analysis

PCB: Polycyclic Chlorinated Biphenyl

PEL: Probable Effect Level

PTFE: Polytetrafluoroethylene

RAC: Risk Assessment Code

RCS: Resuspension of contaminated sediment

REL: Rare Effect Level

SE: Sequential Extraction

SEM: Scanning Electron Microscope

SET: Sequential Extraction Test

SI: Size Index

SPM: Suspended Particulate Matter

SPSS: Statistical Package for the Social Sciences

SQG: Sediment Quality Guideline

T-N: Total Nitrogen

T-P: Total Phosphorus

TBT: Tributyltin

TCE: Trichloroethylene

TDS: Total Dissolved Solid

TEL: Threshold Effect Level

TOC: Total Organic Carbon

XRD: X-ray Diffraction

Chapter 1

1 Introduction

Sediment is a “suspended or deposited solid, acting as a main component of a matrix, which has been or is susceptible to be transported by water” (SedNet, 2004). There is a wide range of applications for sediments in different fields. The unique physiochemical characteristics of sediment have been used in construction and filling material such as hydraulic structure or land reclamation. However, from the environmental point of view, sediment is a key element in the aquatic ecosystem since it contains a variety of habitats and provides the nutrients for different kinds of species. Consequently the quality of sediment has an impact on aquatic species, the food chain and eventually on human health.

1.1 Sources and types of pollution in sediment

Sediments can be found at the bottom of rivers, lakes, estuaries and oceans. They have a close contact with water column and can act both as a source and sink for contamination, which is a valuable feature for sediment. Despite the large effort to clarify the sediment-water interaction in the presence of pollutants, there is still a need to develop a better understanding of complex bindings of different kinds of contamination to the sediment matrix and their mobility and availability in the aquatic environment (Andrade Passos et al., 2010; Rauret, 1998; Tüzen, 2003).

In general, natural events and anthropogenic activities are the main sources of the transportation and distribution of pollutants. Release from volcanoes, earthquakes and forest fires are some examples of natural events. On the other side, agricultural, urban and industrial activities, spill and energy production all contribute the contamination of the sediment by human activities (Mulligan et al., 2009).

Sediments are exposed to many different sources of pollution. Precipitation falling with noxious gases through the atmosphere, pollutant plumes from leaching of waste piles and industrial discharge, runoff of ground surface with nutrients, herbicides and pesticides and finally spills and diffuse discharges from harbour and mining activities are the common sources of contaminants for sediment (Pan and Wang, 2012).

There are two general types of pollution: Organic and inorganic. Organic pollutants cover the wide range of contaminants including hydrocarbons, organohalides, polycyclic chlorinated biphenyls (PCBs) and trichloroethylene (TCE). The most common organic contaminants in the aquatic environment are hydrocarbons and PCBs.

Although heavy metals and nitrogen-phosphorus are the main part of the inorganic pollutants, they have different original sources. Nitrogen and phosphorus usually originate from agricultural activities and animal waste runoff. Accumulation of these elements can lead to eutrophication and subsequent adverse effects on water quality (Fukue et al., 2007). However, heavy metals particularly are generated from industrial and mining activities. Careful attention is needed because of their mobility and availability in aquatic ecosystem. Landfill leaching can be another source of releasing heavy metals such as copper, lead and zinc (LaGrega et al., 2001).

1.2 Contaminated sediments and their issues

Sediment can be exposed to many sources of pollutants (i.e. organic and inorganic) and can cause serious environmental issues. Contaminated sediments increase the risk of eutrophication and changing the color and the taste of water. Consequently, the large biodiversity existing in the water/sediment environment would be affected.

On the other hand, bindings of heavy metals to the contaminated sediment are unstable and can lead to release of those inorganic pollutants. Mobility and availability of heavy metals not only are a short-term threat to biodiversity but the metals also can be spread in the aquatic ecosystem for a long time.

Contaminated sediment can have a significant influence on the aquatic food chain. As a result, their impact on human health and ecosystem is unavoidable. Loss of fisheries, property value, tourism and navigation can happen in the contaminated area (Mulligan et al., 2009).

Therefore, there is still a need to develop new techniques for managing the contaminated sediments in order to confront the challenging issues.

1.3 Challenges of the shallow harbours' management strategy

Harbour areas, particularly on the bank of large rivers, have been facing deposition of sediments. Construction of the breakwaters in those areas can also affect sediment transport. The sedimentation rate for St. Lawrence River's harbours as an example was estimated as 1.5 cm/year according to the Ministère du Développement durable, de l'Environnement et des Parcs du Québec (Pelletier and Rondeau, 2013). On the other hand, over the last decades, significant amounts of pollutants are received at these areas and most of them are adsorbed by sediment. Sewage and wastewater, petroleum and compounds released by antifouling paints that are received from land and river can be adsorbed by up to 99 percent by sediment (Salomons and Stigliani, 1995; Huang et al., 2012). Consequently, shallowness and contaminated sediments in those locations become the challenging issue.

Because of the concentration of pollutants, *ex situ* remediation after dredging is the main viable option and *in situ* techniques are mainly used to reduce the mobility of the contaminants. However dredging the contaminated sediment can increase the risk of mobility and availability of heavy metals in the harbours and impacts on the disposal sites that receive the dredged sediment (United States Environmental Protection Agency, 1991).

Since the shallowness is the main concern, capping with or without reactive amendments (as the most common *in situ* technique) is not applicable. Capping decreases the shallowness and keeps the contamination at the site. The only advantage is to reduce the contact and immobilize the contamination. Moreover, sand capping in some harbours with a fine texture of sediment is not effective since the sand layer can be compromised and the contamination can leach (Fukue et al., 2012; Ghosh et al., 2011). Therefore, developing new techniques with more flexibility for managing contaminated sediment and minimal harm to the surrounding environment is highly desirable. It is worth mentioning that contamination in harbour areas usually comprises organic and in-organic pollutants. Therefore, the remediation technique should be applicable for organic and inorganic contaminants simultaneously.

In order to address these issues in shallow harbour areas, the resuspension technique was introduced as a new approach to remediate contaminated sediments. The concept of the resuspension method is that finer sediments (i.e. clay and fine silt) have a greater tendency to adsorb the contamination (Mulligan et al., 2009). Due to the high specific surface adsorption and ionic attraction, finer sediments tend to have a relatively higher concentration of contaminants (Huang et al., 2012). Suspended sediment and the organic components of sediment can also scavenge organic and inorganic contaminants (Fukue et al., 2007). Therefore, removing the finer sediments without dredging the whole contaminated area is the main goal of the resuspension technique.

In the resuspension method, over a specific period of the time, the air jets in the confined water column create a strong turbulence and force the sediments to suspend. After a while, when the coarser sediments settle, the finer sediments which are still suspended, will be removed by a pump and delivered to the filter system. Consequently, some of the fine sediments containing the most contamination will be eliminated from the aquatic environment. One of the advantages of this method is that the aeration in the water column not only suspends the sediments but also creates an aerobic condition in the lower layers of sediment. Furthermore, it is the main role to prevent the eutrophication and hydrogen sulfide production (Fukue et al., 2012). Another advantage of the resuspension is that it can be applied for remediation of organic and inorganic contamination at the same time. Moreover, no chemical reagents are used in this technique.

1.4 Scope and application

Although some parameters related to organic pollutants were investigated, this research study mainly focused on heavy metal contamination and their remediation. The result of this study can be employed in remediation of contaminated sediment in rivers, lakes and particularly in harbour areas.

1.5 Objectives

Harbour areas receive organic and inorganic input from land, river and boats. Sediments in harbours have a crucial role in capturing the contaminants. However, any disturbance in sediment can lead to an increase in the mobility and availability of heavy metals in ecosystem. Understanding the complex behaviour of heavy metals binding to sediments would be helpful for choosing the proper management technique. Among the various available techniques, the cost, efficiency, sustainability and environmentally friendly factors should be considered. The main objectives of this research thesis are as follows:

- To evaluate the feasibility of the resuspension technique as a new approach for managing the contaminated sediment in harbour areas and introduce it as a viable option in shallow and contaminated harbours.
- To assess the performance (e.g. efficiency to remove the contaminated particles with minimum adverse effect on water quality) of this method in order to compare the resuspension's capability to the other viable options.
- To evaluate the effect of the resuspension method on distribution of heavy metals in sediments and suspended particulate matter. Consequently, the behaviour of the heavy metals bound to the sediment matrix over a short-term resuspension is examined.
- To assess the risk of mobility and availability of heavy metals under the influence of the resuspension technique.

1.6 Thesis organization

This thesis contains 6 chapters. Chapter 1 provides a brief introduction and the objectives of the research. In the second chapter, a comprehensive and concise literature review is presented regarding resuspension of sediments in the aquatic environment from the different point of views. Moreover, influential factors in mobility and availability of heavy metals from sediment matrix were discussed. Chapter 3 presents different physicochemical characteristics of contaminated sediments in a case study (a harbour in St. Lawrence River) in order to appraise various existing management strategies in that particular situation. Therefore, the lack of flexible and viable options for managing and remediation of contaminated sediments were demonstrated. In Chapter 4, the resuspension technique is introduced as a new approach for remediation of contaminated sediment in harbour areas. Feasibility of this method is evaluated in this chapter in order to show its capability to reduce the concentration of contaminants without dredging or applying any chemical substances. Chapter 5 focuses on the details of the resuspension technique on distribution of heavy metals in sediment and suspended particulate matter. The resuspension effects on the heavy metal concentration of each fraction in sediment matrix are evaluated in this chapter as well as applying a statistical tool for supporting the discussions. Chapter 6 is the summary of the conclusions with emphasis on the contributions in this research study. Future work is also presented in this chapter.

Chapter 2

2 Literature review

The crucial role of sediments, which are affecting the level of the contaminants in aquatic environment, has been discussed in this chapter. Heavy metals entering the rivers can be captured up to 99% by sediments in different fractions (Salmons et al., 1995). However, natural events such as waves or tides can resuspend them into the water column. Regardless of the duration and intensity of resuspension, there is a potential risk to release some captured pollutants in rivers. Simultaneously, there is a chance to adsorb contaminants from the water column into the sediment matrix. In this chapter, the different points of view about resuspension of contaminated sediments and also the effective factors on adsorption and desorption of heavy metals in sediments were considered. Additionally, different *in situ* and *ex situ* techniques for remediation of the contaminated sediments were reviewed. Subsequently, the resuspension method was introduced as a viable option, where the common strategies for managing the contaminated sediment are not feasible.

2.1 Antifouling paint particles, one of the main sources of heavy metal contamination in harbour areas

The main focus of this research is on contaminated sediments in harbour areas. Understanding the nature and sources of pollutants is a key component to resolve the issues. Depending on the location of the harbours, sediments are exposed to different sources of contaminations. One the most important sources for leaching the heavy metals into the sediment is antifouling paints (Turner, 2010).

Aquatic biofouling consists of the community of organisms, which grow on the external surfaces of submerged or semi-submerged objects such as port and harbour's structures and hulls of boats (Lewis, 1998; Dafforn et al., 2011). Biofouling causes higher fuel consumption by increasing the drag on the boats and also may compromise safety of static structures by reducing stability and covering structural defects (Turner, 2010). Therefore, antifouling paints are applied by coating the vessel hulls, pontoons, piers, aquaculture nets, buoys, pipeline and drilling plat forms in order to inhibit the attachment of marine organisms (Voulvouilis et al., 2002; Konstantinou and Albanis, 2004; Chambers et al., 2006; Almeida et al., 2007).

The main components of antifouling paints (AP) are biocides and heavy metals (i.e. Cu, Zn, Pb and Cd). However, their concentrations in AP formulations may vary considerably (Sandberg et al., 2007). Widespread applications of AP have led to high levels of pollution in the ecosystem. As an example, during the maintenance of the boats or from abandoned structures and grounded ships, antifouling paint particles (APP) are generated and introduced to the aquatic environment by runoff. Depending on the methods of paint removal (e.g. scraping, sanding, striping, etc.) different sizes of APP are generated with a range of a few microns in diameter to several centimeters in length (Turner, 2010). Despite the practice code, defined in many countries including Canada, large quantities of APP can be found in boat yards and maintenance areas (Figure 2.1**Error! Reference source not found.** and Figure 2.2**Error! Reference source not found.**) during the cleaning seasons (Links et al., 2007; Kotrikla, 2009). Plumes of the particles are generated during the cleaning the boat's hulls, even with a vacuum sander. Consequently, APPs washdown and runoff into the aquatic environment or as airborne dust (Thomas et al., 2003; Tolhurst et al., 2007).

Figure 2.1 Discarded paint fragments remain in a boat repair facility on the island of Gozo (Turner, 2010).

Figure 2.2 Paint fragments in the vicinity of sand flats shed on the Gannel estuary, southwest England (Turner, 2010).

Studies from a variety of recreational boat maintenance facilities within the EU showed that the contemporary composites of APP contain 35% and 15% of dry weight Cu and Zn concentration respectively (Turner et al., 2008; Singh and Turner, 2009). Low concentrations of other trace metals such as Cd, Cr, Ni, Pb and Sn were detected. The crucial part of the research was that the heavy metals leach more rapidly from APP than a painted surface of the static structures or hulls of the boats since APP have a greater surface area of pigments (e.g. $PbCrO_4$, CdS) and additives exposed to the environment (Turner, 2010).

Although the APPs are one of the main sources of inorganic and non-degradable contaminants in harbours, the literature suggests that there have been other sources responsible for contamination. Sewage, wastewater and petroleum released from motorboats are the other sources of organic and inorganic pollutants. Additionally, deposition of suspended loads of large rivers in the vicinity of the large cities and industrial regions, which mainly contain fine particles with high concentrations of contaminants, is another contamination source in those areas.

2.2 Remediation of contaminated sediment

This research focused on heavy metals among the various contaminants due to their mobility, environmental persistence and ecological risks. Therefore, the methods, which have been reviewed in this section, concern heavy metal removal and stabilization.

Remediation of contaminated sediment can be classified based on two strategies. The first strategy concerns the immobilization of metals on sediment particles and chiefly functions by enhancing metal sorption precipitation and complexation capacity on sediment. Methods with this concept are called '*in situ*' remediation (Susana et al., 2005).

The main concept of the second strategy is to extract the heavy metals rather than immobilization. Therefore, the polluted sediment first must be removed from the river bed or lake bed and then through a series of chemical, physical and/or biological procedures heavy metals will be extracted. Obviously this kind of remediation technique is mostly carried out 'ex situ' (Alfredo et al., 2005, Rafael et al., 2006).

2.2.1 *In situ* remediation technologies

Over the past decades, *in situ* methods have been rapidly developed since they are low-cost and usually non-disruptive to the environment. It should be noted that, although *in situ* technologies reduce the mobility of heavy metals in sediments, the total concentration of metals does not decrease. Moreover, there is a possibility of releasing some parts of those immobilized metals into the environment after a while. The following techniques are the most common and feasible *in situ* remediation technologies for contaminated sediment:

2.2.1.1 Amendments

This is a common method used in soil remediation as well. In this method, some inexpensive amendments such as minerals (e.g. apatite, zeolite, etc.) are used to reduce mobility and bioavailability of heavy metals in sediment. These materials contain high cation exchange capacity, which can lead to adsorption or precipitation of some metals and thereby decreasing their solubility. Compared to the same technology used in soil, for sediment remediation the amendments usually have a higher sorption capacity and lower water solubility (Raicevic et al., 2006).

2.2.1.2 Capping

In situ capping is usually applied to immobilize and reduce the release of contaminants from sediments. In this technique a clean suitable isolating material covers the contaminated sediment in order to decrease the direct contact area between water and sediment. Those materials can be soil, sand or a geosynthetic substance. In the case of sediment with limitations for open water disposal, the most economic approach is sand capping. It is worth mentioning that the effect of capping decreases with time and in a few years the chance of heavy metal release is significant (Mulligan et al., 2010).

2.2.1.3 In situ sorbent amendments

This is a modern capping method by supplementation with active amendments such as activated carbon (AC). Practically, it has the advantages of an *in situ* technique (i.e. simplicity and cost-effectiveness), with more strength to adsorb and immobilize the contamination. In other words, this new capping technique increases contaminant binding and consequently reduces their exposure risk to the aquatic environment. Ghosh et al. (2011) conducted a series of laboratory tests, which demonstrates that the effectiveness of the sorbent amendment on decreasing the level of bioavailability of contaminants increases with decreasing AC particle size, increasing doses of AC and greater mixing and contact time.

The typical dosing of AC was about 2 - 5% by weight of dry sediment in top of 10 - 30 cm of sediment. As a result, 70 - 90% reduction of biouptake of hydrophobic organic compounds (HOCs) was recorded. This technique is more attractive where dredging is not feasible such as under piers or around piling and in areas with very ecologically sensitive situations (Ghosh et al., 2011). Despite the advantages of this method, it cannot decrease the total sediment concentration of pollutants as it is mentioned earlier. Additionally, the risk of leaching the contaminants from the clean sediment layer will increase over time.

2.2.1.4 Phytoremediation

Phytoremediation is the most ecologically responsible alternative for remediation of contaminated sediment. This method usually takes advantage of plants to extract or detoxify pollutants (Meagher, 2000). Although this technology is mostly applied in soil remediation, removal of heavy metals by phytoremediation in some shallow rivers and wetlands is significant. Beside the direct effect by plants themselves, there are some indirect reactions happening during phytoremediation. Metal uptake by hydrophytes, stimulation of microbial activity and redox reaction/formation of insoluble metal compounds in the rhizosphere are some particular phenomena, taking place in phytoremediation (Clemente et al., 2005).

2.2.1.5 In situ slurry vortex in a reactor vessel

There is also a theoretical method for managing of contaminated sediments, submitted as a patent in United States (Zaiger, 2003). This is an *in situ* technique introduced for generating a slurry vortex inside a reactor in an underwater environment such as the ocean floor, which was specifically designed for a hot spot (limited area with severe contamination).

In this method the reactor vessel is set at the hot spot and by removing seawater a negative pressure is created, which enables the reactor to penetrate into the ocean floor. Then a pressurized fluid is injected into the reactor vessel, which creates a slurry vortex of the contaminated sediment material. At the final stage, a remediation fluid (corresponding to those particular contaminants) is injected and mixed with the slurry materials. A sufficient amount of remediation fluid (depending on the type and magnitude of contaminant) needs to be delivered in the reactor to provide non-contaminated sediment materials. Eventually by injecting the pressurized seawater into the interior of the reactor vessel, a positive pressure is generated and helps to lift and transfer the reactor to another location (Zaiger, 2003). The whole remediation procedure is actually done at the site but the materials (i.e. treated sediments and the chemical substances) will remain at the site. No scientific results have been recorded under the name of this method. Also, no environmental impact assessment was performed after applying this technique.

2.2.2 *Ex-situ* remediation technologies

For the highly polluted sediments, which are distributed to a large extent, *ex situ* remediation becomes the first choice (Mulligan et al., 2001). Most of the techniques for *ex situ* sediment remediation are similar to soil remediation techniques. Since sediments have a close contact with water and aquatic ecosystem, guidelines and regulations impose more strict limitations for the minimum amounts of the concentration of contamination in sediment. Moreover, dewatering and handling the high organic content materials usually increase the cost of the remediation. The most applicable *ex situ* methods are introduced as follows.

2.2.2.1 Washing

The washing technique is a relatively simple *ex situ* method. After dredging the contaminated sediment, through adding washing water, some fractions of heavy metals are transferred from the dredged sediment to the wash solution. Usually for increasing the heavy metal removal some additive substances are employed. Acid washing (e.g. H_2SO_4 and HNO_3), chelating agents (e.g. ethylenediaminetetraacetic acid (EDTA)) and surfactants (e.g. rhamnolipid) are some examples of additive agents. Acid washing is applied to solubilize and mobilize the heavy metals to the washing solutions. Chelating agents mostly can assist in removing the heavy metals by combining with aqueous metals to form chelate complexes and consequently reduce the concentration of heavy metals in water. However, surfactants desorb the contaminants from dredged sediment and remove them from the environment. The target of this technique is the weaker metal bonds that mostly exist in the exchangeable, hydroxide and reducible oxide fractions. For fine grain sediments that have a stronger bond to heavy metals, decontamination through washing is not an ideal method (Ortega et al., 2008).

2.2.2.2 Electrokinetic remediation

This method uses a low DC current or low potential gradient to electrodes, which are inserted into the sediment and encompass the contaminated zone. The DC electric field causes migration of charged ions. Positive ions are attracted to the negatively charged cathode and negative ions move to the positively charged anode (Virkutyte et al., 2002). This technology is more suitable for fine-graded sediment since the fine particles carry the highest electric conductivity and hence contain the most adsorbed metals.

2.2.2.3 Flotation

Flotation is a hetero-phase separation method that uses gaseous bubbles to disperse fine particles. Various metal ions are adsorbed onto the fine inorganic and then the formed aggregates are floated and eventually separated from the dispersing medium (Dobias et al., 1995). This technique can also be applied as an *in situ* method particularly for anaerobic fine-texture sediment (20-50 μm) with a significant percentage of metal sulfides. In some cases up to 80% of removal efficiency was reported for most metals in sediment. However, like most of the techniques, flotation can be either advantageous or disadvantageous depending on the oxidation degree of sulfur (Kyllonen et al., 2004). Low oxidation and high oxidation intensity can lead to lower particle resuspension and excessive sulfide to sulfate, respectively. Both would decrease the removal efficiency.

2.2.2.4 Ultrasonic-assisted extraction

High-energy acoustic cavitation is normally applied in the ultrasound system in order to encourage formation, growth and implosive collapse of bubbles in liquids. The cavitational collapse generates the intense heating in hotspots with 5000 ºC, 500-atmosphere pressure and lifetime of a few microseconds. As a result, most of the metals are melted and sunk in an area of low pressure caused by cavities. Removal efficiency of this method for heavy metals completely depends on the particle size of sediments. For coarse grains, almost all metals can be separated from sediment (around 92%). However, for fine particles (i.e. < 2µm) no significant removal can be found (Meegoda et al., 2001) and the reason is that metals associated with clay are too stable to be removed in most remediation techniques (Peng et al., 2009).

2.2.2.5 Solidification / Stabilization

The purpose of the solidification / stabilization process is to reduce the mobility and stabilize the heavy metal contaminants by adding an agent (e.g. cement or pozzolan). The amendment used in *in situ* remediation can also be applied to immobilize the metals in dredged sediment. Although this technique just minimizes the mobility of heavy metals and cannot remove them from the sediment, due to their low-cost and fast effect it is still applied frequently (Peng et al., 2009).

2.2.2.6 Vitrification

Vitrification is another form of immobilization but instead of employing amendments, contaminated sediment is melted in a glassy matrix. Heavy metal pollutants are immobilized in a glassy matrix and the chance of leaching is almost zero. Basically inserting the electrodes into the dredged sediment and providing the electric energy can produce a temperature of about 1200 ºC. Under this circumstance, all organic compounds are volatilized and the rest of sediment is melted. During vitrification, toxic gases can be generated, which must be treated by activated carbon to not release them to the atmosphere (Mulligan et al., 2001).

Adoption of different remediation techniques depends on some special characteristics of the sediment and the site. Metal loads, sediment size distribution and metal species are some important features of sediment that should take into consideration. On the other hand, the type and source of pollutants as well as depth and biodiversity in sediment influence the decision regarding the most appropriate remediation strategy.

2.3 Metal partitioning in sediments

At present, it is widely recognized that the total concentration of heavy metals in sediment does not show complete information and history of the adsorbed metals. In general, metal ions in sediment are partitioning between different phases. To clarify the details of the adsorbed metals, the sequential extraction test is recommended. The results of the sequential extraction cover some information about toxicity and bioavailability of heavy metals to aquatic biota, risk assessment and anthropogenic sources of the metal species in sediments (Filgueiras et al., 2002). Therefore, it is quite instructive to know the concentration of metals in each fraction. There are different methods for sequential extraction, but most of them contain four to six steps mainly established by Tessier et al. (1979).

2.3.1 Water soluble fraction

Heavy metals extracted by H_2O may be the most potentially bioavailable metals in the aquatic environment. Free ions and ions complexed with soluble organic matter are the most significant part of this phase. The water-soluble fraction is obtained by two ways; 1) sampling of sediment pore solution by *in situ* filtration or 2) by laboratory procedure (*ex situ*) such as centrifugation, filtration or displacement. In a nutshell, this fraction constitutes the most mobile and potentially the most available metal and metalloid species (Filgueiras et al., 2002).

2.3.2 Exchangeable fraction

Weakly adsorbed metals, retained on the solid surface that can be released by ion-exchange processes will be categorized as an exchangeable fraction. The metals corresponding to this fraction are usually extracted with magnesium chloride solution or sodium acetate solution (1M) at pH 8.2 for 1 hour. They normally can be replaced by neutral salts (Mall et al., 1996; Rauret, 1998).

Extraction efficiency in this fraction is dependent on the cation properties. Based on the literature, efficiency increasing in the order of: $H^+ < Ca^+ < Mg^+ < Na^+ < NH_4^+$, and this is a reason for widely employing $MgCl_2$ and NH_4OAc (ammonium acetate-$C_2H_7NO_2$) at 1 $mol.dm^{-3}$

concentration as a reagent for leaching (Narwal et al., 1999). Normally this fraction and the water-soluble fraction are used to represent the environmentally available components.

2.3.3 Acid soluble fraction

This phase contains the metals that are precipitated or co-precipitated with carbonate (Clevenger, 1990). Generally the carbonate form is a weakly bound phase and sensitive to environmental condition. Thus, this phase is susceptible to a change in pH (Zorpas et al., 2000). That is the main reason the carbonate fraction is targeted by a mild acid. Adsorbed metals in this phase are extracted with sodium acetate (NaOAc) or acetic acid solution (1M) at pH 5.0 for 5 hours. It should be noted that under the more acidic condition, the solubilization of Fe-Mn oxides could take place (Van Valin et al., 1982). However, with the same pH and same duration, 99.9% of metal content associated with carbonate in sediment can be extracted (Tessier et al., 1979).

2.3.4 Reducible fraction

Metals adsorbed by hydrous oxides of manganese and iron are the main target in this fraction. Adsorbed metals in this phase can be extracted by 25% (v/v) acetic acid containing $NH_2OH.HCl$ at 96 ^{o}C for 6 hours. Usually Mn-Fe oxides exist in a large proportion in soil and sediments. However, they are thermodynamically unstable under anoxic conditions (Tokalioglu et al., 2000). Reduction of Fe (III) and Mn (IV) under anoxic circumstances can release some adsorbed heavy metals (Marin et al., 1997).

The most popular reagent used for leaching the reducible fraction is hydroxylamine hydrochloride in a nitric acid medium. The important part in extracting this fraction is to control the pH. If the pH of extraction solution falls below 1.5, the reagent might release some metals associated with the silicate fraction (Tessier et al., 1979).

2.3.5 Oxidizable fraction

The oxidizable fraction is associated with various forms of organic material through complexation or the bioaccumulation process. Organic materials can be found as a form of living organisms, detritus or coating on mineral particles (Tokalioglu et al., 2000).

Experiments show that the organic substances demonstrate a high level of selectivity for divalent ions. The binding strength for metal ions onto organic matter is following this order: Hg

> Cu > Pb > Zn > Ni > Co (Jonasson, 1977). This fraction, particularly in contaminated sediment and sewage sludge, plays a key role in heavy metal distribution (Ridgway et al., 1987). However, heavy metals bound to organic matter can be easily released under oxidizing conditions. The most common oxidants are hydrogen peroxide in acid medium. Precisely, with 0.02 M nitric acid and 30% hydrogen peroxide at pH 2.0 and 85 °C most of the metals will be extracted from this fraction (Tessier, 1979). Metals extracted from this phase exist in sediment for longer periods compared to the previous fractions. Metals in this fraction can be released through decomposition of organic matter (Peng et al., 2009).

2.3.6 Residual fraction

The residual fraction represents the metals still remaining in the sediment after the above extraction steps. They have a relatively strong and stable bond and do not show significant transformation under different conditions. Acid digestion is the method used to extract remaining metals in this fraction.

To conclude, water-soluble and exchangeable fractions can be used to assess the risk of bioavailability of heavy metals in aquatic ecosystem. Metals exist in the acid-soluble and reducible fractions are representative of the potentially mobile components under changing conditions. These two fractions are the most important ones in contaminated sediment remediation. The last one is the residual fraction that is related to metals with stable forms. They usually have less influence on the ecosystem due to their unavailability.

2.4 Factors affecting the release and mobility of heavy metals in sediment

Availability of heavy metals in the water column depends on complex interactions between aqueous (i.e. pore water, overlying water) and solid phases (i.e. sediment, suspended particulate matter). The distribution and partitioning behavior of pollutants are regulated by some general factors such as hydrodynamics, biogeochemical processes and environmental conditions (Samiullah, 1990; Cantwell et al., 2002; Eggleton et al., 2004). The following parameters were recognized as influential factors on adsorbing and desorbing the contaminants (i.e. heavy metals) from sediments.

2.4.1 pH

The pH probably is the most important parameter to control the mobility of heavy metals in sediment. As it is understood, with a pH decrease in the environment the quantity of H^+ increases and consequently causes the competition between H^+ and dissolved metals for ligands. As a result, mobility and availability of heavy metals becomes more and more significant. Gundersen et al. (2003) reported that with a few lower pH units, desorption of heavy metals from sediment particles may range from almost 100% to negligible amounts.

Generally in the sediment, because of the organic matter (OM) degradation and acid volatile sulfide (AVS) oxidation, pH usually decreases and results in some metals being released into the water column even under a stable condition (Kraus et al., 2006; Bonnissel-Gissinger et al., 1998).

For different heavy metals, there exists a different limit of pH to control the mobility. In other words, under similar pH conditions the potential of desorption and mobility of heavy metal is considerably different. Peng et al. (2009) provided the approximate ranges of pH for heavy metals. Below these limits, leachability of the metals from sediments can increase significantly (Table 2.1).

Table 2.1 Limit of the pH for different metal desorption (Peng et al., 2009)

Metals	pH limit range
Zn	6.0 - 6.5
Cd	6.0
Ni	5.0 – 6.0
As	5.5 – 6.0
Cu	4.5
Pb	4.0
Al	2.5
Fe	2.5

2.4.2 Oxidation-reduction potential

Element cycling in the environment is directly affected by reduction and oxidation. ORP controls bioavailability, toxicity and mobility of many major elements and heavy metals (Borch et al., 2009). ORP is also directly related to dissolved oxygen in the water column. In anaerobic sediment, when acid volatile sulfide (AVS) plays a key role in controlling some divalent cation metals, aeration causes the increase of the oxidation rate of metal sulfides and degradation rate of organic compounds. Therefore, the amount of ORP increases and eventually it can affect the pH. The result is that a secondary release of heavy metals happens. However, some part of released metals will be re-adsorbed by sediment fractions. Zoumis et al. (2001) and Kelderman et al. (2007) reported that with increasing ORP in sediment, Cd bound to organic sulfide (i.e. stable form) would decrease from 65% to 30% and form a more mobile form. In another case in the Mulde reservoir (Saxony, Germany), because of the disturbance and oxidation of sediment during a flood, a significant amount of Zn was released in to the water (Zoumis et al., 2001).

2.4.3 Organic matter (OM)

In natural rivers and lakes, organic compounds in sediment can be found significantly in particle form. The bodies of the aquatic plants, which are decomposed by the microorganisms, are the sources of the OM. They have a major role in heavy metal transformation. In some cases, OM becomes the largest fraction in the sediment in terms of adsorbing the metals. Mobility of metals in this fraction is directly determined by solubility of OM. Complexation of metal ions with insoluble organic compounds can drastically lower their mobility. In contrast, dissolved organic compounds can adsorb soluble metal complexes and consequently enhance their mobility (Amina et al., 1999).

2.4.4 Other factors

Beside the factors mentioned, some other parameters can also influence the release and mobility of heavy metals. Salinity, temperature, metal species and retention time are implied in the literature.

Garnier et al. (2006) showed that increasing the salinity in pore water decreases the total adsorption content of heavy metals, because of the competition among metals and other cations.

They also reported that the temperature is a factor affecting the release of heavy metals. With a temperature increase, the adsorption on sediment often decreases gradually.

Time is another parameter affecting the mobility of metals. Long-term experiments in kinetic adsorption-desorption showed that the metal freshly adsorbed by sediment usually are less stable and more available than those associated for a long time (Peng et al., 2009). Liang et al. (2014) conducted a series of experiments by coupling the diffusive gradients in thin-films (DGT) technique with two sequential extraction methods in order to investigate the influence of aging on As and Pb fractionation and availability in soils. Their results clearly indicated that during aging, As and Pb moved from available fractions to more stable fractions. Particularly for Pb, it moved from carbonate and Fe-Mn hydroxide to the organic fraction.

Grain size distribution, microbial activity and amount of acid volatile sulfide (AVS) and total organic carbon (TOC) existing in sediment are the other parameters, which can be counted as the effective factors. As an example, daily study on seasonal variations of trace metals in the Deûle River (northern France) suggested that acid-leachable concentration of Cd, which is environmentally available under changing pH, is mainly bound to light particles such as clay and carbonates (Superville et al., 2015).

2.5 Sediment quality criteria in Quebec-Canada

The quality criteria of sediment in Quebec-Canada is described in a document presented by Environment Canada and the Quebec Ministère du Développement durable, du l'Environnment et des Parcs (2007). To protect the aquatic life, two reference values have been suggested for about 30 substances (included heavy metals) in freshwater and marine sediment. In this research, the main concern is the quality of sediment in fresh water such as rivers and lakes and is mainly focused on St. Lawrence River as a source of sampling.

The Threshold Effect Level (TEL) and Probable Effect Level (PEL) are two values, which have been adopted as a basic level for assessment of sediment quality in Quebec. In addition, another three levels were presented for those sediments need for management and remediation. These three levels are: the Rare Effect Level (REL), the Occasional Effect Level (OEL) and the Frequent Effect Level (FEL). For substances below the TEL, the incidence of biological adverse effects is less than 10%. Therefore, there is no need to monitor and manage the sediment. In the range of heavy metal concentrations above the PEL, biological effects are frequently observed and particularly for fresh water, the incidence of adverse effects varies considerably among chemicals and is usually lower than 50%.

The concentration of pollutant in the range of OEL and above is considered as the sediment that needs to be managed and treated before dredging process. In this category adverse effects are anticipated in many benthic species. In the FEL range, adverse effects are anticipated for the majority of species. Therefore, open-water disposal of dredged sediment is prohibited. Precisely, OEL and TEL are the two values governing the management of dredging sediment from rivers and lakes. According to this guideline, three groups are defined to classify the contaminated sediments.

Group one: the concentration of heavy metals in this group should be below the OEL. There is little probability of adverse biological effects in this category but open-water disposal is allowed.

Group two: for substances about and above OEL and below the FEL there is a probability of detecting adverse effects. Open-water disposal is conditionally permitted if the toxicity test indicates that the heavy metals in sediment are not bioavailable and will not adversely affect the environment.

Group three: if the concentration of heavy metals in sediment is at or above the FEL, the sediment is categorized as highly contaminated sediment. Clearly, disturbance of the highly contaminated sediment increases the risk of mobility and bioavailability of heavy metal in aquatic environment. Table 2.2 presents the concentration of some trace metals at different levels based on Environment Canada and Quebec regulations.

Table 2.2 Concentration of heavy metals (mg/kg) at different levels (Environment Canada, 2007).

Levels	Cr	Ni	Cu	Zn	As	Cd	Pb
TEL	37	-	36	120	5.9	0.6	35
OEL	57	47	63	170	7.6	1.7	52
PEL	90	-	200	310	170	3.5	91
FEL	120	-	700	770	230	120	150

It should be mentioned that different standard levels of Ni were not reported in Canadian guidelines. However because of the importance of this element in the sediment and its effects in the aquatic environment, the geometric mean of the natural concentration of Ni in pre-industrial sediment (29 mg/kg) and the natural concentration in postglacial clay (75 mg/kg) in St. Lawrence River were chosen as the OEL in Table 2.2 (Environment Canada 2007).

2.6 Metal release under the resuspension process

Resuspension is introduced mainly as an occurrence with adverse effects on aquatic ecosystem in the literature. Different aspects of resuspension at contaminated sites were reported, which mostly are about the risk of releasing the heavy metals in aquatic environment (Cantwell et al., 2002, 2004 and 2008; Simpson et al., 1998, Atkinson et al., 2007). They evaluated the partitioning behaviour of metals bound to sediment (mainly anoxic) during resuspension under equilibrium and non-equilibrium conditions.

Salinity, pH and redox potential have been indicated as the effective factors in metal desorption (Kiratli et al., 1996). However, physical and chemical properties of resuspended sediments were described as the primary variables, which regulate the mobility of metals in dissolved phase (Cantwell et al., 2002). Cantwell et al. (2002) designed an instrument to simulate the particle entrainment (Figure 2.3). Their results presented the key role of resuspension energy and duration on the release and re-distribution of sediment bound metals. It is worth mentioning that, they used 0.2 to 0.5 Pa to resuspend the sediments with duration of 1 to 12 hours. Details of the particle entrainment simulator are available in Figure 2.3.

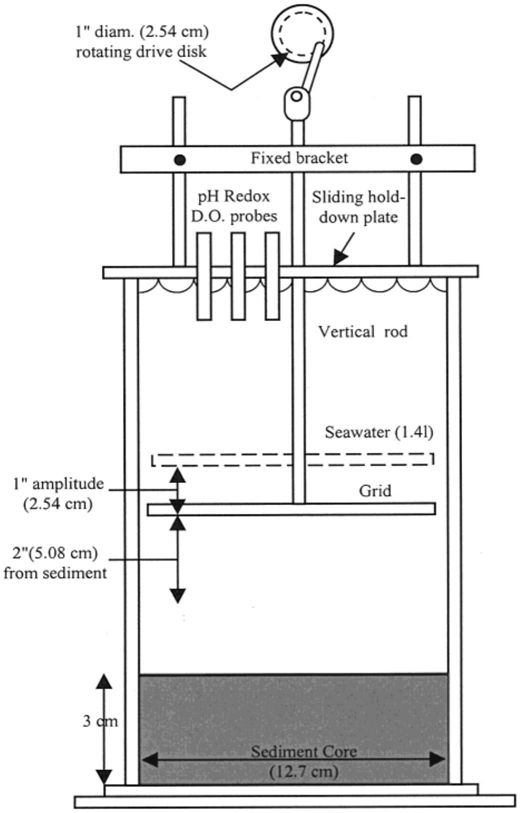

Figure 2.3 Diagram of particle entrainment simulator (PES) after Cantwell et al. (2002)

Solubility of metals in anoxic sediment during aeration was another subject that was considered (Caille et al., 2003). In estuaries and seas most of the contaminated sediments are anoxic with a high level of sulfides (Simpson et al., 2000). Therefore, aeration at some locations will be performed to enhance the quality of water and sediments. Caille et al. (2003) reported that during the early steps of aeration, the solubility of Al, Cu, Fe, Hg, Pb and Zn increased rapidly but over time this was followed by fast re-adsorption. The results also indicated that Cu and Zn were the only metals leached into the dissolved phase.

Short-term resuspension was investigated by Simpson et al. (1998). They did some research on trace metal speciation in anoxic contaminated sediment. Their results showed that FeS and MnS were particularly unstable and will be oxidized quickly in aerated water. Therefore, aeration in highly anoxic sediment with significant amounts of sulfide led to the release most of the adsorbed iron and manganese in the aqueous phase. However, CdS, CuS, PbS and ZnS were kinetically stable over a short-term resuspension. They used an 8 h resuspension to monitor the distribution of metals associated with sulfide fraction, since it has strong implication in assessing of sediment quality. Rapid decrease in AVS was also reported upon sediment resuspension.

Cantwell et al. (2008) resuspended different types of sediment for 6 hours by PES (Figure 2.1). Their results presented the role of particle grain size and total organic carbon (TOC) and AVS to regulate the release of heavy metals. However, they implied that AVS had the greatest effect.

Zheng et al. (2013) achieved different results. They simulated resuspension of contaminated sediments in Taiha Lake (China) by using a pneumatic annular flume. Six different wind forces were employed to simulate resuspension. Increasing the wind speed and also the duration of the experiment increased the total concentration of metals in overlying water. Furthermore, a remarkable increase in metal concentration was observed in SPM by increasing the wind speed and duration.

2.7 Contaminated harbours in Canada

Canada, the world's second-largest country has over 300 commercial ports and thousands of harbours for small and leisure boats. Transportation sector made up 4.2% of Canada's gross domestic product (GDP), in which 3% of this sector belongs to water transportation (Dunlavy et al., 2005). Keeping the harbours and ports clean and efficient with proper management strategy is the key element in sustainable development in Canada. Sediment remediation projects in Hamilton harbour and decontamination in the port of Montreal – Sector 103 – are the successful examples in Canada.

Hamilton Harbour lies at the western end of Lake Ontario with area of 2,150 ha. This area was exposed to many sources of pollution. Long history of industrial activities caused elevation in metals and organic compounds levels in bottom sediments. It took 13 years (1996 - 2009) to complete a comprehensive study on remediation options in the harbour and to determine the most contaminated area located along the south shore of Hamilton harbour. Dredging of sediment in some contaminated area with metals and PAHs as well as capping the other highly contaminated locations were proposed along with long-term monitoring at the site. In total, approximately 500,000 m^3 of contaminated sediment were dredged and 130,000 m^3 were cover through the *in situ* capping. The estimated cost for sediment remediation project in selected area (Figure 2.4) was about $139-million (Randle Reef Sediment Remediation Project, 2012).

Figure 2.4 Selected area of Hamilton harbour for restoration-Randle Reef (http://www.randlereef.ca).

Montreal harbour decontamination, however, was launched in 1988 as a part of St. Lawrence Action Plan (SLAP). This harbour also had suffered from decades (1920 – 1970) of toxic effluent discharge into the river (upstream of the site) by the 50 most polluting industrial plants. Sediment characterization was started in June 1989. Sector 103 (one of the most contaminated locations along the St. Lawrence bank) was contaminated with heavy metals (mainly Cd, Pb, Cu and Zn) and PAHs and PCBs. Petrochemical industries, metal refineries, and discharge of sewage from collector in Ville d'Anjou and Montreal East were the main sources of pollutants. Reduction of the contamination sources was the first action. It took almost 15 years to get all the stakeholders together for conducting the essential studies and developing the best action strategy. Eventually, the fieldwork containing the total volume of 50,000 m^3 for dredging and remediation of contaminated sediment took place a few months in 2007 with the total cost of approximately $10 million (Environment Canada, 1993; Environment Canada, 2013).

Figure 2.5 Dredging operation by using specialized machinery -Sector 103- Montreal port (Photo: Jacques-Cartier, Environment Canada website)

2.8 Environmental impacts of a dredging operation

Dredging of sediment is an unavoidable operation for expansion purpose or facilitating the passage of large vessels in canals, ports or rivers and it has also increased in demand in the past few decades (Thacker, 2007; Schexnayder, 2010). In general, dredging lead to increase oxygen demand and turbidity levels while it makes a strong resuspension of sediment. Monitoring the studies implies that dredging, scooping and dumping acts could cause a decrease of invertebrate species and have an adverse effect on aquatic ecosystem (Crowe et al., 2010; de Leeuw, 2010; Manap and Voulvoulis, 2015). Dredging operations are comprised of three subsequent steps: excavation, transport, and disposal of dredged materials.

Excavation of sediments at the site is widely performed by a hydraulic and/or mechanical dredge (Du and Li, 2010; Klein, 1998). Precisely, for extracting the sediment from riverbeds and lakes, pit excavator and bar skimmer are commonly used (Padmalal, 2008). Excavation may cause changes in the riverbeds, generation of dredging plumes and more importantly exposure of benthos and fishes to contamination in the case of dredging of contaminated sediment (Manap and Voulvoulis, 2015).

Transport of dredged materials to the intended disposal site is the next step of the operation. Depending on the volume of dredged sediment, hopper barges, conveyor belts or bucket can be employed. Pipelines using suction pipes, however, for expansion or dredging in huge projects are normally used (Duran Neira, 2011). Contamination exposure, changing of the sediment type and distribution, as well as increase in turbidity level are the most noticeable environmental impacts of transporting the dredged materials (Manap and Voulvoulis, 2015). Clearly, using the appropriate controls (e.g. silt curtains or booms) would minimize the adverse impacts of dredging to the resident biota. However, there may still be some impacts to biota close to the controlled area (Su, 2002). As an example, Otto et al. (1996) examined the level of PCB uptake in caged rainbow trout during dredging of the St. Lawrence River at Massena, New York, USA. The fish were located close but outside of the silt curtain. The results showed that the total PCB body burden in fish was increased after 42 days of dredging.

Disposal is the last step of the dredging of sediment operation and it can be done through several methods. Agitation dumping, side casting, dumping in rehandling basin or direct dumping ashore can be named as the common disposal technique. However, open water disposal is known as the most popular and economical method for sediment disposal (Katsiri et al., 2009). As it is mentioned earlier, toxicity tests must be performed in this case to show that there is no potential risk in dredged sediment posed to the intended disposal site. Previous research suggested that environmental impacts of dredging are highly dependent on the intensity of contamination in sediments and technologies used for dredging them at the site (Manap and voulvoulis, 2015). Another concern about open water disposal is generating plumes and diffusion of contamination. Although silt curtains or booms are mainly used to prevent contamination dispersion, there is still a serious concern due to the risk of pollution leakages through the media (Morton, 2001; Su, 2002). Therefore, applying a proper management strategy for reducing the contamination level in sediment prior dredging can provide a favorable environment for benthic organisms and lead to safer and more cost-effective dredging. If the toxicity tests show that disposal is not a safe method for handling the dredged materials, an appropriate treatment on the dredged sediment should be performed (refer to section 2.2.2). In that case, dewatering normally is the first step.

2.9 Resuspension as a remediation of contaminated sediment

Japanese scientists were the first to employ resuspension as a remediation technique for contaminated sediments. Fukue et al. (2012) applied resuspension in Fukuyama city port in order to decrease the rate of eutrophication and improve the water-sediment quality. They designed a pilot test for cleanup of the Fukuyama canal port sediments. Their technique consisted of three stages.

In the first stage, water-air jets resuspended the sediment in a water column surrounded by a silt protector. Because of the jet forces, finer and lighter particles moved from bottom to top, while coarser and heavier sediments remained near the bottom (Figure 2.6). They used pumps, in the second stage, to remove some fractions of the suspended solids near the top. In the third stage, the separation of water and solids was performed by condensation, sedimentation and filtration. Details are presented in Figure 2.6 such as adding a reagent (i.e. inorganic proprietary agglomerate, before bag filtration), filtering and dewatering procedures.

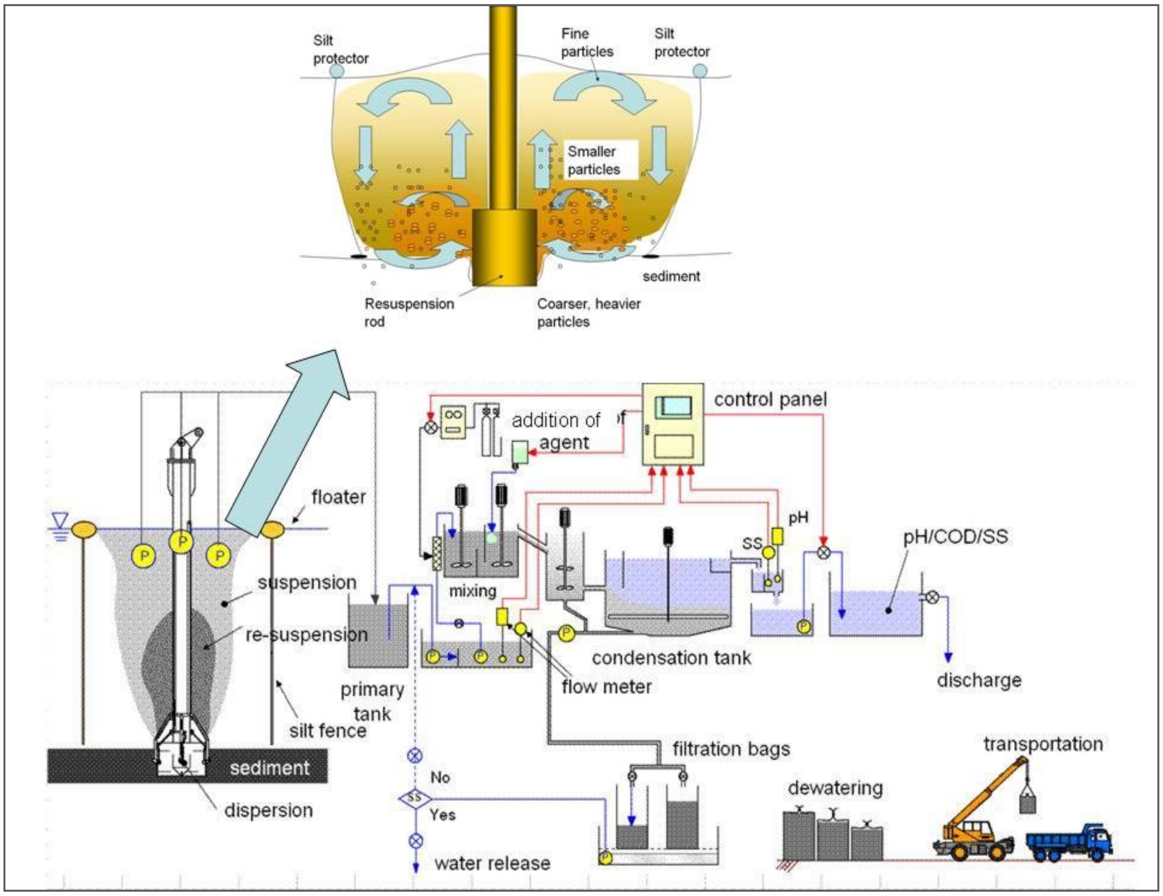

Figure 2.6 Resuspension procedure performed by Fukue et al. (2012)

Since smaller particles have a larger specific area, they have a great tendency to adsorb the contamination. Therefore, finer sediments should contain more pollutants than coarser in contaminated sediment. Moreover, organic matter (consisting of a significant amount of nutrients) as a main reason of eutrophication and hydrogen sulfide production can be removed in the resuspension procedure. As it is understood, organic matter is lighter than sediment particles and easily can be resuspended in the water column.

They removed 3% of the sediment at the bottom of the canal instead of the whole sediment in dredging method. Their results indicated that the resuspension was successful in reducing 31%, 14% and 27.6% of the total nitrogen (T-N), total phosphorous (T-P) and chemical oxygen demand (COD), respectively. However, they implied that by removing about 10% of resuspended sediment, reduction of T-N, T-P and COD could be around 100%, 50% and 95% respectively. Furthermore, dissolved oxygen and ORP during the resuspension test significantly increased. Consequently, decomposition of organic matter in the canal would be under more aerobic and hydrogen sulfide production will not occur (Fukue et al., 2012). It should be mentioned that, they used a 0.7 to 3 MPa pressure to resuspend the sediment and deliver the oxygen into the bottom of that canal for 2 weeks. The total area of the site was 3000 m^2 and 50 cm of the bottom layer was resuspended.

2.10 Summary of the literature

Review of the previous studies made clear the different views in the resuspension event. Understanding the factors and conditions affecting the adsorption and desorption of heavy metals can be helpful to improve the existing method and design the new techniques for managing the sediment in contaminated areas. The resuspension technique performed by Fukue et al. (2012) was the only scientific research applying resuspension as a remediation method for contaminated sediment. Despite the valuable research done on the contaminated sediment, there is a need to better understand the complex interaction between water and sediment in the presence of pollutants. Moreover, not all existing technologies for managing the contaminated sediment are suitable for any situation. Developing new techniques with more flexibility for managing contaminated sediment and minimal harm to the surrounding environment is always desirable. The resuspension technique, as a novel method for remediation of contaminated sediment with heavy metals is a viable and effective method in shallow harbours, where the common techniques cannot be applied. Avoiding the use of any chemical substances, the simplicity of the resuspension method for remediation of organic and inorganic contaminants and reduced amounts of contaminated sediment that must be managed are its unique features.

Chapter 3

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

Mehdi Pourabadehei, Catherine N. Mulligan

Department of Building, Civil and Environmental Engineering, Concordia University, 1455 de Maisonneuve Blvd. W., Montreal, Qc, Canada, H3G 1M8

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 heavy 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 heavy metals by applying an appropriate action.

Keywords: Contaminated sediment, Remediation strategy, Heavy metals, Harbour.

3.1 Introduction

Harbours have a vital role in the economy through the transport of the 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 enormously harmful. For many years antifouling paints are applied to the hulls of boats and to many static submerged structures. Since fouling (i.e. a layer of slim, algae or any aquatic microorganisms) may compromise the safety, stability and fuel consumption of boats, antifouling paints are a compulsory part of the boating business (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 runoffs 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). However, recently by ultimately banning triorganotin (e.g., TBT) formulations, Cu (I)-based biocidal pigment in combination with zinc oxide (mainly as a booster) has been used in marine antifouling paints (Tuner, 2010). New formulations of antifouling paints also contain some additives and non-biocidal pigment made by lead antimonates [$Pb(SbO_3)_2$], lead chromates and cadmium yellow (Abel, 2000). Nevertheless, leaching of biocides from APP in marine systems (e.g. harbours) has been previously reported (Turner, 2010).

Contamination is not the only issue that harbours have to tackle with. Construction of breakwaters (either permanent or floating) for protecting boats and dock areas from waves causes changes in the sediment transport, and leads to deposit of significant amounts of sediments annually. In the quasi-stationary water situation around the dock areas suspended sediment in the river gradually settle. The sizes of the settled sediments are fine and because of their specific surface area, they have a great tendency to adsorb the contamination (Mulligan et al., 2009). Subsequently, sediments are a sink for the contaminants that have been entered into the water. Accordingly, shallowness and contaminated sediment with organic and inorganic contaminants become challenges for 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, 2008). 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, 2008). A management strategy is normally 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). Consequently, for numerous cases, the risk of availability of trace metals, for instance, is often overlooked. Walker et al. (2013) showed with some additional information from a sediment leachate test, a more cost-effective disposal management can be achieved by minimizing the contaminated cell disposal method.

Additionally, new developments in managing the contaminated sediment are not always sustainable or suitable for this particular case. For instance, new *in situ* sorbent amendments designed and developed by Ghosh et al. (2011) cannot be applied in shallow areas. *In situ* management could be beneficial over dredging due to a reduction in costs and solid disposal requirements. However, they are not applicable in this case.

E*x 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, 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).

Selecting a suitable management approach for reducing the level of contamination could provide a favourable environment for benthos. 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 insufficient information, provided by SQGs to identify the actual contaminants, could lead to choosing a destructive or potentially ineffective method for risk reduction in contaminated sediment. In other words, 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 Quebec province, 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 is suggested to manage the contaminated sediment for shallow aquatic environments.

3.2 Materials and methods

3.2.1 Site details and relevant information

The study area was a harbour in the province of Quebec, Canada, which is located on the north bank of the St. Lawrence River. This river flows in a north-easterly direction, passing through large cities and industrial regions and eventually drains into the Atlantic Ocean. The site was a harbour for leisure boats with an area of approximately 15,000 m^2 (Figure 3.1-a). Two floating and one solid breakwaters 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 suspended sediment load in the harbour (Figure 3.1-b).

The semi-motionless areas, like this case study, are the perfect destination for over loaded suspended sediments in the rivers to be settled, which make the harbours shallower each year. 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 14 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.

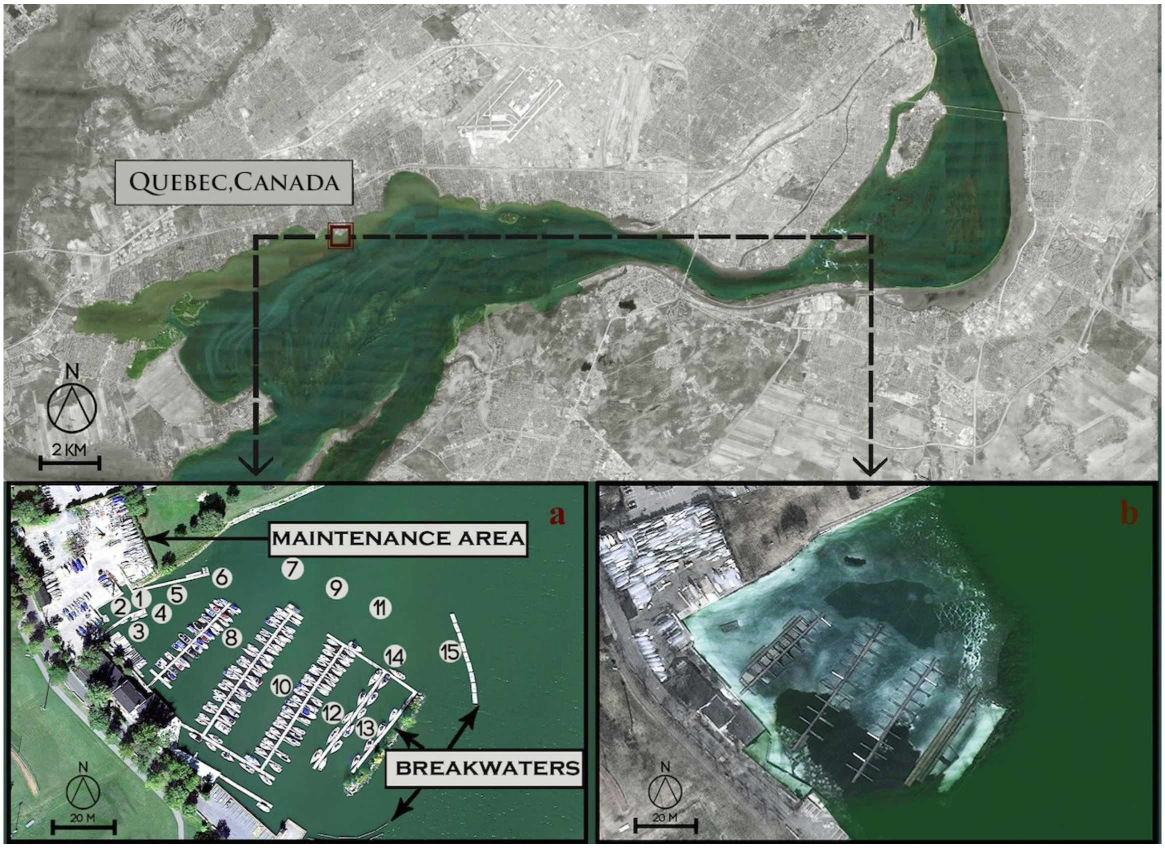

Figure 3.1-a) Study area on the north bank of the St. Lawrence River with 15 selected stations as the potential places for dredging. Two floating and one permanent breakwater protect the harbour from the waves. b) Arial photo of the site in wintertime that presents the most stationary (frozen) water locations (Source: Google Earth).

The water depth varied between 0.6 (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 Figure 3.1-a.

3.2.2 Sampling operation

Two sets of sediment samples were obtained at the selected stations (Figure 3.1-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 were taken with a Birge-Ekman sampler from the surface of the sediments to a maximum depth of 10 cm. Each sample was about 1±0.2 kg. The surface sampler consists of a stainless steel box with a pair of jaws and free-moving hinged flaps (Gouws and Coetzee, 1997). The jaws can trap sediments as soon as they reach the river bottom and keep the sediments in the stainless steel box to prevent washout during retrieval.

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 sediments were trapped in a stainless steel cylinder with a capacity of around 500 ml. 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. They were transferred to the freezer at the Environmental Engineering laboratory at Concordia University and were used for subsequent experiments. It should be noted that sediment samples were mixed and homogenized before analysis.

River water sample collection was carried out with a motorboat in the harbour. The samples were obtained from up to 20 cm depth from river water surface at five different locations (stations 1, 5, 6, 8 and 10) in the harbour and they were stored in the pre-cleaned polypropylene bottles. For dissolved metal analyses, they were 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 were 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 μΩ cm). For quality control, all sediment samples were analyzed using a blank, control and duplicates.

3.2.3 Heavy metal analysis

The concentrations of heavy 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. The EPA 3050B method was the protocol used to digest the solid samples and prepare them for analyses by ICP-MS. For digestion, 1 or 2 g of wet sample or 1 g of the dried sample were digested with repeated additions of nitric acid (HNO_3, 70% - trace metal grade) and hydrogen peroxide (H_2O_2, 30%) as well as hydrochloric acid (HCl, 35% - trace metal grade) at the end of the digestion (USEPA, 1996). The digested samples were kept in the fridge around 4 ^{o}C and were analyzed later.

3.2.4 Analytical parameters

Among the physical characteristics of sediments, information about their texture and the size distribution are most useful. Particle size analysis was performed in this study to determine the sedimentation process history and the texture of the samples. Moreover, understanding the fine particle percentage (i.e. clay and fine silt) in sediment samples would be helpful to estimate the capability of sediment to adsorb the contamination. Analysis of the particle size distribution of sediment samples was done by a laser scattering analyzer (HORIBA, LA-950V2). D_{50} (50% of the particles are less than this size) and the percentage of clay, silt and sand for each sample was determined.

pH, oxidation-reduction potential (ORP) and dissolved oxygen (DO) of the river water were measured by a multiparameter meter (HANNA HI 9828) at the site. For sediment samples, however, quality assessment was performed in laboratory. A ratio of 1:10 (v/v) sediment to the river water was used in each sediment sample to determine the pH. River water (100 ml) was poured in a beaker and then slowly the sediment sample (equal to 10 ml) was added. The slurry was mixed slowly and then the probes were located inside the beaker. Loss on ignition (LOI) was another parameter chosen to estimate the organic carbon and carbonate content in the sediment. According to the ASTM D2974-00 method (American Society for Testing and Material, 2000), oven dried sediment samples (105 ^{o}C) were placed in a furnace at 550 ^{o}C for 4 h. After the sediments were cooled in a desiccator and their weights (w) were measured, loss on ignition (%) in each sample was calculated based on the following equation:

$$LOI\ \% = \left({(W_{105^{o}C} - W_{550^{o}C})}/{W_{105^{o}C}} \right) \times 100\% \qquad [3.1]$$

3.2.5 Sequential extraction test

A sequential extraction test (SET) was employed on the basis of Yong et al. (1993). Heavy metal ions in sediments are partitioned between different fractions. Determining the concentration of metals in each fraction can provide detailed information about their physicochemical availability and mobilization (Filgueiras et al., 2002). The most available metals were found in the water soluble and exchangeable fractions by adding 8 ml of 1 M $MgCl_2$, pH 7, to 2 g dried sediment sample with shaking for 1 hour at room temperature (23 ^oC). Metals associated with carbonate were extracted by adding 8 ml of sodium acetate, pH adjusted to 5 with acetic acid, with 5 h shaking at room temperature. Metals bound to Fe-Mn oxide and hydroxide were removed by adding 20 ml of 0.04 M $NH_2OH.HCl$ in 25% (v/v) acetic acid at 96 ^oC in a water bath for 6 h. To extract metals from organic and sulphide matter, 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 (pH 2) were added at 85 ^oC for 2 h, followed by 3 ml of 30% H_2O_2 (pH 2) at 85 ^oC for 3 h. Finally 5 ml of 3.2 M ammonium acetate in 20% (v/v) HNO_3 was added and then diluted to 20 ml at room temperature 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 solution (50 ml HCl + 200 ml HNO_3 + 750 ml deionized water) for 3 h at 96 ^oC. After each extraction step the suspensions were centrifuged with 1478 x g (Thermo Scientific IEC HN-SII 58012) for 20 min. The supernatant was then filtered through a 0.45μm polytetrafluoroethylene (PTFE) syringe filter, before analysis in ICP-MS to remove any remaining particles. Those samples that contain high amounts of a metal concentration were diluted. It should be noted that the SET is relatively highly operational. All chemical reagents must be carefully prepared and applied in sequence to extract the targeted elements. Limitations and pitfalls of the SET were previously reported (Filgueiras et al., 2002).

3.2.6 Geoaccumulation index

The index of geoaccumulation (I_{geo}) is a criterion to assess the intensity of heavy metal contamination. This index was originally presented by Müller (1979) as follows:

$$I_{geo} = log_2(C_m/(1.5 \times B_m))$$

[3.2]

Where, C_m is the metal concentration detected in sediment samples and B_m is the background value of that metal at the site. A factor of 1.5 corresponds to possible variation of crustal contribution in sediment mainly by weathering or bank erosion in the rivers.

Table 3.1 presents a qualitative scale of contamination intensity for sediment samples with 7 classes. The classes of zero and one, as it is noticeable from equation (2), show the background/unpolluted levels. For those samples with I_{geo} values above unity, early signs of contamination are expected. Subsequently, the higher classes in sediment samples, shows a higher contamination intensity of heavy metals in the sediment. For classifying the sediment samples by this index, the worst pollutant is actually considered. In other words, if a sample showed a higher index for a single metal, it would be ranked based on that element (Buruaem et al., 2012).

Table 3.1 Scale of contamination intensity for geoaccumulation index values - I_{geo} (Müller, 1979).

I_{geo}	Class	Contamination intensity
>5	6	Very strongly polluted
4-5	5	Strongly polluted
3-4	4	Moderately to strongly polluted
2-3	3	Moderately polluted
1-2	2	Unpolluted to moderately polluted
0-1	1	Unpolluted
<0	0	Background levels

3.2.7 Multivariate statistical analysis

Principal component analysis (PCA) is the most common type of multivariate analysis, which has been widely used in environmental studies (Abollino et al., 2002; Liu et al., 2003; Lucho-Constantino et al., 2005; Sundaray et al., 2011). PCA is a powerful statistical tool for pattern recognition, which is designed to reduce the number of variables into a few new components. Precisely, PCA transform the original variables into new and uncorrelated variables, called principal components (Chabukdhara and Nema, 2013). The new principal components (PCs) explain the major part of the variance of the data set (normally more than 75% of the cumulative of the variance). Therefore, PCs enable recognition of the actual influential factors for selecting a proper contaminated sediment management option, which lead to a balanced and viable outcome.

Cluster analysis (CA) is another tool that allows grouping sampling stations on the basis of the similarities of contaminants' characteristics such as availability or contamination intensity of heavy metals (Sundaray et al., 2011). Both PCA and CA analysis were carried out using SPSS statistical desktop 23.0 software.

3.2.8 Sediment Quality guidelines

Qualities of the sediment and water samples were assessed based on Canadian standards. The provincial and federal approaches to identifying the reference values for assessing the quality of sediment result are introduced in five different levels. For management of dredged sediment and remediation of contaminated aquatic sites, three distinct levels were suggested, which are occasional effect level (OEL), probable effect level (PEL) and frequent effect level (FEL), from low to high concentration of substance level, respectively. These concentration levels are calculated based on different intensities of the adverse effects observed in aquatic species (Table 3.2).

According to the guidelines (Environment Canada and Ministère du Développement Durable, de l'Environnement et des Parcs du Québec (MDDEP), 2007), the level of contamination for the management of dredged sediment was evaluated based on the OEL and FEL. For substances 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 subsistence). For heavy metal content equal or exceeding the FEL, open-water disposal is banned without any further tests. Sediments containing elements exceeding the FEL are highly contaminated and the site must be treated before any action as adverse effects are expected for the majority of benthic species (Environment Canada and MDDEP, 2007).

On the other hand, for remediation of contaminated aquatic sites, the PEL and FEL are the two threshold values that can be used to provide guidance for remediation decisions. The PEL shows the contaminant level within which adverse biological effects are frequently observed. Based on the standard, the level of contamination below the PEL does not justify initiation of site remediation. However, for those above the PEL, evaluation of the contamination, risk assessment and determination of the remediation is required (Environment Canada, 2007). The presence of a single heavy metal in sediment samples that exceeds the quality criterion is sufficient to categorize sediments as contaminated. Table 3.2 presents the criteria for assessing the quality of sediment samples for heavy metals.

Table 3.2 Environment Canada criteria for assessment of sediment quality [mg/kg] (Environment Canada and MDDEP, 2007).

Level	Cr	Ni	Cu	Zn	As	Cd	Pb
OEL	57	47	63	170	8	1.7	52
PEL	90	-	200	310	17	3.5	91
FEL	120	-	700	770	23	12.0	150

To assess the quality of the river water samples, the Canadian Water Quality Guidelines (CWQG) were employed (CCME, 1999). Comparing to the EPA (United States national recommended water quality criteria, 2009), the levels of reference standards for water quality in the Canadian guidelines were found to be more strict and closer to the chronic effect levels rather than the acute levels.

3.3 Results and discussion

3.3.1 Physical characteristics of sediment samples

Table 3.3 presents the results of the particle size analysis and loss on ignition (LOI) as a representative of organic and carbonate contents. Both surface and core samples texture were pretty fine with D_{50} about a µm. The distribution of particle size in both samples was determined as poorly graded (i.e. clay and fine silt were the dominant particle sizes).

The differences between clay, silt and sand percentages in surface and core samples were not significant. Surface and core samples contained a significant amount of clay and colloids (<2 µm), which is an indication of the capability of this sediment to adsorb pollutants. The sample from station 1, in the vicinity of the entrance gate to the harbour, was coarser than the rest of sediment samples (with 17.5% sand). Additionally, large gravels and some boulders were observed at stations 1 and 2, which were not considered in the particle size analysis. The presence of natural organic materials (NOM) such as algae in the surface sediment, particularly in the stations with semi- stationary water, was noticeable and indicated by the higher LOI in the surface samples.

Images of surface samples taken by scanning electron microscope (SEM) clearly showed the micron-size particles and tiny NOM pieces in sediment samples (Figure 3.2). Those fine particles (i.e. clay and very fine silt) cause a cohesiveness condition in some sediment samples, which can cement different sizes of sediments together. On the other hand, the presence of NOM (or organic components of sediment) and very fine particles could act as strong adsorbents for contaminants in the harbour (Fukue et al., 2007).

Table 3.3 Particle size analysis and loss on ignition results for surface and core sediment samples.

	LOI	D_{50}	Particle Size Distribution (%)		
	(%)	(μm)	Clay	Silt	Sand
Surface Sample					
Mean (n=15)	11.8	0.9	74.5	22.3	3.2
Min	4.4	0.3	41.0	8.8	0.0
Max	31.0	6.2	88.6	41.5	17.5
S.D.[1]	6.0	1.5	13.4	10.9	4.2
Core Sample					
Mean (n=12)	9.2	1.3	72.7	22.9	4.4
Min	2.5	0.2	23.0	10.4	0.0
Max	22.7	6.6	89.0	60.8	16.2
S.D.[1]	5.8	2.0	20.4	15.9	4.9

[1] Standard Deviation

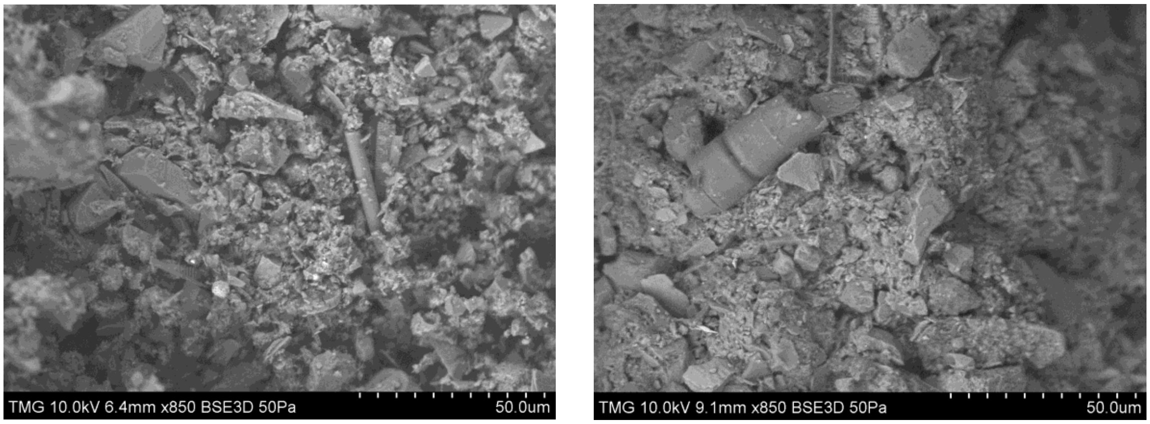

Figure 3.2 Scanning electron microscope images from surface sediment samples of stations 12 and 13. Distinction of very fine particles and tiny pieces of NOM from the rest of sediment particles was the purpose of these images.

3.3.2 Quality of the river water samples

Five river water samples were obtained from stations 1, 5, 6, 8 and 10 at the site. Common physicochemical characteristics of water samples were measured on the site and in the laboratory. Table 3.4 shows the physicochemical features of the river water samples on average. pH was between 7.5 and 8.5 with an average of 8.04, which was in the normal range for the St. Lawrence River (Environment Canada, EHD, 1997). The average value of the oxidation-reduction potential (ORP) and dissolved oxygen (DO%) for all selected stations implied that the quality of water is significantly above the average of this river (CCME, 2002). The presence of aquatic plants (e.g. algae), which were alive and actively producing oxygen, could be the reason of oversaturated dissolved oxygen in the water. The results of total dissolved solid (TDS), electric conductivity (EC) and turbidity revealed the high quality of freshwater at the site. Any management option for remediation of sediments should consider this level of quality.

Table 3.4 Physicochemical characteristics of the river water sample.

pH	ORP[1] (mV)	DO[2] (%)	TDS[3] (mg/L)	EC[4] (µs/cm)	Turbidity (NTU)
8.04 ±0.1	126.7±1.0	103.2±1.5	0.11±0.01	220 ±1.0	2.77±0.1

[1] Oxidation-Reduction Potential

[2] Dissolved Oxygen

[3] Total Dissolved Solids

[4] Electrical Conductivity

Seven metals and metalloids were selected for determination, which were Cr, Ni, Cu, Zn, As, Cd and Pb. The results of the dissolved metals in river water samples are presented in Table 3.5 with the standard values of heavy metals in fresh water in rivers recommended by Canadian Water Quality Guidelines (CWQG).

Table 3.5 Dissolved concentration of heavy metals (µg/L) in water samples from the site. Canadian Water Quality Guidelines (CWQG) for fresh water rivers was used as a standard reference (CCME, 2009).

	Cr	Ni	Cu	Zn	As	Cd	Pb
Ave.River water (Mean± S.D.) (n=5)	0.95±0.6	2.01±1.2	10.14±7.3	5.59±2.9	2.64±0.5	0.01±0.01	0.51±0.2
CWQG (CTC[1])	(11-16)[2]	65	(variable)[3]	30	5	0.8	2

[1] Chronic Toxicity Criterion.

[2] Adopted from National Recommended Water Quality Criteria, EPA. 2009.

[3] The CWQG for Cu is related to water hardness (as $CaCO_3$). Normally ranging between 2 to 4 µg/L. No fact sheet created.

Except for Cu, the concentration of dissolved heavy metals in water samples was below the chronic toxicity criterion (CTC) on average. Copper was the only element that had a concentration of almost 2.5 times of the upper CTC level. According to the EPA standard, the mean acute value of dissolved Cu in freshwater ranged from 2.37 µg/L for the most sensitive species to more than 107 mg/L for the least sensitive ones (USEPA, 2009). Therefore, assessment of the toxicity of this level of dissolved copper in river water depends on the species exist on the site.

3.3.3 Total concentration of heavy metals in sediment samples

Before measuring the total concentration of heavy metals, it is important to determine the background level of each heavy metal in the harbour. Beside the different standard levels of contaminant values provided by Environment Canada and MDDEP, having the natural level (NL) of the elements in St. Lawrence River is required to detect the actual contaminants.

Two types of sediments were detected and characterized in St. Lawrence River. Postglacial clay, which were deposited over 8000 years ago, and pre-industrial sediment that dating back before 1920 (pre-industrial era). They can be identified based on their physical and chemical properties (Environment Canada, 2007). Table 3.6 presents both the concentration of NL for selected heavy metals in sediment from the fluvial section and fluvial estuary of St. Lawrence

River. If the concentration of a substance did not exceed 1.5 times of their NL, it implies that the substance is entirely provided from crustal contribution in sediments (Zhang and Liu, 2002; Yuan et al., 2012). However, for concentration's values greater than 2 times of their NL, anthropogenic influences are considered.

Table 3.6 Natural levels of selected heavy metals in pre-industrial and postglacial sediment in St. Lawrence River (mg/kg).

	Cr	Ni	Cu	Zn	As	Cd	Pb
Pre-industrial	60	29	19	86	6.6	0.2	13
Postglacial clay	150	75	54	150	8	0.2	16

Total concentration of heavy metals in sediment samples was determined and presented in Table 3.7. Highlighted cells present the concentration value more than two times higher than the NL (i.e. postglacial clay) presented in Table 3.6. Those cells with borders are the elements exceeding probable effect level (PEL) as well. It is worth noting that for those stations containing the heavy metals exceeding PEL, risk assessment and determination of remediation is required according to the Canadian guidelines (Environment Canada and MDDEP, 2007). Concentrations above FEL were not detected in sediment samples.

Results from Table 3.7 indicated that Cr and Ni did not exceed two times their natural levels (TTNL) and PEL, neither in surface sediments nor in the core samples. Conversely, Cd exceeded TTNL in almost all stations and no concentration exceeding PEL was detected in any station. Since the reference level for initiating the site remediation is PEL, those stations with the bordered cells should be the focus.

Generally, the surface sediments were slightly more contaminated than the core sediment samples. For all stations and selected heavy metals, surface sediments were about 10% more polluted. However the concentrations of Pb and As in core samples were determined as higher than the surface sediment (mainly because of C3 and C14). Zn was the main contaminant followed by Pb and Cu. Arsenic was detected above the PEL just at station S13. However stations in the vicinity of maintenance area were the most contaminated locations. Zn, Cu, Cd and Pb are the main inorganic elements used in antifouling paint formulae. The high concentrations of Cu and Zn were mainly found in the surface sediments and Cd and Pb (with relatively higher concentration than their NL) were detected in both surface and core samples.

Antifouling paint particles can be a source of trace metals since they mostly were found with high concentrations in stations near the maintenance area. APP normally wash off and runoff into the aquatic environment and become a source of contamination (Thomas et al., 2003; Tolhurst et al., 2007).

Table 3.7 Total concentrations of selected heavy metals in sediment samples (mg/kg). Highlighted cells present the concentration value more than two times higher than the natural level (TTNL), and the cells with borders are the elements exceeding the probable effect level (PEL).

St. No.	Cr	Ni	Cu	Zn	As	Cd	Pb	Year
S1	37	22	219	204	6.1	0.5	134	2013
S2	60	47	159	303	7.0	0.8	51	2013
S3	74	64	138	563	6.6	0.8	77	2013
S4	71	39	137	372	9.4	0.9	69	2013
S5	79	41	69	173	7.3	0.7	42	2012
S6	62	37	68	188	6.8	0.6	33	2012
S7	62	38	87	202	6.5	0.8	42	2012
S8	72	46	59	305	8.4	0.9	37	2013
S9	59	33	96	149	6.7	0.8	30	2012
S10	67	43	70	266	6.4	0.8	33	2013
S11	62	38	59	185	6.3	1.3	58	2012
S12	62	38	47	205	6.0	0.8	33	2013
S13	99	46	67	334	18	1.1	55	2013
S14	74	39	75	201	11	0.8	34	2013
S15	51	30	77	121	4.6	0.6	25	2012
Mean ±S.D.[1]	66 ±14	40 ±9	95 ±47	251 ±112	7.8 ±3.3	0.8 ±0.2	50 ±28	
C1	44	28	149	223	6.3	0.46	72	2014
C2	54	27	49	225	8.1	0.69	97	2014
C3	91	45	92	364	14	1.3	212	2014
C4	71	40	42	238	9.4	0.8	51	2014
C5	52	31	107	224	7.6	0.6	48	2014
C6	33	25	27	151	4.5	0.2	25	2014
C9	37	22	24	111	7.1	0.4	35	2012
C10	62	40	52	213	9.5	0.9	80	2012
C11	56	50	69	110	4.5	0.1	13	2012
C13	76	39	53	268	11	0.9	56	2014
C14	94	39	59	247	17	0.7	60	2014
C15	31	32	28	66	4.8	0.1	11	2012
Mean ±S.D.[1]	58 ±21	35. ±8	63 ±37	203 ±81	8.6 ±3.8	0.6 ±0.4	63 ±54	

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[1] Standard Deviation

3.3.4 Geoaccumulation index analysis

Results of the geoaccumulation index were determined for the core sediment metal analysis. Figure 3.3 presents the I_{geo} of selected heavy metals in eight core samples. The results clearly showed that Cu and Zn in core samples were not contaminants as well as Cr, Ni and As. However, Cd and Pb were categorized as moderately polluted in 5 and 4 stations, respectively. Only Pb in C3 was identified as a moderately to strongly contaminated (Class 3). Although Zn in C3 exceeded the PEL, the I_{geo} values indicated that Zn was not a contaminant in core samples. Although the geoaccumulation index shows the intensity of contamination, it cannot assess the actual risk posed by metals in the aquatic environment. Sequential extraction is required in order to evaluate the risk of mobility and availability of heavy metals in sediment samples. It should be noted that SQGs do not require any risk assessment based on sequential extraction tests or measuring/calculating the NL of heavy metals in sediments. The NL is considered in some cases especially where high NL levels are known (e.g. Cr in the St. Lawrence River).

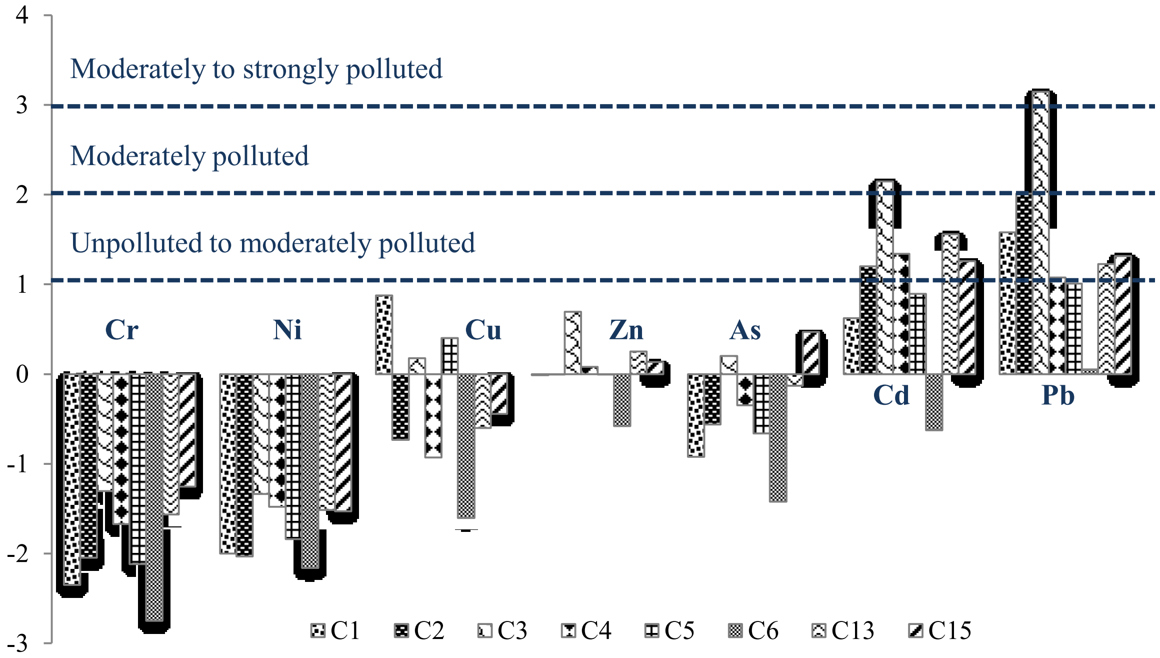
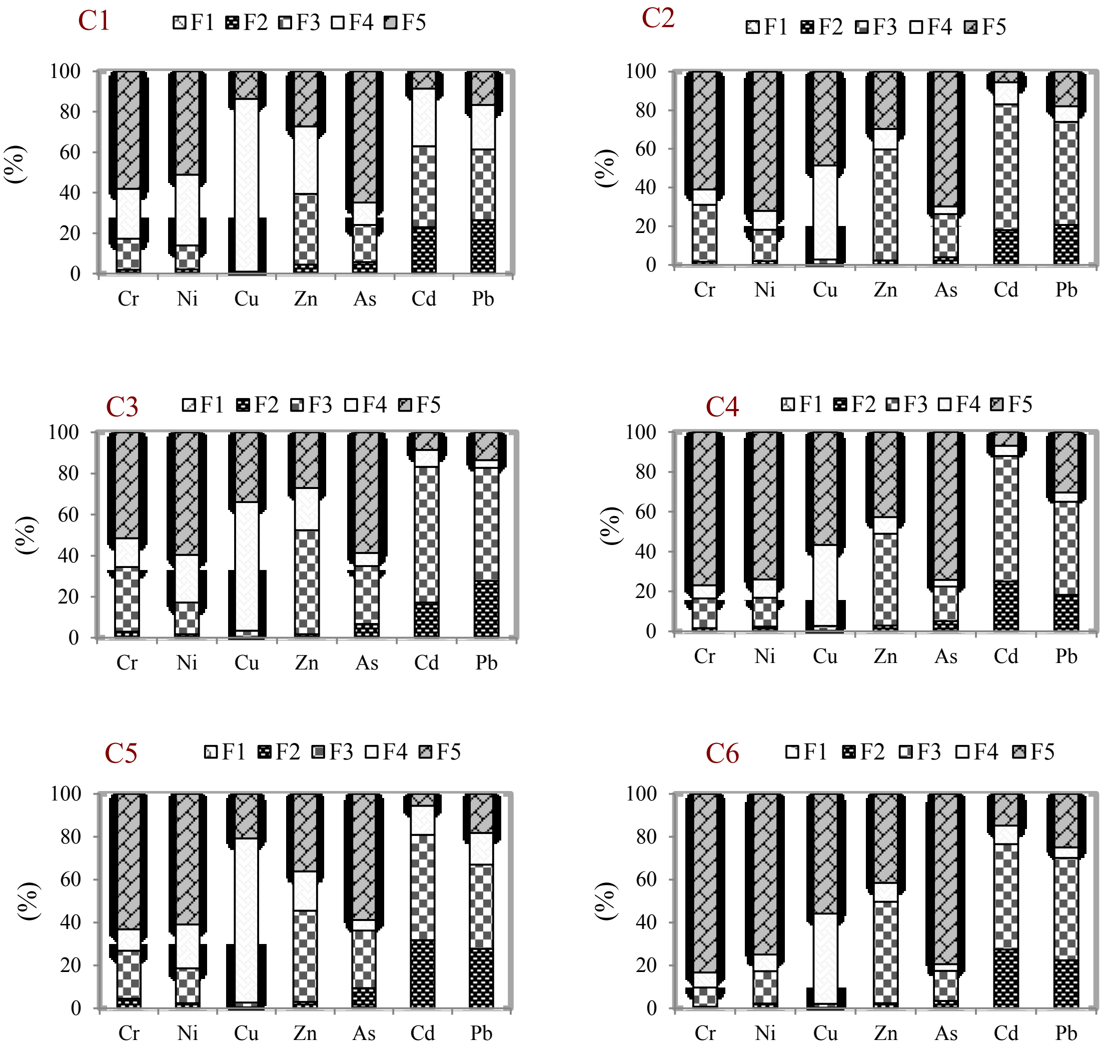


Figure 3.3 Geoaccumulation index (Igeo) of heavy metals for selected core sediment samples.

3.3.5 Results of sequential extraction of selected heavy metals

Since the shallowness was an issue in the harbour, a depth of 50 cm of sediment should be taken into account for any remediation strategy. This depth is required for future dredging in order to facilitate the passage of the large boats. Subsequently, the core samples, which cover the required depth, were chosen for the sequential extraction test (SET). Core sediment samples from stations 1, 2, 3, 4, 5, 6, 13 and 15 were chosen for the SET.

Five distinct fractions were determined in the sediment matrix and are presented in Figure 3.4 for selected core sediment samples. Fractions 1 to 5 (F1 to F5) are representatives of the exchangeable, acid-soluble (carbonate), reducible (Fe-Mn oxides), organic and residual fractions respectively.



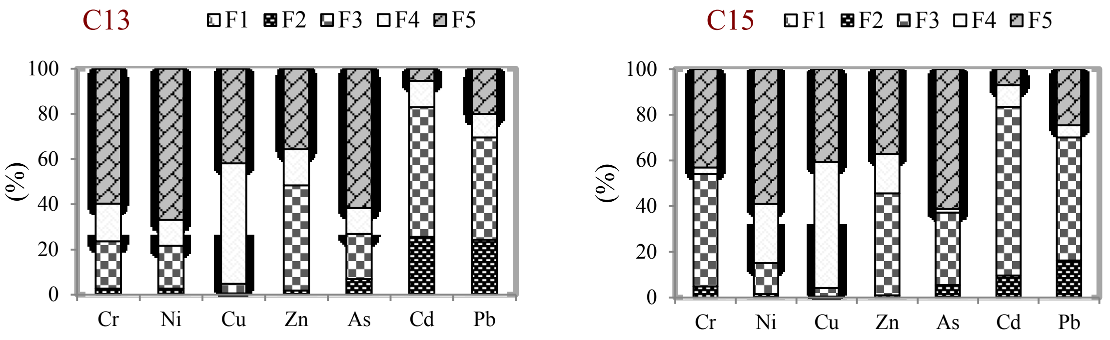


Figure 3.4 Results of the sequential extraction test for selected core sediment samples. F1 to F5 are representatives of exchangeable, carbonate, Fe-Mn oxides, and organic and residual fractions respectively. The concentrations of elements in F1 in all selected sediment samples were below 1%.

Chromium, nickel and arsenic as indicated earlier, were not considered contaminants. The results of the SET also indicated that their concentrations were mainly found in the most stable fractions (F4 and F5). Therefore, the risk of availability of Cr, Ni and As in the aquatic ecosystem is negligible in the case of contaminated sediment disturbance. On the other hand, cadmium and lead mainly existed in F2 and F3. Precisely, the concentrations of Cd and Pb in F2+F3 were around 80% and 70% of their total respectively. Since the carbonate phase is susceptible to changes in pH (Coetzee, 1993; Gauthreaux et al., 1998), significant concentrations of Cd and Pb may be re-introduced to the aqueous phase upon an uncontrolled resuspension of contaminated sediment.

Copper was mainly bound in the organic fraction, which is consistent with previous research (Sundaray et al., 2011; Pagnanelli et al., 2004) and consequently was not environmentally available. Although more than half of the zinc concentration was in the F4 and F5 fractions, the other half was in F3. In general, except for Cd and Pb, all selected heavy metals were not environmentally available according to the SET. It should be noted that, since sediment samples were exposed to oxic waters in the reactor, the results of SET reflects the partitioning of metals after the oxidation of the sediment.

To assess the potential mobility and availability of heavy metals in the sediment, the risk assessment code (RAC) was used. The RAC is defined based on the total of the exchangeable and carbonate-bound fraction percentages (Perin et al., 1985) and is categorized into five different classes (Table 3.8).

Table 3.8 Classification of risk assessment code -RAC (Perin et al., 1985).

RAC	F1+F2 (%)
No risk	< 1
Low risk	1 - 10
Medium risk	11 – 30
High risk	31 – 50
Very high risk	> 50

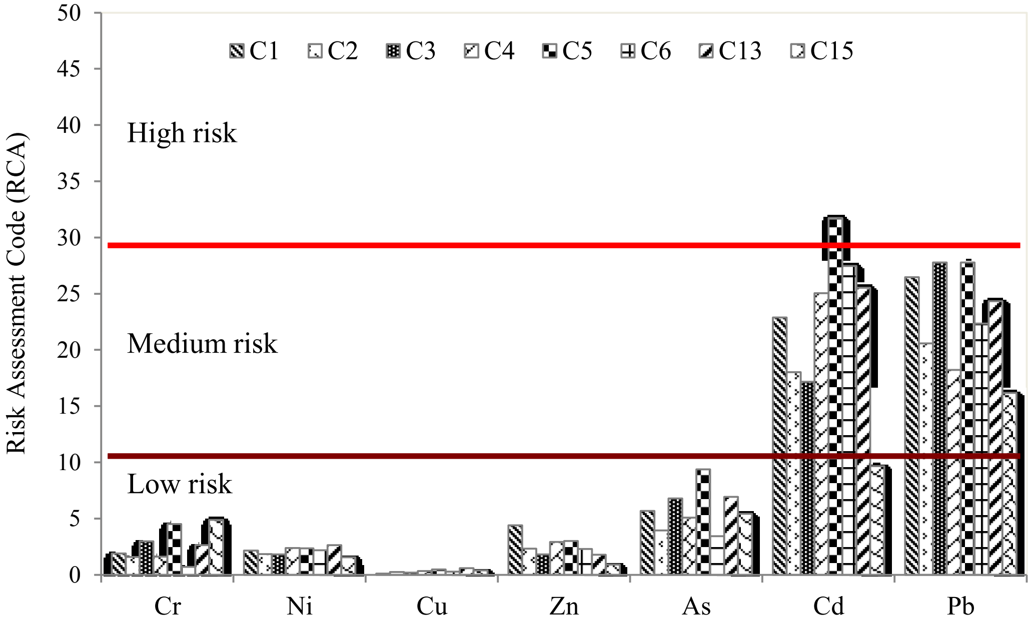


Figure 3.5 Risk assessment code for selected core samples.

Figure 3.5 shows the RAC of heavy metals in core sediment samples. According to the RAC, mobility and availability risk of Cd and Pb were at least four times more than the rest of the metals. They were at the medium risk category with an average of 22 and 23 percent, respectively. The risk of availability of the other metals was negligible.

Monitoring the previous studies revealed that clays and carbonates are known to be an effective adsorbent of Cd (Shirvani et al., 2006; Zheng et al., 2007). These minerals are of low density and can be easily resuspended (Superville et al., 2015). Dredging the contaminated sediment with a fine texture (medium size around a micron) and medium to high risk of Cd mobility could pose a real danger to the aquatic environment. Silt curtains or booms are normally employed to contain suspended sediments during the dredging operation, which have successfully prevented sediment dispersal in numerous projects. Yet there is a major concern regarding their use due to the risk of contamination leakages in polluted areas containing very fine particles (Manap and Voulvoulis, 2015; Morton, 2001; Su et al., 2002). For instance, Otto et al. (1996) examined the level of PCB uptake in caged rainbow trout during dredging of the St. Lawrence River at Massena, New York, USA. The fish were located close to but outside of the silt curtain. The results indicated that the total PCB body burden in fish was increased after 42 days of dredging.

Although more than 23 percent of Pb was detected in labile fractions (medium risk), more than 47 percent of its concentration was found in the Fe-Mn oxide/hydroxide fraction. Dynamic behaviour of Pb in the Deule River (in northern France) showed that remobilized Pb from the reductive dissolution of iron hydroxide was effectively scavenged by particulate organic matter and unlike Zn, it is bound by more stable fractions (Superville et al., 2015). Therefore, the potential risk posed by Cd to the ecosystem is more serious than Pb in the case of a dredging operation. In fact, Zn and Pb, which were the only elements exceeding the PEL based on their total concentrations in core samples, are not as available as Cd. This is the reason that risk assessment based on SET should be taken into consideration when contaminated sediment management options are evaluated.

3.3.6 Identifying the main influential factors using PCA

A principal component analysis was carried out to identify the actual factors (i.e. PCs) affecting the management of contaminated site. In other words, PCs provide reliable information for making a balanced and viable decision.

The variables employed in this study in the PCA process were: 1) the availability of the selected heavy metals (F1+F2%). They presented the weakly bound elements to the sediment matrix, which probably were recently adsorbed by the sediment. Sundaray et al. (2011) termed this group of variables as an ‘anthropogenic factor’ since they found the majority portion of the metals associated with the available fractions were contributed by anthropogenic activities. 2) The concentration of the metals in F3 (%). This group of variables showed the importance of Fe-Mn oxides/hydroxides in retaining the metals and its role in this study. 3) The concentration of the metals in the most stable fractions (F4+F5%). This set of variables presented those metals with strong bonds to the sediment matrix, which were either the aged pollutants or the metals originating from crustal contribution (Liang et al., 2014). 4) Contamination intensity of all selected metals (I_{geo}) was another group of variables. They presented the difference of concentration of the elements in the sediment and their natural levels. 5) Texture of core sediment samples (percentage of clay and silt in this study) was the last group of variables. In total, 30 unit-less variables were employed with 8 subjects for each variable, which were representative of the 8 stations in the harbour for core sediments.

The R-mode varimax factor analysis was used to determine the PCs. The rotation method was Oblimin with Kaiser normalization. PCs were the components with eigenvalues greater than one and the data set was sorted by the contribution of more significant variables (>0.3 factor score). The results of the rotated factor loading score along with eigenvalues, percentage of variance and cumulative percent are presented in Table 3.9.

Table 3.9 Structure matrix of PCA for heavy metals features in core sediment samples.

Variable	PC1	PC2	PC3	PC4	PC5
Cd (I_{geo})*	**.973**				-.498
Zn (I_{geo})	**.969**				-.526
Cr (I_{geo})	**.943**			-.349	-.626
Ni (I_{geo})	**.920**				-.426
As (I_{geo})	**.906**			-.403	-.726
Pb (I_{geo})	**.763**	-.412	-.370		-.423
Cu (F3)**	.687	-.437	**.617**	-.373	-.508
Zn (F3)		**-.958**			
Zn (NA)***		**.930**			
Pb (F3)	.422	**-.901**		-.535	
Pb (NA)	-.495	**.861**			.329
Zn (A)****	-.414	.645	-.450	.548	.488
Cu (I_{geo})	.328	.503	-.430	.493	-.468
Cu (A)			**.948**		
Ni (NA)			**-.881**		
Ni (F3)		-.394	**.862**		

Variable	PC1	PC2	PC3	PC4	PC5
Cu (NA)	-.647	.389	**-.684**	.354	.490
Cd (NA)	-.484	.593	-.612	.348	
Ni (A)		.451	.604	.491	.551
Pb (A)				**.955**	
Silt				**-.884**	-.414
Clay				**.865**	.441
Cd (A)	-.488	.421	.391	**.693**	.552
Cd (F3)	.635	-.668		-.669	-.481
As (A)	.400	.387	.335	**.576**	**-.518**
As (F3)	.614				**-.981**
As (NA)	-.623				**.964**
Cr (A)	.470				**-.934**
Cr (NA)	-.582			.510	**.917**
Cr (F3)	.578	-.343		-.543	**-.890**
Eigen value	13.14	5.47	5.15	3.10	1.58
% of variance	43.79	18.23	17.16	10.27	5.26
Cumulative	43.79	62.02	79.18	89.44	94.70

I_{geo} *Geo accumulation index

F3 **Fe-Mn oxide/hydroxide fraction

NA ***Non-available fractions (organic and residual fractions)

A****Available fractions (exchangeable and carbonate fractions)

Five principal components were determined, which explained more than 94 percent of the total variance. The first PC with 43.8% of variance is the most influential factor affecting the management option in the contaminated harbour. As shown in Table 3.9 with the bolded numbers, the first PC (contain more significant variables) is representative of the contamination intensity (I_{geo}) in core sediment samples. The sorted variables with the highest factor scores clearly indicated that the first significant component is contamination intensity. The geoaccumulation index is a reliable tool to assess whether the contribution of heavy metals in sediment is due to lithogenic effects or not. In other words, the signs of anthropogenic activities in contaminated sediment can be clarified by calculating this index (Buruaem et al., 2012). The significance of I_{geo} to provide a more accurate appraisal of river contaminated sediment management options was reported in previous studies (Chabukdhara and Nema, 2012; Zhiyuan et al., 2011).

The second and the third PCs were almost the same percentage of variance (18.2% and 17.2%, respectively). These PCs cannot be termed with certainty as the first component. However, considering the variables with higher factor scores in the second component implies that the concentration of Zn and Pb (as the only elements exceeding the PEL in core sediments) in the non-labile fractions can be the next influential factor in the management decision. It is worth mentioning that the positive and negative scores of bolded numbers in PC2 show an inverse relationship between the Fe-Mn oxide/hydroxide and organic-residual fractions. This shows the importance of the Fe-Mn oxide/hydroxide fraction for Zn and Pb, which comprises a significant percentage of their concentrations. F3 also can play a crucial role in the case of uncontrolled resuspension of contaminated sediment that leads to changes in the environmental conditions (e.g. pH). Fe-Mn oxides scavenge the potential remobilized metals (caused by a dredging operation for instance) from the aquatic environment (Eggleton and Thomas, 2004). Moreover, as mentioned earlier, metals (e.g. Pb) released from the reductive dissolution of iron hydroxide (F3) can be re-adsorbed by a more stable fraction (mainly organic fraction). Subsequently, the constructive role of F3 in heavy metal fractionations should be taken into consideration as the PCA suggested.

The third component implies the contribution of non-contamination elements (i.e. Cu and Ni). Heavy metals with higher concentrations in stable fractions pose an insignificant threat to the aquatic ecosystem due to a short-term resuspension event (Cantwell et al., 2008). However, identifying the non-contamination elements could be as important as determining the actual contaminants for selecting a proper management option.

The fourth component with 10.3% of the explained variance is mainly representative of the textural factor and available Pb and Cd in the sediment samples. The results are consistent with some previous studies' outcome, which indicated the importance of the textural factor in river sediments (Lucho-Constantino et al., 2005; Sundaray et al., 2011). The presence of a significant amount of clay and colloids in the sediment texture is the most important physical control on adsorption and also distribution of heavy metals in non-labile fractions (Francois, 1998; Helena et al., 1999). Additionally, fine particles (i.e. clay and silt) actively can adsorb the contaminants entering to the rivers due to their specific surface area and ionic attraction (USEPA, 1991). It is well understood that fine particles have negative electrostatic charges on the surface, which attract divalent metals ions with positive charges.

The last component is the least significant factor with only 5.3% of the variance. The role of crustal contribution in metal concentration in sediment can be termed for this factor. As and Cr not only showed high concentrations in the total but also the main part of their total was detected in the most stable fractions. Evidence of human activities was not noticed in fractionations of Cr and As in the core sediment samples.

3.3.7 Stations grouping using hierarchical cluster analysis (HCA)

Hierarchical cluster analysis was performed in order to categorize the contaminated or non-contaminated stations on the basis of the similarities of contamination intensity (I_{geo}). Since the PCA results have suggested that the intensity of contamination is a significant factor in sediment management strategy, HCA was performed according to the similarity of I_{geo} in 27 sediment samples across the harbour, including both surface and core sediments. Identifying the contaminated spots could reduce the cost of operation in the case of dredging and also reduce the risk of remobilization of heavy metals by applying a suitable management method for the contaminated spots.

HCA was employed by means of the Ward's method, using Euclidean distances as a measure of similarity, which is a widely accepted method for grouping mechanism (Sundaray et al., 2011). According to HCA analysis (Figure 3.6), 4 groups were recognized to describe the stations with similar levels of contamination.

Group one contains both surface and core sediment samples from stations 1 to 5, which are mainly affected by effluents from the maintenance area. In this group Cu, Zn, Cd and Pb were found at more than their natural levels. Cu and Zn may present the mixed origin (anthropogenic and lithogenic). However Cd and Pb in this group appear to be mainly associated with human activities (particularly Pb). This group, termed as the most contaminated area in the harbour, comprises S1, S2, S3, S4, C1, C3 and C5. These locations are in the most stationary water in the harbour as shown in Figure 3.1-b in the wintertime.

Group two, comprises the surface sediments from stations 5, 6, 7, 8, 9, 10, 12, 14 and 15. Unlike the first group, Cd is the only element in this group with noticeable I_{geo} (the results of surface sediment I_{geo} are not presented). Contamination intensity of Cu, Zn and Pb in this group was negligible. The locations of the sediment samples in this category are in the pathway of the boats traveling to the main dock. This group is named as slightly contaminated sediment with Cd.

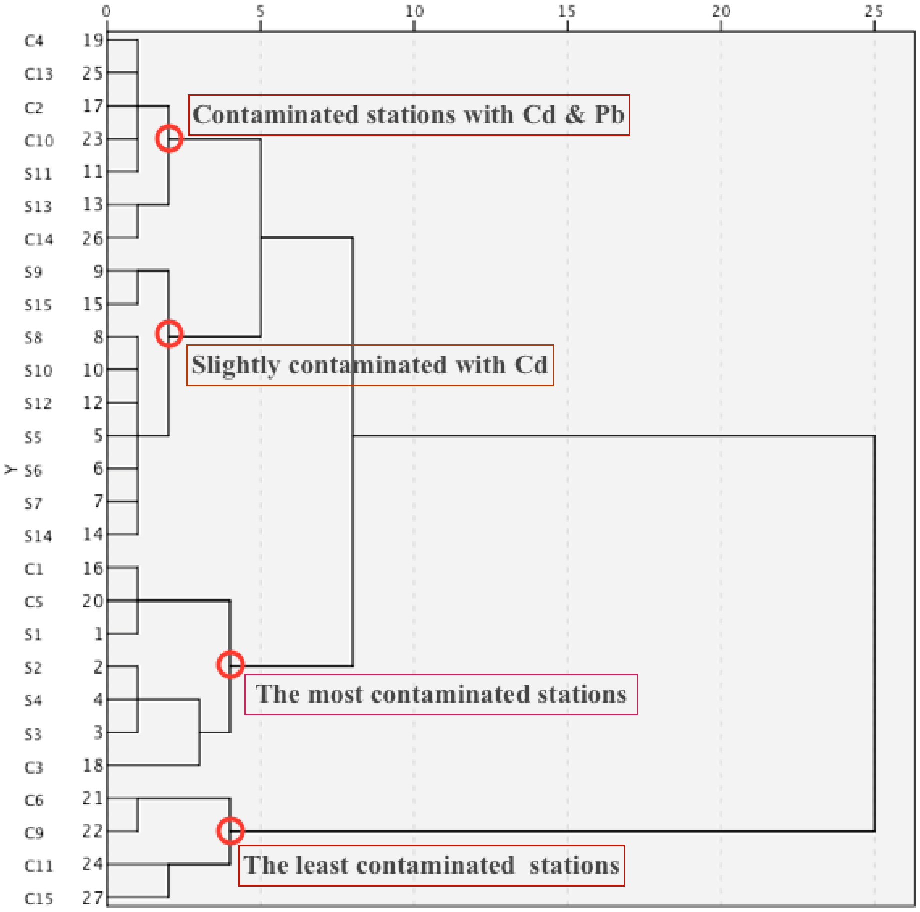


Figure 3.6 Dendrogram using the Ward Linkage, clustering of stations based on the contamination intensity of heavy metals in sediment samples.

The third group is comprised of those contaminated stations polluted with Cd and Pb. There was no sign of contamination with Cu and Zn in this group of stations. S11, S13 and C2, C4, C10, C13 and C14 are classified in this group. As it is noticeable, unlike the first group, core samples are the majority of this group and Cd is the main focus. This cluster of stations was termed as contaminated locations with Cd and Pb. Since the core sediments are included in this category, the contaminants might be the aged elements adsorbed and retained in sediments for decades. Choosing a proper management option for contaminated sediments in this group as well as the first group is crucial due to the high percentage of Cd and Pb concentrations in the labile fractions.

The last group is comprised of the core sediment with negligible intensity of contamination. This group displays the least contaminated stations included C6, C9, C11 and C15, which are relatively far away from the docks and the maintenance area.

3.3.8 Evaluation of the contaminated sediment management strategies

Different influential factors are involved in selecting the right strategy in a contaminated area. A comprehensive study and evaluation of the quality of water and sediment should be done before making any decision. Determination of the pH, organic matter contents, oxidation-reduction potential, temperature of the water, metal species and their concentration in each fraction in sediment matrix could be helpful in making the right decision. SQGs criteria do not provide sufficient and comprehensive information to identify the real contaminants. Risk assessment analysis of heavy metals provides valuable information about the mobility and availability of contaminants. Data analysis through PCA and HCA also enables more cost effective and balanced decision making for managing the contaminated area. For instance, stations in group one (in the vicinity of the maintenance area) were recognized as the only stations needing remediation management for reduction of heavy metals, according to the RAC, I_{geo} and HCA. Conversely, locations in the last group were identified as the stations without any noticeable contaminants in the core sample, which do not need any management and open water disposal would be a viable option following dredging. Open water disposal, as the most economical and widely used method for disposal (Katsiri et al., 2009), for C2, C4, C13 and C15 is allowed if the toxicity test shows there is no threat for benthic organisms. Further tests on surface sediment samples must be done to avoid remobilization of metals in the water column.

For stations 1 to 4, a capping strategy cannot be applied since shallowness is an issue. An *ex situ* strategy on the other hand requires dredging, which can result in the destruction of existing benthic ecosystem (USEPA, 1991; Mulligan et al., 2009). Besides the fact that the total concentrations of Zn and Pb were noticeably high in these stations, the concentrations of Cd and Pb in labile fractions were also high enough to cause serious adverse effects on aquatic species. If the toxicity test indicates that disposed sediment is a threat to the benthic ecosystem, open water disposal is not allowed and sediment should be dewatered, transported and treated or delivered to the secure landfill, which would be costly. Therefore, for dealing with contaminated sediment at these locations, a less destructive and more cost-effective technique with minimal waste production is highly desired.

A resuspension technique is an alternative for dredging since unlike the other common *in situ* methods, this technique can reduce the concentration of contaminants. Japanese scientists were the first to employ resuspension as a remediation technique for organic pollutant removal from contaminated sediments. Fukue et al. (2012) applied the resuspension in a Fukuyama city harbour in order to decrease the rate of eutrophication and improve the quality of water and sediment. Since the finer sediments carry higher concentrations of pollutants, in the resuspension process, finer sediments are targeted for removal by a suspension mechanism in a confined water column for a short period of time. Fine particles ultimately are removed through a pumping and filtering process and consequently the concentrations of contaminants (including heavy metals) decrease (Pourabadehei and Mulligan, 2016a). In the resuspension method, some lighter substances such as APP and tiny pieces of NOM can be removed from the ecosystem as well. The quality of the water must be monitored during and after the test. Details of the resuspension procedure in shallow aquatic environment and its performance for potential risk reduction were described in previous studies (Fukue et al., 2012; Pourabadehei and Mulligan, 2016a, 2016b).

The resuspension technique can be applied as a remediation method for stations categorized in group one in the vicinity of the maintenance area and station 13 in the third group. These locations are the shallowest places in the study area and cannot be treated by the common *in situ* remediation methods. To avoid the environmental impacts of dredging as well as the cost of handling significant amounts of contaminated sediment, the resuspension technique is suggested as a viable alternative for those stations. Figure 3.7 shows the general remediation plan at approximate locations across the study area. The ‘R’ in the red circle is a representative of those areas suggested for applying the resuspension technique to reduce the concentration of contaminants. Considering the level of contamination, open water disposal is not recommended for these stations. However, since the removed materials’ volume through the resuspension method is about 5 to 15 percent of the sediment of the whole contaminated areas (Fukue et al., 2012), handling the removed materials in this method is much more convenient than the significant amounts of contaminated sediment removed by dredging.

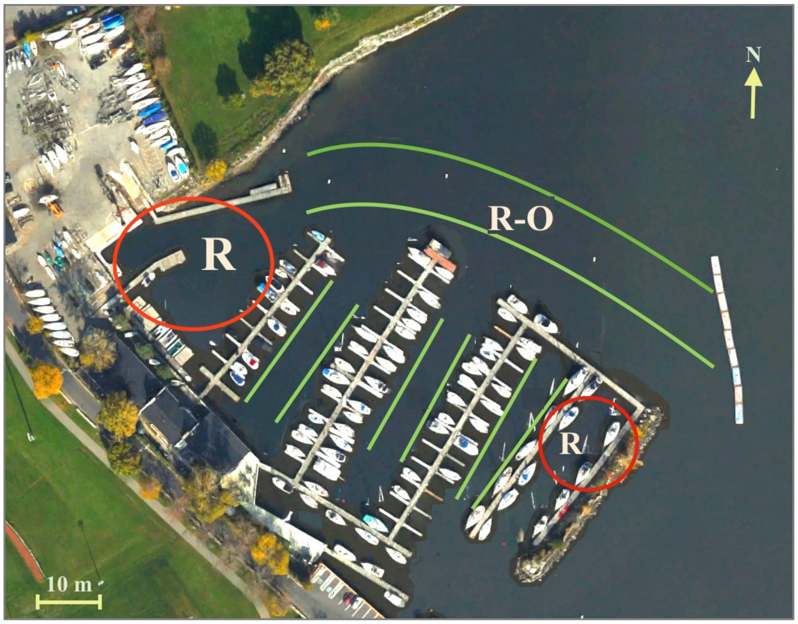


Figure 3.7 General remediation plan for contaminated locations across the harbour. 'R' in red circles presents the areas, which are recommended for applying the resuspension method as a remediation technique for contaminated sediment. The green lines, however, are the representatives of the areas that resuspension is suggested to eliminate the need for dredging with the possibility of open water disposal ('R-O').

On the other hand, the pathways for moving the boats in the study area mainly cover those locations with sediments categorized in group two. Dredging of the sediment in those stations can be performed if the toxicity test confirms that there would be no threat to the ecosystem of the aquatic environment.

On the other hand, for those areas that need to be dredged for facilitating the passage of large vessels, the resuspension can also be suggested to eliminate the need for dredging. Similar to previous situations, if the toxicity test confirms that Cd would not pose a threat to aquatic species, open water disposal of the removed materials (probably by a suction pipe) is recommended. As a result, less destruction would be made in ecosystem and the quality of the harbour sediment would be enhanced. Further tests (e.g. leaching tests and toxic effects on the living organisms) are required with emphasis on Cd in the sediment samples. The pathways presented in Figure 3.7 with green lines are representatives of the locations, where the resuspension technique is recommended with an open water disposal option.

3.4 Conclusions

Physicochemical characteristics of the water and sediment samples from a shallow harbour on the bank of the St. Lawrence River were determined in order to evaluate the best management strategy for contaminated sediments. Canadian standards and regulations were used for assessing the quality of water and sediment of the study area as well as applying the standard methods for measuring and sampling. Although the water samples showed a high level of water river quality, the dissolved concentration of Cu was 2.5 times more than the chronic toxicity criterion.

Sediment samples were highly organic and contaminated mainly by Zn, Cu, Pb and Cd. The results of the sequential extraction test indicated that Cd and Pb were the most environmentally available elements in core sediment samples, while their total concentrations were more than two times of their natural levels. Conversely, Cu was the least environmentally available since most of its concentration was in the organic and residual fractions. Zn as a main contaminant exceeds the PEL in some surface and core samples and was mostly bound to the Fe-Mn oxide/hydroxide fractions.

In general surface samples were slightly more polluted than the core samples and contain a finer texture according to the particle size analysis results and images of the SEM. Residues of the boat painting washout from the maintenance area could be the main source of the contamination.

The geoaccumulation index was found as the most influential factor affecting the management option for core samples followed by concentration of Zn and Pb in Fe-Mn oxide/hydroxide fraction. The percentage of clay and silt in sediments was another factor, which could show the sediment's capability to be a sink or/and source of contaminants. HCA indicated that the stations near the dock area contained the most contaminated sediment, which required an appropriate remediation strategy. C6, C9, C11 and C15, however, were not found to be contaminated. Among the diverse range of the management strategies, the resuspension technique is suggested as a viable alternative in this specific case for stations in the vicinity of the maintenance area and other shallow contaminated locations. For those locations in the pathways of the larger boats, the resuspension also is suggested to eliminate the need for dredging. Further tests are required to assess the risk of mobility of heavy metals in the surface sediments over a short-term resuspension of contaminated sediment.

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Chapter 4

In Chapter 3, through a comprehensive assessment on the sediment samples obtained from the contaminated harbour, resuspension technique was recommended for addressing the issues according to the Japanese previous research. However, this method has not been evaluated for remediation of contaminated sediment with heavy metals in previous studies. Moreover, the mechanism of metal removal through removing the suspended particulate matter has not been elucidated. Chapter 4, however, focuses on evaluating the feasibility of the resuspension method for reducing the concentration of heavy metals for the first time and explaining the mechanism of contamination removal.

4 Resuspension of sediment, a new approach for remediation of contaminated sediment

Mehdi Pourabadehei, Catherine N. Mulligan

Department of Building, Civil and Environmental Engineering, Concordia University, 1455 de Maisonneuve Blvd. W., Montreal, Qc, Canada, H3G 1M8

Abstract

Natural events and anthropogenic activities are the reasons of undesirable resuspension of contaminated sediments in aquatic environment. Uncontrolled resuspension could remobilize weakly bound heavy metals into overlying water and pose a potential risk to aquatic ecosystem. Shallow harbours, with contaminated sediments are subjected to the risk of uncontrolled resuspension. Remediation of sediments in these areas cannot be performed by conventional *in situ* methods (e.g. capping with or without reactive amendment). *Ex situ* remediation also requires dredging of sediment, which could increase the risk of spreading contaminants. Alternatively, the resuspension technique was introduced to address these issues. The concept of the resuspension method is that finer sediments have a greater tendency to adsorb the contamination. Therefore, finer sediments, believed carry more concentration of contaminants, were targeted for removal from aquatic environment by a suspension mechanism in a confined water column. The objective of this study was to evaluate the feasibility of the resuspension technique as a new approach for remediation of contaminated sediment and a viable option to reduce the risk of remobilization of contaminants in harbours due to an undesirable resuspension event. Unlike the common *in situ* techniques, the resuspension method could successfully reduce the total concentration of contaminants in almost all samples below the probable effect level (PEL) with no significant change in the quality of overlying water. The results indicated that removal efficiency could be drastically enhanced for metals in sediment with a higher enrichment factor. Moreover, availability of metals (e.g. Cd and Pb) with a high concentration in labile fractions was higher in finer sediments with a high enrichment factor. Consequently, removal of contaminants from sediment through the resuspension method could reduce the risk of mobility and availability of metals under changing environmental conditions. Potential dredging in harbours could be performed safer and more cost-effective afterward.

Keywords: Resuspension, Contaminated sediment, Harbours, *In situ* remediation, Heavy metals.

4.1 Introduction

Sediments, particularly at the bottom of large rivers, act as a sink for anthropogenic contaminants. Sediments are exposed to significant amounts of pollutants from the land and/or transport by rivers and up to 99 percent of contaminants can be adsorbed (Salomons and Stigliani, 1995; Huang et al., 2012). However, sediments can be a source of contaminants when they are disturbed, moved or relocated by natural events or human activities (Latimer et al., 1999).

Traditionally, resuspension of contaminated sediments (RCS) has been known as an unplanned event, and has led to remobilization of some contaminants into the aqueous phase and eventually release in to the aquatic environment. RCS also may disturb the remediation process and management of contaminated sediment in industrial regions (Friedman et al., 2009). Many occurrences can cause sediment resuspension; Natural events such as waves and storms, tidal currents, bioturbation or human activities like dredging or vessel movements and trawling (Olsen et al., 1982).

The literature on the research studies on RCS suggests that the majority of contaminant release in the aquatic ecosystem has occurred by natural disturbance (Roberts, 2012). As an example, monitoring of suspended particulate matter and the total concentration of pollutants in Port Jackson in Australia indicated that large storms and waves resulted in significant RCS with the potential for mobility and availability of contaminants (Birch and O'Hea, 2007). Additionally, remobilization of sediment-bound contaminants due to tidal currents, particularly in areas with a large natural tidal range, has frequently occurred (Duquesne et al., 2006). Another natural disturbance is bioturbation and bio-irrigation. According to Gilbert et al. (1994) and Dahl Rasmussen et al. (1998), bioturbation enhances the adsorption of contaminants by sediments and also releases dissolved and particulate contaminants from contaminated sediment into the water column.

Dredging and disposal of contaminated sediments are the common anthropogenic activities causing RCS in the aquatic environment. As a result, substantial quantities of contaminants (e.g. heavy metals) may be released from contaminated sediment into the water column (Latimar et al., 1999; Olsen et al., 1982). Although in many cases, oxygenated water during resuspension event may oxidize iron and manganese, which can scavenge some contaminants into the bound forms (Jones-Lee and Lee, 2005), the majority of studies indicated that mobility and availability of contaminants in aquatic environments typically was enhanced during dredging and disposal of contaminated sediments. Adverse effects of contaminated sediment dredging, however, are limited in spatial and temporal extents (Roberts, 2012). Vessel movement is another type of human activity causing RCS, which is more noticeable in shallow harbours. Propeller wash is the frequent mechanism for RCS in this case (Gucinski, 1982). Large vessels can also generate solitary waves. Studies conducted by Schoellhamer (1996) in a shallow bay in Florida suggested that the waves created by large vessels persist for only a few minutes. However, high recurrences at the site considerably caused RCS.

Resuspension of contaminated sediments is an uncontrolled and unavoidable event in many cases. In this study, a shallow harbour was the focus where deposition of sediments has occurred with significant amounts of pollutants. Therefore, shallowness and contaminated sediments in this area are the challenging issues. Since in most of the cases, harbours are protected by breakwaters, storms and waves are not the primary reason for RCS in these areas. However, periodical dredging of sediments and movement of the vessels maybe the main cause of RCS.

Dredging the contaminated sediment can increase the risk of mobility and availability of contaminants in the harbours and off site migration due to the generation of sediment plumes. Additionally, the disposal of contaminated dredged material can be very costly and not every landfill has space (Zaiger, 2003). Therefore, development of a new technique offering greater flexibility to reduce the adverse effects of natural RCS, and reduce the need for dredging and disposal of contaminated sediment is highly desirable.

In order to address these issues at shallow harbours, a new management strategy is introduced and evaluated in this research, which is called 'resuspension technique'. This is an *in situ* physical separation technique, which targets and removes highly contaminated sediment from the aquatic environments. The concept of the resuspension method is that finer sediments (i.e. clay and silt) have more tendency to adsorb the contamination (Mulligan et al., 2009). Due to the high specific surface adsorption and ionic attraction, finer sediments tend to have a relatively higher concentration of contaminants (Zhang et al., 2009). Suspended sediment and the organic components of sediment can also play the role of scavengers for organic and inorganic contamination (Fukue et al., 2007). Therefore, the finer sediments carry higher concentrations of pollutants. In the resuspension process, finer sediments are targeted for removal by a suspension mechanism. Through a powerful air jet, in a confined water column, sediments are resuspended over a short period of the time and then will settle based on size. The suspended solids containing higher concentrations of heavy metals can then be removed from the aquatic ecosystem by pumping and filtering.

Japanese scientists were the first to employ resuspension as a remediation technique for organic pollutant removal from contaminated sediments. Fukue et al. (2012) applied the resuspension in a Fukuyama city harbour in order to decrease the rate of eutrophication and improve the quality of water and sediment. In this study, however, heavy metal removal from contaminated sediment was evaluated. Heavy metals adsorbed by sediments are of particular concern due to their mobility and toxicity in the aquatic ecosystem. Binding of heavy metals to the contaminated sediment may not be permanent and can release those inorganic pollutants through uncontrolled RCS. Contaminated sediments with heavy metals are not only a short-term threat to biodiversity but they also can serve as long-term exposure sources to ecosystems (Ghosh et al., 2011).

To improve the quality of sediments, the resuspension technique is designed to remove a small percentage of sediment, believed to contain the largest concentration of contaminants. Risk of mobility and availability of heavy metals in future dredging operations can be reduced and handling fees for disposal of contaminated sediments in landfills can be minimized. Considering this fact that open water disposal of highly contaminated sediments is not allowed in many countries, this method could be a solution to reduce dewatering, transport and landfill tipping fees for contaminated sediment, which are the major costs in the dredging operation. Moreover, the threat of RCS at the site posed to the aquatic environment can be reduced. The objective of this study was to evaluate the feasibility of resuspension technique as a new approach for remediation of contaminated sediment and viable option to reduce the risk of remobilization of contaminants in harbours due to RCS.

4.2 Materials and methods

4.2.1 Study area

A harbour on the northern bank of the St. Lawrence River in the province of Quebec, Canada, was selected for this study. The area of the harbour was approximately 15,000 m^2. Two floating and one solid breakwaters have protected the harbour from the waves. Consequently, there was a quasi-steady flow around the passageways and dock area, which led to deposition of sediments (Figure 4.1). The boat maintenance area was located at the northwest part of the harbour and was mainly used for repairing and repainting in the summer and storing the boats in the winter.

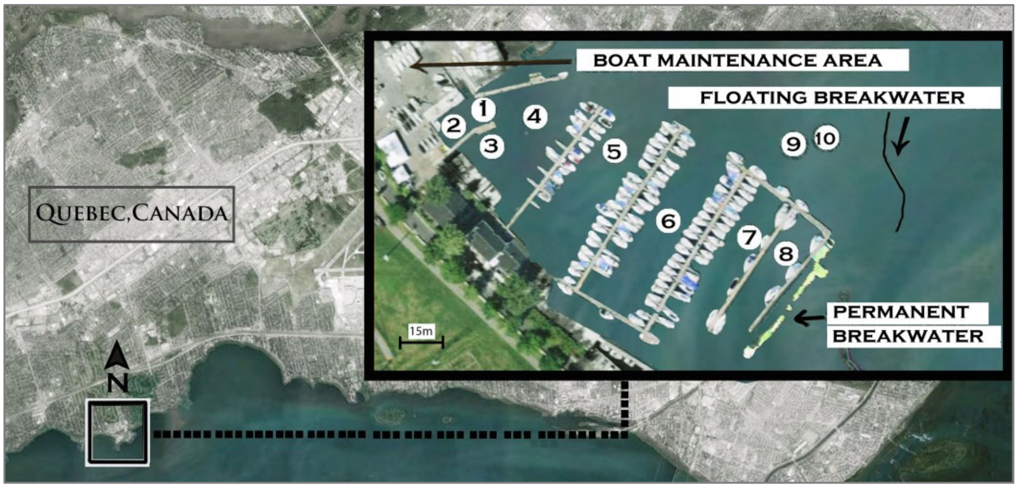

Figure 4.1 Selected stations for sampling in the harbour area. Quebec, Canada.

Station numbers (1 to 10) are representative of sample locations. Those places are potential locations for dredging the sediments.

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 14 years since dredging was employed in this harbor. The water depth varied between 0.6 meters (around the dock area) and 3 meters (around the floating breakwater). However, prior to dredging, the quality of sediments needed to be assessed to evaluate management options. Ten different stations along the passageways and the dock area, which are the most potential places for dredging, were chosen for analysis. The selected stations also covered the paths, where yachts usually take for accessing the docks. These stations are shown on the map in Figure 4.1. Assessment of the quality of sediment samples from selected stations was performed according to the guidelines issued by Environment Canada and the Ministère du développement durable, de l'environnement et des parcs (Environment Canada and MDDEP, 2007).

4.2.2 Sampling

A set of surface sediment samples was obtained at the selected stations (Figure 4.1) based on the sediment-sampling guide for dredging and marine engineering projects in the St. Lawrence River (Environment Canada, 2002). The samples were taken with a Birge-Ekman grab from the surface of the sediments to a vertical distance to a maximum depth of 10-centimeter. Each sample was about 1±0.2 kilogram. The sampler consists of a stainless steel box with a pair of jaws and free-moving hinged flaps (Gouws and Coetzee, 1997). The jaws can trap sediments as soon as they reach the river bottom and keep the sediments in the stainless steel box to prevent washout during retrieval. Sediment samples were transferred and kept in the airtight polyethylene bottles and placed in an ice-cooled box. They were transferred to the freezer at the Environmental Engineering laboratory at Concordia University and were used for subsequent experiments.

River water sample collection was carried out using a motorboat in the harbour and samples were stored in the pre-cleaned polypropylene bottles. For dissolved metal analyses, they were passed through a 0.45 μm filter and then acidified with 0.5 M HNO_3 and 0.3 M HCl (U.S. Environmental Protection Agency, 1992).

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

4.2.3 Experimental design

The setup for resuspension of sediment contained three parts. The first part is resuspension/aeration, which was performed by an air jet connected to the central compressing air system in the laboratory. The central air compressor provided up to 400 kPa. However, the velocity of the air injected to the water was around 10 meter per second, to create a strong turbulence in a reactor. The head of the air injector was submerged and fixed about 5 cm above the sediment in the reactor. The reactor was a vertical plexiglas cylinder with 20 and 60-centimeter in diameter and height, respectively (Figure 4.2). The sediment sample was deposited first into the reactor followed by adding tap water. The ratio of the sediment sample to tap water was 1:10 (v/v) in the reactor. Tap water was used in all experiments since it has relatively similar characteristics to the river freshwater samples. Sediments were suspended in the reactor over the air injection for two hours. The air injection caused increasing approximately 30% in the volume of the water/sediment in the reactor.

Figure 4.2 Reactor with a Plexiglas cylinder and air jet arm connected to the central air compressor.

For the second part, aeration was stopped after two hours of suspension and the coarser sediments were allowed to settle. In about 15 minutes, the sand and coarse silt were almost completely settled. Then, by using a pump above the reactor, 30% of the slurry in the reactor containing the water and suspended particulate matter (SPM) and some insoluble organic matter was removed and in the third part of experiments they were conveyed to the filter system. The filter system was comprised of two layers of a non-woven geotextile (Titan TE-GTP 250) with apparent opening size of 90 microns. Fukue et al. (2012) suggested that 15 percent of the suspended solids should be removed after resuspension for the best result at that site (Fukuyama city harbor) to achieve the desired decontamination level. However, in this study 30% of the slurry volume including water and SPM in the reactor was removed by the pump with maximum flow rate of 22 liters per minute. The suction pipe for pumping was located in the middle of the water column depth and it took less than a minute to remove 30% of the slurry from the reactor. The removed slurry contains between 10 to 15 percent solids.

It should be noted that surface sediments, in some stations, contained a significant amount of natural organic matter (NOM) such as algae (up to a quarter of the weight). NOM was not removed prior to the resuspension test since naturally they are a part of the surface sediment at the site. A sample of sediment was obtained for each experiment (about 20 g) from the reactor before and after the test and analyzed. Additionally, a SPM sample was taken from the reservoir. Almost all SPM was settled in the reservoir 48 hours after filtration. Filtration chiefly trapped the tiny pieces of NOM and likely the SPM larger than 90 microns that were pumped into the filtration system. A schematic of the whole resuspension procedure is presented in Figure 4.3.

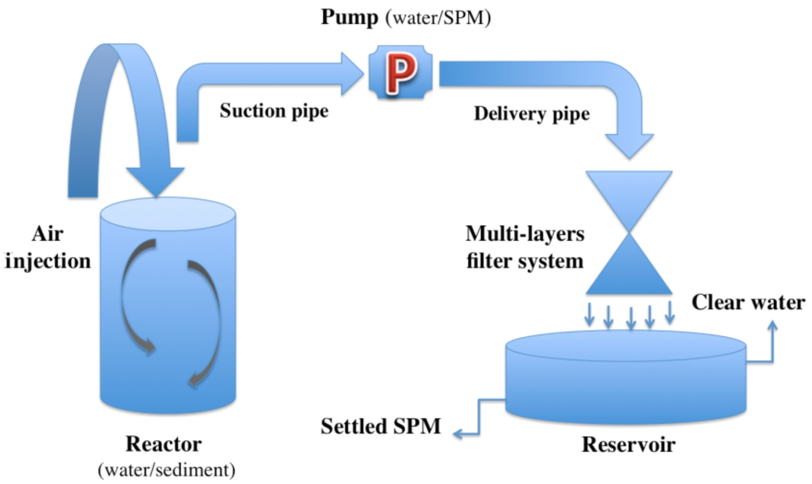

Figure 4.3 Schematic of the procedure for resuspending the sediments contains 3 steps: aeration, pumping the slurry and filtration.

4.2.4 Analytical parameters

Among the 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 a laser scattering analyzer (HORIBA, LA-950V2). D_{50} (50% of the particles are less than this size) and the percentage of clay, silt and sand for each sample was determined.

pH, oxidation-reduction potential (ORP) and dissolved oxygen (DO) were measured during the resuspension test by a multiparameter meter (HANNA HI 9828). They are common parameters measured for water quality purposes. Loss on ignition (LOI) was another parameter chosen to estimate the organic and carbonate content in the sediment. According to the ASTM D2974-00 method (ASTM, 2000), oven dried sediment samples (105°C) were placed in a furnace at 550° C for 4 hours. After the sediments were cooled in a desiccator and their weights (w) were measured, loss on ignition (%) in each sample was calculated based on the following equation:

$$LOI\ \% = \left(\left(W_{105^oC} - W_{550^oC}\right)/W_{105^oC}\right) \times 100 \qquad [4.1]$$

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 (i.e. sediment), acid digestion was required. The EPA 3050B method was the protocol used to digest the solid samples and prepare them for using in ICP-MS. For digestion, 1 or 2 grams of wet sample or 1 gram of the dried sample were digested with repeated additions of nitric acid (HNO_3, 70% - trace metal grade) and hydrogen peroxide (H_2O_2, 30%) as well as hydrochloric acid (HCl, 35%) at the end of the digestion (U.S. Environmental Protection Agency, 1996). The digested samples were kept in the fridge around 4°C and were analyzed later.

Measurement of acid-volatile sulfide (AVS) concentrations in selected sediment samples was made according to the direct method described by Simpson (2001). Briefly, sediment samples thawed and dried overnight in a nitrogen gas-filled glove box. About 0.1 g (dry wt.) of a sample (accurately weighted), transferred to a 50 milliliters centrifuge tube. 5 ml of methylene blue reagent (MBR - Simpson, 2001) was added to the sample and mixed in the tube with closed cap. Then it was centrifuged (by a Thermo Scientific IEC HN-SII-58012 Rotor System) for 2 min with 754 x g. The sample was allowed to sit for 90 min for the methylene blue color development. Sulfide standard solution (containing 0 to 0.1 M Na_2S), on the other hand, was prepared and 5 ml of MBR was added. Again after 90 min, both standards and samples were diluted with 1 M H_2SO_4 and then analyzed with a UV light spectrophotometer.

4.2.5 Sequential extraction test procedure

A sequential extraction test (SET) was employed on the basis of Yong et al. (1993). Heavy metal ions in sediments are partitioned between different fractions. Determining the concentration of metals in each fraction can provide detailed information about their physicochemical availability and mobilization (Filgueiras et al., 2002). The most available metals were found in the water soluble and exchangeable fractions by adding 8 ml of 1 M $MgCl_2$, pH 7.0, 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, with 5 hours shaking at room temperature. Metals bound to Fe-Mn oxides and hydroxides were removed by adding 20 ml of 0.04 M $NH_2OH.HCl$ 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 HNO_3 and 5 ml of 30% H_2O_2 (pH 2.0) were added at 85°C for 2 hours, followed by 3 ml of 30% H_2O_2 (pH 2.0) at 85 °C for 3 hours. Finally 5 ml of 3.2 M ammonium acetate in 20% (v/v) HNO_3 was added and then diluted to 20 ml at room temperature 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 HNO_3 + 750 ml deionized water) for 3 hours at 96°C. After each extraction step the suspensions were centrifuged with 1478 x g for 20 minutes. The supernatant was then filtered through a 0.45 μm polytetrafluoroethylene (PTFE) syringe filter to remove any remaining particles, before analysis by ICP-MS. Those samples that contain high amounts of a metal concentrations were diluted.

4.2.6 Sediment quality guidelines (SQG)

According to the guidelines (Environment Canada and Ministère du développement durable, 2007), the level of contamination for the management of dredged sediment was evaluated based on the Occasional Effect Level (OEL) and Frequent Effect Level (FEL). For substances 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 subsistence). For heavy metal content equal to or exceeding the FEL, open-water disposal is banned without any further tests. Sediments containing elements exceeding the FEL are highly contaminated and the site must be treated before any action as adverse effects are expected for the majority of benthic species (Environment Canada, 2007).

On the other hand, for remediation of contaminated aquatic sites, the PEL (probable effect level) and FEL are the two threshold values that can be used to provide guidance for remediation decisions. The PEL shows the contaminant level within which adverse biological effects are frequently observed. Based on the standard, the level of contamination below the PEL does not justify initiation of site remediation. However, for those above the PEL, evaluation of the contamination, risk assessment and determination of the remediation is required (Environment Canada, 2007). It is worth noting that the remediation target is the OEL for those contamination levels exceeding the PEL or FEL. Moreover, the presence of a single heavy metal in sediment samples that exceeds the quality criterion is sufficient to categorize sediments as contaminated. Table 4.1 presents the criteria for assessing the quality of sediment samples for heavy metals.

Table 4.1 Environment Canada (2007) criteria for assessment of sediment quality (mg/kg).

Standard levels	Cr	Co	Ni	Cu	Zn	As	Cd	Pb
OEL	57	18	47	63	170	8	1.7	52
PEL	90	-	-	200	310	17	3.5	91
FEL	120	-	-	700	770	23	12.0	150

The standard levels of Co and Ni were not reported. However because of the importance of those elements in sediment and its effects in aquatic environment, the geometric mean of the natural concentration of Co and Ni in pre-industrial sediment (13 and 29 mg/kg) and the natural concentration in postglacial clay (27 and 75 mg/kg) in St. Lawrence River were chosen as the OEL in Table 4.1, respectively (Environment Canada, 2007).

4.3 Results and discussion

4.3.1 Physicochemical characteristics of sediment samples before resuspensin

General characteristics of sediment samples were determined before the tests. Table 4.2 presents the physicochemical features of sediment samples from selected stations. Generally speaking, the pH was neutral at almost all stations. As it is expected, the surface samples contain significant organic materials as the loss of ignition (LOI) implies. The presence of organic materials in those stations located at the stationary parts of the harbour was more noticeable. Particle size distribution showed also the texture of the samples was very fine with D_{50} around 1.2 microns on average. Nevertheless, S1 had the coarsest texture and lowest organic content. The texture of this area was completely different from the rest of the stations. S1 is the area that usually receives the runoffs from land particularly from the maintenance area and this can be the reason for the presence of a significant percentage of sand (i.e. 17.5%). Therefore, if the D_{50} of S1 is not considered as a normal value, the average D_{50} of the sediment samples would be 0.61 microns.

The values of the ORP and DO in Table 4.2 implied that the surface sediments are oxic. According to the previous studies, a significant amount of acid-volatile sulfide (AVS) was not expected in the oxic sediment with positive redox potential values (Simpson et al., 2013; Fukue et al., 2007). However, AVS was measured in this study for four selected stations on the basis of Simpson (2001). The mean values of the AVS (± standard deviation) for stations 1 to 4 were 2.3±0.2, 1±0.2, 0.5±0.1 and 1.6±0.3 $\mu mol.g^{-1}$, respectively. It has been discovered that the presence of living aquatic plants can significantly decrease AVS concentration in sediment (Jacob and Otte, 2004; Almeida et al., 2005). This can explain a relatively higher AVS concentration in S1 than the other stations and generally low concentration of AVS in the harbour sediment. Additionally, Simpson et al. (2013) indicated that AVS is an ineffective factor in releasing the trace metals from contaminated sediments where they have been in a close contact with a more oxidized overlying water. Therefore, AVS was not considered as an influential factor for releasing the contaminants into overlying water during the resuspension tests in this study.

Table 4.2 Physiochemical characteristics of sediment samples.

St. No.	pH	ORP (mV)	DO (%)	LOI (%)	D_{50} (µm)	Particle Size Distribution (ASTM, 2006)		
						Clay[1] %	Silt[2] %	Sand[3] %
S 1	7.0	20.3	30.4	4.4	6.18	41.0	41.5	17.5
S 2	7.7	87.4	27.9	12.8	0.49	62.8	35.1	2.1
S 3	8.0	124.4	86.7	12.4	0.47	67.0	32.0	1.0
S 4	6.9	86.9	38.2	11.4	1.51	66.7	30.8	2.5
S 5	6.9	-61.3	27.5	10.7	0.48	66.9	32.0	1.1
S 6	6.6	33.7	0.0	12.5	0.43	75.3	23.5	1.2
S 7	7.0	116.0	23.2	7.6	1.59	65.5	30.1	4.4
S 8	7.0	99.4	52.3	11.1	0.44	70.0	25.4	4.6
S 9	7.1	60.7	12.1	7.9	0.37	80.8	19.2	0.0
S10	7.2	76.5	48.7	8.6	0.32	88.6	10.4	1.0

[1] Clay: < 2 µm

[2] Silt: 2 – 62.5 µm

[3] Sand: 62.5 – 2000 µm

4.3.2 Physicochemical characteristics of sediment samples during the test

The percentage of dissolved oxygen (DO) and the amount of oxidation-reduction potential (ORP) indicated that surface sediments were not anoxic before the test. However, during the resuspension, ORP not only remained positive but also improved after 48 hours. The enhancement of ORP was likely attributed to a rapid and significant increase in oxygen concentration in water during the resuspension. Figure 4.4 shows the variation of pH, ORP and DO during the resuspension and Table 4.3 also presents the changes of those parameters after 48 hours. The accuracy of the parameter's values is presented in Table 4.3 as well. The results of S10 were not shown in this table.

The pH was above 7 on average for all samples during the test. Additionally, it rose slightly after air injection in all experiments. The increase in the pH of the water is in agreement with some previous studies. As an example, Simpson et al. (1998) evaluated the effects of short-term resuspension on trace metal speciation. They employed seawater at first with initial pH 8.0, and upon addition of sediment the pH dropped to 7.7. However, adding the sediment to river water (similar to this study with initial pH 7.0) caused the pH to increase to 8.4 and then slowly during the resuspension pH decreased at a rate of 0.0009 pH.min^{-1}. The increase in pH upon adding the contaminated sediment to freshwater was mainly recognized to a significant increase in alkalinity of aquatic environment (Simpson et al., 1998). Generally, pH played a constructive role in the resuspension process in this study since keeping the pH above 7 - 7.5 could prevent remobilizing of heavy metals in the aqueous phase. The DO rapidly increased and reached about 80% ten minutes after air injection. However, the DO gradually decreased and reached the initial percent after 48 hours. In S4 exceptionally, DO drastically dropped. The increase of the oxygen demand in this sediment sample mainly by decomposition of natural organic materials was likely the reason.

ORP of the sediment samples was positive before the test except for S5 due to the shallowness of the water in the harbour. However the decomposition of a significant amount of organic matter can cause an adverse effect on the quality of water and the possible negative value of ORP.

Table 4.3 Variation of pH, ORP and DO during the resuspension test.

Parameters	S1	S2	S3	S4	S5	S6	S7	S8	S9
pH (±0.1)									
Mean (n=10)	7.7	7.8	8.0	7.4	7.4	7.1	7.3	7.5	7.5
Min.	7	7.5	7.4	6.6	6.9	6.5	6.8	7.0	7.1
Max.	7.9	7.9	8.2	7.8	7.7	7.4	7.6	7.7	7.8
Change after 48 h (%)	6.9	-2.1	-8.2	-1.2	0.7	-1.7	-2.9	2.2	0.6
ORP (±1.0 mV)									
Mean (n=10)	80.4	87.4	123.2	108.8	102.7	103.8	120	128.7	85.2
Min.	20.3	65.9	111.4	86.9	-61.3	33.7	85.2	99.4	60.7
Max.	99.5	137.2	152.4	127.3	173.3	138.3	165.7	175.3	105.0
Change after 48 h (%)	74.1	36.3	17.5	0.3	135.4	75.6	30.0	43.3	17.5
DO (±1.5 %)									
Mean (n=10)	70.8	76.4	84.1	62.7	63.9	61.8	65.9	75.0	59
Min.	30.4	27.9	50.2	5.8	13.5	0.0	23.2	52.3	0.0
Max.	88.6	94.9	96.4	87.7	85.4	87.5	80.8	85.6	83.5
Change after 48 h (%)	46.5	37.7	-72.7	-558.6	42.1	100.0	38.1	4.0	56.8

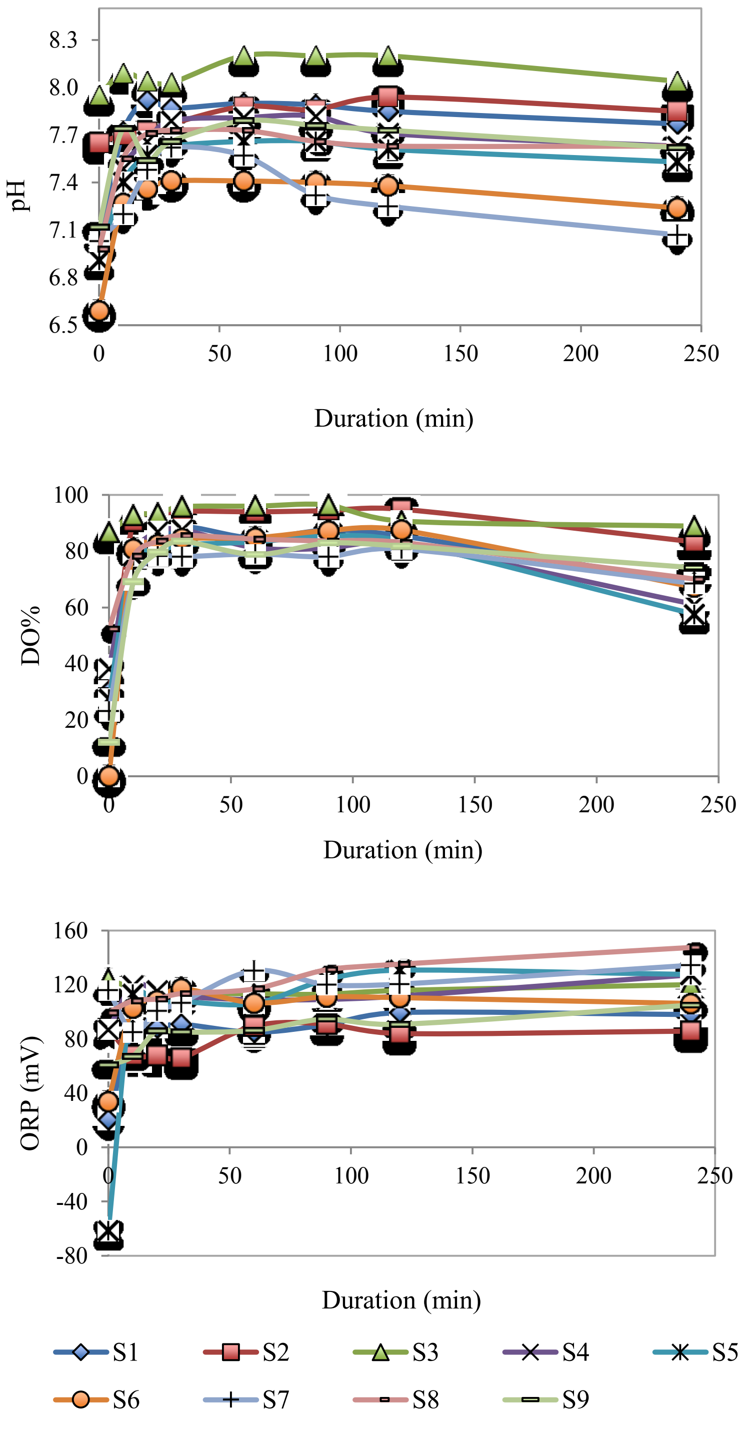

Figure 4.4 Variation of pH, DO (%) and ORP during 2 hours of resuspension of sediments.

4.3.3 Quality of the sediment before the test

To assess the quality of sediment samples, the total concentrations of the eight heavy metals and metalloids were determined. The references for quality assessment were OEL, PEL and FEL according to the Environment Canada guidelines. Table 4.4 shows the total concentration of selected heavy metals. Bolded and highlighted numbers are the concentrations exceeding the OEL and PEL respectively. Concentrations above FEL were not detected.

Table 4.4 Total concentrations of selected heavy metals before the resuspension test (mg/kg).

St. No.	Cr	Co	Ni	Cu	Zn	As	Cd	Pb
S1	37	9	22	**219**	**204**	6.1	0.5	**134**
S2	**67**	14	37	**165**	**311**	7.5	0.8	**53**
S3	**74**	13	**64**[1]	**138**	**563**	6.6	0.8	**77**
S4	**71**	15	39	**137**	**372**	**9.4**	0.9	**69**
S5	**72**	18	46	59	**305**	**8.4**	0.9	37
S6	**67**	17	43	**70**	**266**	6.4	0.8	33
S7	**62**	15	38	47	**205**	6.0	0.8	33
S8	**99**	18	46	**67**	**334**	**18**	1.1	**55**
S9	**74**	15	39	**75**	**201**	**11**	0.8	34
S10	**62**	13	38	59	**185**	6.3	1.3	58

[1] This value was about 35% more than the OEL (the only Ni reference value that is reported).

Based on the total concentration of heavy metals shown in Table 4.4, Zn, Cr and Cu are the main contaminants detected in the sediment samples. Pb and As also showed high concentrations in some stations. Half of the samples (five stations) contained the elements exceeding the PEL. The other stations, however, were categorized as contaminated sediments within which dredging is allowed but open water disposal can only be considered an acceptable option if the toxicity test demonstrates that the sediment will not adversely affect the receiving environment (Environment Canada, 2007).

Beside the different standard levels, the background levels of elements also should be taken into account to determine the actual contamination. According to the definition, if the concentration of substances exceeds the background level observed prior to industrialization, and is high enough to have an adverse effect on benthic organisms, they can be called contamination (Environment Canada, 1993). Results from X-ray diffraction (XRD) for some sediment samples, implied that the mineral fractions and physical properties (i.e. particle size distribution) of sediments in the harbour is relatively similar to postglacial clays in the St. Lawrence River rather than pre-industrial sediments. These clays typically were deposited earlier in a marine context. However bottom and bank erosion and deposition in the inner part of the river contributes significantly to the supply of fine particles in recent sediments (Pelletier and Lepage, 2002). Therefore, the natural levels of heavy metals in postglacial clays were employed as a reference concentration (Table 4.5).

Table 4.5 Natural level of selected heavy metals in postglacial clay-St. Lawrence River (mg/kg) (Environment Canada, 2007).

	Cr	Co	Ni	Cu	Zn	As	Cd	Pb
Postglacial Clay	150	27	75	54	150	8	0.2	16

The Exceeding Index (EI) is defined based on the definition of enrichment factor applied by Zhang and Liu (2002) and Yuan et al. (2012). The EI is the proportion of total concentration of each metal compared to its natural concentration in postglacial clays. If the value of EI is equal or less than 2, this indicates that the heavy metal is provided from crustal contribution in the sediment mainly by weathering or bank erosion in the river. On the other hand, the EI value greater than 2 can be considered as the contribution of non-crustal resources delivered by either natural process (i.e. biota activities) and/or anthropogenic activities. Figure 4.5 presents the EI for eight selected heavy metals in the sediment samples.

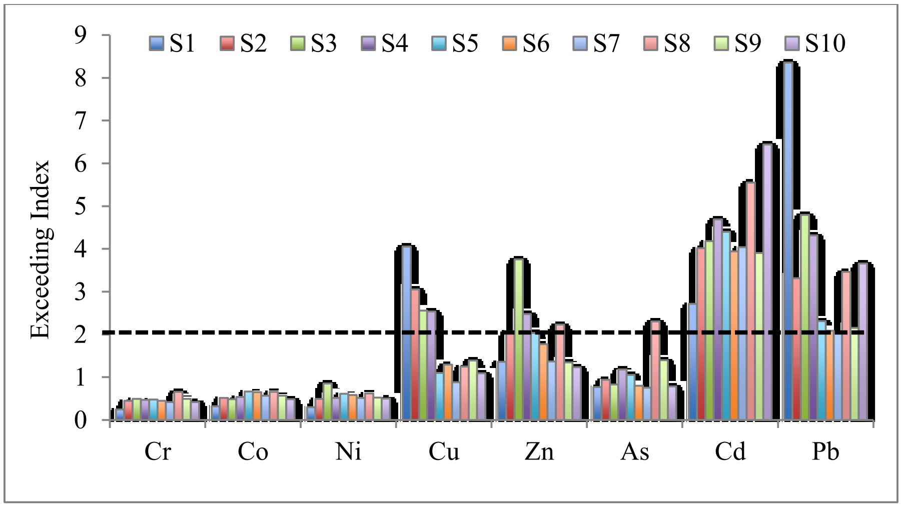

Figure 4.5 EI for selected heavy metals in sediment samples.

According to the EI results, Cd and Pb are the main elements that exceed their natural levels followed by Zn and Cu. Since Zn, Cu and Pb already passed OEL and PEL in some stations, they are considered as contaminants. Cd also showed a high EI in all stations on average (i.e. about 4.3), although its concentration did not exceed even the OEL. Generally, stations 1, 3 and 4 were the most contaminated locations as expected. These stations received the runoffs from the maintenance area, which mainly contain the components of antifouling paint. Antifouling paint is usually applied on the hull of the boats to prevent the growth and colonization of river microorganisms (Yebra et al., 2004; Braithwaite et al., 2007). Copper, zinc, lead and cadmium are the most common components of many antifouling paint formulations (Simpson et al., 2013). Recently due to the 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 cadmium play a key role as an anti-corrosive in anti-rust paints. 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 and eventually adsorption by the sediments.

4.3.4 Resuspension effects on the quality of contaminated sediment

Table 4.6 shows the total concentration of heavy metals in the sediment samples after two hours of resuspension and removing suspended particulate matters (SPM) from the reactor. Similar to Table 4.4, Table 4.6 shows bold and highlighted numbers that are the concentrations exceeding the OEL and PEL respectively. The results indicated that resuspension technique was successful in reducing the concentration of heavy metals in all samples on average. More precisely, all metal concentrations were decreased below the PEL except for Zn at S3, which is slightly above the PEL. There were 6 heavy metals with concentrations above the PEL on 5 stations before the test and they were decreased to one metal (i.e. Zn) in one station. Even in some cases (e.g., nickel) the PEL was reduced to below the OEL and for S6, for example, open water disposal is allowed without any further tests (i.e. toxicity test) after resuspension.

Table 4.6 Total concentration of selected heavy metals after the resuspension test (mg/kg).

St. No.	Cr	Co	Ni	Cu	Zn	As	Cd	Pb
S1	24	6	14	**160**	110	5.7	0.3	**65**
S2	**60**	13	**47**	**159**	**303**	7.0	0.8	51
S3	**72**	13	37	**108**	**331**	7.4	0.9	**73**
S4	41	8	20	**89**	157	4.4	0.5	41
S5	**60**	14	37	**65**	**224**	6.4	0.8	35
S6	36	9	22	29	137	3.7	0.4	19
S7	**60**	15	37	40	**199**	5.4	0.8	32
S8	**79**	14	**49**	61	**240**	**10**	0.8	45
S9	**59**	15	36	42	**195**	6.7	0.8	41
S10	51	14	34	41	**181**	5.7	0.8	36

The total concentrations of heavy metals in SPMs were also determined (Table 4.7). It is worth mentioning that the SPM size distribution was between 0.1 and 1 micron (clay and colloids) in all sediment samples. To assess the quality of SPMs, similar to the previous samples, OEL and PEL were used as references, which are shown by bold and highlighted numbers, respectively. SPMs were more contaminated than the bulk sediment samples as it was expected. To compare the metal concentrations in SPMs and sediments after the test, the enrichment factor (EF) was used as applied by Zheng et al. (2013). EF was calculated using the formula EF = M_{SPM} / $M_{Sed\text{-}A}$, in which M_{SPM} and $M_{Sed\text{-}A}$ are the concentrations of heavy metals in SPM and sediment samples after the resuspension tests. Therefore, for those metals with EF value above unity, removal of SPM from aquatic environment by the resuspension process was useful for reducing the contamination. If more SPM is removed, fewer contaminants remain in the environment.

Table 4.7 Total concentration of selected heavy metals in SPMs (mg/kg).

St. No.	Cr	Co	Ni	Cu	Zn	As	Cd	Pb
S1	**79**	**18**	**54**	**208**	**359**	**10**	1.0	**119**
S2	**72**	**17**	46	**84**	**272**	5.5	0.6	39
S3	**77**	**15**	44	**109**	**379**	7.3	0.8	**66**
S4	**73**	**17**	**48**	**144**	**342**	**8.4**	0.8	**62**
S5	**76**	**19**	**50**	**95**	**237**	6.5	0.6	34
S6	**73**	**19**	38	**79**	158	**25**	0.7	15
S7	**75**	**18**	**50**	**110**	**340**	5.7	0.6	38
S8	**67**	**15**	**60**	**132**	**310**	**8.5**	0.6	38
S9	**72**	**17**	**47**	**92**	**234**	**8.1**	0.7	52
S10	**74**	**17**	**65**	54	**264**	5.9	0.8	37

Table 4.8 presents the EF values of heavy metals for sediment samples and shows that the EF appeared in the following order: As > Ni > Cu > Co > Cr > Zn >> Cd > Pb. For all elements, average EF values were above one. However EF values of Cd and Pb were significantly lower than the rest of elements (more than 33% lower than the average of other metal's EF), which implied that the removal of Pb and Cd in some stations might not be very effective by the resuspension process. Those EF values of less than unity mainly belonged to Cd and Pb. However there was an EF = 0.5 for Cu in S2, which seems unusual. The presence of organic matter in the reactor may cause a lower EF value in this sediment sample since Cu more than any other heavy metals has a tendency to be adsorbed by organic matter (Sundaray et al., 2011). However, further tests are required to show the role of OM in S2. In contrast, the high EF values (e.g. S1, S4 and S6) could be because of the higher percentage of postglacial clays in some sediment samples, particularly for Ni and As.

Table 4.8 Values of Enrichment Factor for selected heavy metals in sediment samples.

St. No.	Cr	Co	Ni	Cu	Zn	As	Cd	Pb
S1	3.3	3.1	3.9	1.3	3.3	1.9	3.8	1.8
S2	1.2	1.3	1.0	0.5	0.9	0.8	0.8	0.8
S3	1.1	1.1	1.2	1.0	1.1	1.0	0.9	0.9
S4	1.8	2.1	2.4	1.6	2.2	1.9	1.9	1.5
S5	1.3	1.4	1.3	1.5	1.1	1.0	0.8	1.0
S6	2.0	2.3	1.7	2.8	1.2	6.9	1.6	0.8
S7	1.3	1.2	1.4	2.8	1.7	1.1	0.8	1.2
S8	0.9	1.1	1.2	2.2	1.3	0.8	0.8	0.9
S9	1.2	1.2	1.3	2.2	1.2	1.2	0.9	1.3
S10	1.4	1.3	1.9	1.3	1.5	1.0	1.0	1.0
Mean	**1.5**	**1.6**	**1.7**	**1.7**	**1.5**	**1.8**	**1.3**	**1.1**

Removal efficiency (RE) was also used (equation 2) to present the capability of resuspension method for removing pollutants from aquatic environment. A positive value of RE shows that resuspension was successful for reducing the concentration of that contaminant.

$$RE\ (\%) = \frac{(M_B - M_A)}{M_B} \times 100 \qquad [4.2]$$

In equation [4.2], M_B and M_A are the total concentrations of heavy metal before and after resuspension, respectively. Table 4.9 presents the RE values for all sediment samples. Generally, RE values on average were positive for all heavy metals (with a minimum 17.6% for Co and a maximum for 25.9% for Zn), which endorsed the capability of this technique to reduce the concentration of pollutants. Zinc, as the main contaminant, had positive RE values for all sediment samples. However, the RE values for a few metals in some samples were negative, which means that the resuspension for a few sediment samples had an adverse effect. This can be explained by the natural level of metal concentrations in the sediment. According to the results from Figure 4.5, Cr, Co, Ni and As (except S8) were below EI = 2 and considered as non-contaminants. Basically, the metal content in sediment at or around the background level varies considerably from one site to another (Environment Canada, 1993), which means that even in multiple samples from one station, the concentration of a metal could show different values about or below background level. Consequently, RE values can be negative or positive after resuspension for those elemental concentrations around the natural levels (NL). RE negative values for Cu, As and Pb at S5, S3 and S9 respectively, corresponded to those concentrations below or around background levels. In particular, As after resuspension at S3 was still below NL. The Cu level at S5 slightly increased above NL after resuspension but the difference was not significant.

Table 4.9 Removal efficiency (%) for selected heavy metals in sediment samples.

St. No.	Cr	Co	Ni	Cu	Zn	As	Cd	Pb
S1	36.1	33.7	38.2	26.9	46.1	7.7	49.8	51.2
S2	10.3	3.6	-27.4	3.8	2.5	7.5	2.9	3.7
S3	2.2	-2.8	42.6	21.5	41.3	-12.5	-11.1	5.2
S4	41.6	46.6	48.4	34.8	57.9	53.6	51.2	40.4
S5	16.1	22.6	18.8	-9.4	26.6	23.6	9.5	4.5
S6	46.7	50.8	49	59.1	48.3	41.9	45.1	43.2
S7	4.1	3.3	4.3	16.2	3.1	9.8	5.2	3.4
S8	20.8	19.9	-6.6	9.9	28.1	43.9	24.0	19
S9	19.5	4.0	6.8	43.7	3.0	39.9	2.9	-20.2
S10	17.5	-5.9	9.4	31.1	2.2	9.0	37.9	37.9

In general, high removal efficiency of heavy metals was mainly observed for sediment samples with high EF values (i.e. S1, S4 and S6). Conversely, low RE was achieved in sediment samples with low EF values (i.e. S2, S3 and S9) in the resuspension experiments. Analysis of sequential extraction tests of sediment samples was then performed to better understand the removal mechanisms through SPMs.

4.3.5 Sequential extraction test analysis

The sequential extraction test (SET) was employed to determine the heavy metal fractionations in sediment samples before the resuspension as well as in the SPMs. SET provides information on potentially available metals bound to the sediment matrix (Stone and Marsalek, 1996). In this study, having knowledge on the distribution of the heavy metals in the SPM fractions was crucial. Regardless of the efficiency of this technique to reduce the total concentration of heavy metals in sediment, the mechanism of metal removal through SPM should be evaluated. In other words, the fractionation of metals, which were removed by SPM, can be quite helpful to examine the capability of this technique for remediation of different heavy metals with different bonds to the sediment.

Stations number one to four, which had the most contaminated sediment samples, in the vicinity of the maintenance area were selected for SET. Sediment samples before the tests, which were shown in Figure 4.6 by Sed-B, and SPM after the resuspension test were analyzed by SET. Five distinct fractions were identified as it is mentioned in section 4.2.5. However in Figure 4.6, three categories were presented for the main contaminants (i.e., Cu, Zn, Cd and Pb).

The first category is the potentially available heavy metals bound to fractions one and two (i.e. exchangeable and acid soluble fractions). These fractions are susceptible to changes in pH, and are considered readily and potentially available through changes in the environmental conditions (Wong et al., 2002; Gauthreax et al., 1998). The second category is metals bound to the reducible fraction. Heavy metals associated with hydrous oxides of iron and manganese are represented in this category by F3 in Figure 4.6. Iron and manganese oxides play a crucial role in scavenging the contaminants in aqueous phase through mechanisms such as coprecipitatation, surface complex formation, adsorption and etc. (Gwendy, 1996). However, under some circumstances (e.g. aeration of anoxic sediment), reduction of Fe (III) and Mn (IV) could occur and some adsorbed heavy metals could be released into the aquatic environment (Filgueiras et al., 2002). The third category belongs to the most stable fractions under normal sediment condition, which are oxidizable (organic) and residual fractions. The metals bound to these fractions are environmentally unavailable and release of the bond could happen under harsh oxidizing conditions with a drastic drop in pH (Clevenger, 1990; Gauthreaux et al., 1998; Davidson et al., 1998).

In Figure 4.6, the left column presents the SET results of sediment samples for selected stations before the resuspension treatment and the right column shows the corresponding SPM in those stations. It is worth mentioning that the performance of the resuspension technique is quite dependent on the heavy metal removal through SPM. Therefore, identifying the metal fractionations in SPM is crucial in this study.

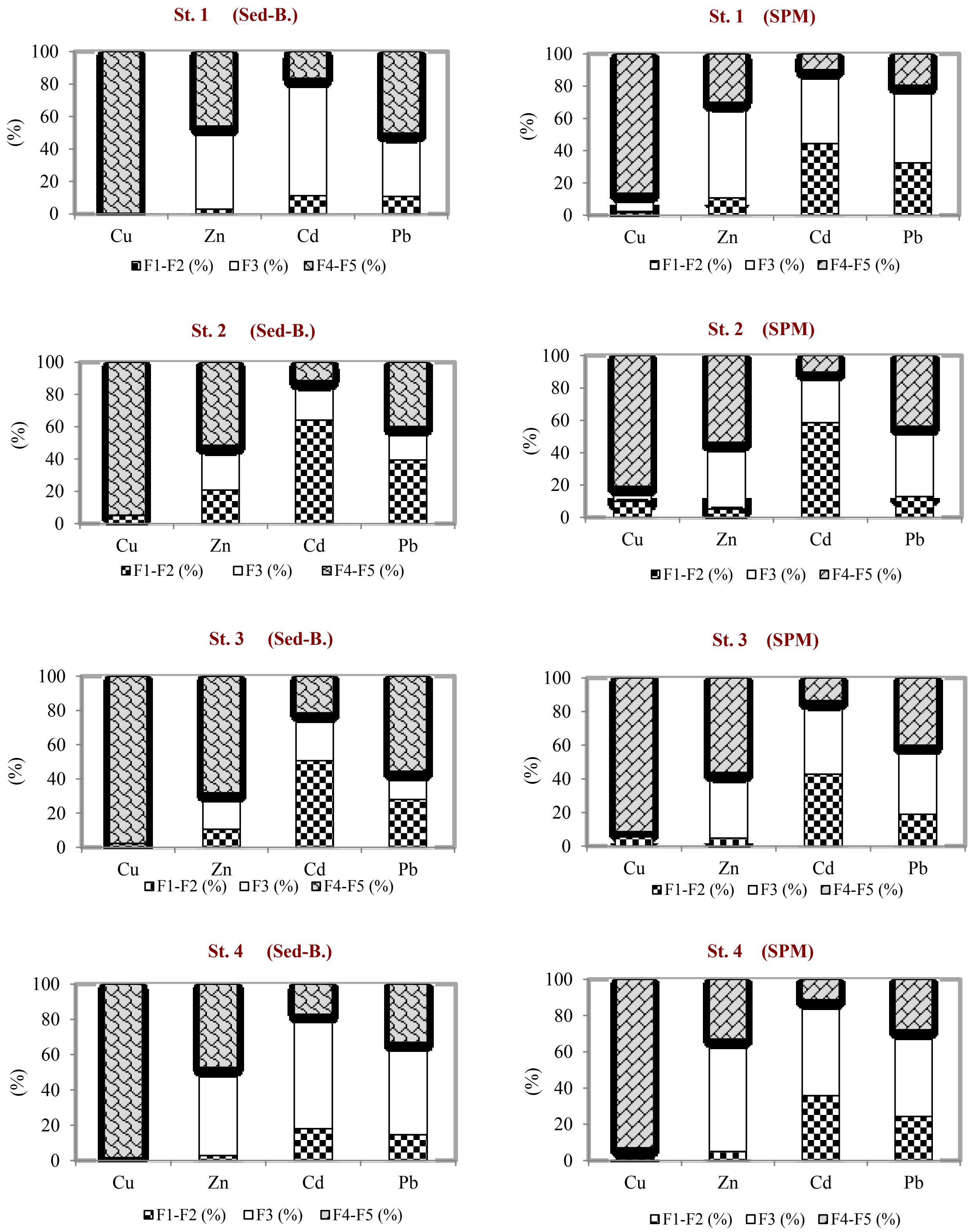

Figure 4.6 Results of sequential extraction test (SET) for selected stations. [F1-F2 (%): potentially available metals in exchangeable and acid soluble fractions, F3 (%): metals bound to Fe-Mn oxides/hydrous oxides, F4-F5 (%): the most stable fractions contain metals bound to organic and residual fractions]

Based on Figure 4.6, the percentage of copper and zinc concentrations in F3 (Fe-Mn hydrous oxides) were higher in SPM than the bulk sediment samples, particularly for zinc. Moreover, copper was found mostly in stable fractions (organic and residual fractions) in bulk sediment with average of about 97%. However in SPM, copper concentrations was found in more available fractions (9% more than the bulk sediment), mainly in F3, on average. Previous studies on metal fractionation during resuspension indicated the fact that by increasing the particle-particle collision during the resuspension it is very likely that some metals such as copper, zinc and lead in the SPM were transferred from more stable to more labile fractions (Huang et al., 2012). Additionally, resuspension potentially can facilitate desorption and release of weakly bound metals in the water column. On the other hand, metal fractionation showed a high variation in changing environmental conditions such as pH and redox potential (Apps et al., 2011). pH, particularly in resuspension, played a key role by influencing the rate of oxidation of Fe (II) and Mn (II) and also the binding of metals to the organic based metal binding phase (Atkinson et al., 2007). Since pH in this study only slightly increased during the resuspension (by 7.5% on average) and then remained above 7.0, metal scavenging could be elevated mainly by iron and manganese oxides. Monitoring has shown that under the increase of the concentration of oxygen in the overlying water, in the sediment with ORP > 80, Fe (II) and Mn (II) oxidize and become Fe (III) and Mn (IV) and precipitation may occur. As a consequence, metals that became available in the aqueous phase can be adsorbed to these precipitates (Borch et al., 2009; Simpson et al., 2004). Another study on contaminated coastal sediment under changing pH condition illustrated that the mobility of metals from sediment matrix to the overlying water was correlated with reduction in pH and vice versa (Wang et al., 2015). This procedure may explain the reason that F3 in SPM had a critical role than the bulk sediment. In other words, the released metals during the resuspension in water column could probably re-adsorb or coprecipitate by Fe-Mn oxide and because of the high specific surface area of SPM, they were all removed through SPM removal from the aquatic environment.

Cadmium and lead behaved differently. The percentage of Cd and Pb concentrations in the stable fractions in SPM were slightly lower than the bulk sediment samples. In stations number one and four, the availability of Cd and Pb was significantly higher than the bulk sediments. It is worth mentioning that the available concentrations of Cd and Pb in bulk sediment samples were drastically higher, which could pose a potential risk to aquatic ecosystem health in the river.

Therefore, in those stations the resuspension technique was successful for removing a portion of contaminants with high levels of concentration in environmentally available fractions through SPM removal. Moreover, EF values in these stations were relatively high, which subsequently led to a higher RE. Therefore, for those sediment samples with high EF values, SPM have greater tendency to adsorb anthropogenic sources' contaminants. Since more recently added metals were expected to be enriched in outer layers or adsorbed to more labile fractions (Simpson et al., 1998), SPM could show better performance than the bulk sediment and adsorbs Cd and Pb mainly in environmentally available fractions.

On the other hand, in stations number two and three, the availability of Cd and Pb in SPM is slightly lower than the bulk sediment, although they were still significantly high. Fe-Mn oxide-hydroxide in these stations again showed a dominant role in enhancing the metal scavenging during the resuspension. F3 in stations two and three in SPM were higher than bulk sediment by 29% and 54.5% on average for Cd and Pb, respectively. The same procedure more likely happens for weakly bound Cd and Pb in these stations. They remobilized in the aqueous phase and after that because of the Fe-Mn oxide presence most of them are scavenged through a combination of coprecipitation, adsorption and surface complex formation mechanisms. The results are in agreement with previous studies in oxic sediment, which demonstrated that Fe and Mn oxide/hydroxides along with organic matter are important binding sites for heavy metals (Zoumis et al., 2001; Fan et al., 2002). Unlike the sediment samples from stations one and four, sediment samples in stations two and three showed low EF values and subsequently low RE. Therefore, SPM did not adsorb contaminants from the rest of the bulk sediments. As a result, concentrations of Cd and Pb in SPM were lower than the bulk sediment and consequently showed lower RF values.

Since the EF results indicated that the SPM are suitable for removing the contaminants in this study, the resuspension process showed acceptable results for reducing the concentration of contaminants and enhancing the quality of sediments. However, the quality of water should be assessed after employing the resuspension technique.

4.3.6 Resuspension effects on the quality of water

The quality of water after two hours of resuspension of contaminated sediments was evaluated. As long as leaching of heavy metals in the aqueous phase is in the acceptable range, the resuspension process can be recommended as an alternative for remediation. To assess the quality of water after the test, the Canadian Water Quality Guidelines, CWQG (CCME, 1999) and national recommended water quality criteria (U.S. Environmental Protection Agency, 2009) were employed. The amounts of heavy metals, which were transferred to the overlying water in the reactor, mainly included the free ions in the pore water and weakly bound metals at the sediment surface. As an example, results of a study by Wang et al. (2015) indicated that the dominant source of dissolved metals in water column in contaminated costal sediments was the exchangeable metal form. It should be noted that in SET results in Figure 4.6, for Cd and Pb as the most potentially bioavailable metals, less than 0.5% of F1-F2% belonged to exchangeable fraction and almost all of the percentage of that category have belonged to the acid soluble fraction.

Contaminant leaching in each sample in this research was denoted as the difference between the concentration of heavy metals in the overlying water before and after the test. Table 4.10 presents the average values of leaching and the reference standards as well as detected dissolved heavy metals in the river and the tap water samples.

In general, the CWQG is a more restrictive standard than those of the EPA. However, the various standard values provide a wider view of short-term and long-term effects of contaminants in aquatic life and offer more options to compare. Results indicated that for Cr, Ni, Zn, As and Cd the concentrations of heavy metals in the overlying water were below the criterion continuous concentration (CCC or the chronic effect level) in both standards, while for Cu, it was more than the chronic effect level for some sensitive species. Water quality data collected in a Brazilian estuary also showed that Cu, Zn and As were slightly elevated in surface water after resuspension caused by anthropogenic activities (Urban et al., 2010). Zheng at al. (2013) illustrated that dissolved Zn in overlying water can be easily adsorbed by SPM. Cu is the only metal that showed levels higher than the CCC and CMC for the most sensitive species (Table 4.10).

Table 4.10 Leaching amounts and reference standards for assessment of water quality after resuspension test (μg/L)

	Cr	Co	Ni	Cu	Zn	As	Cd	Pb
Leaching								
Ave. (n=10)	0.41	0.05	0.46	6.06	1.53	0.51	0.02	0.76
Min.	0	0	0	0	0	0	0	0
Max.	1.53	0.26	1.67	28.25	6.99	2.72	0.07	3.46
Ave. River water (n=5)	0.95	0.19	2.01	10.14	5.59	2.64	0.01	0.51
Ave. Tap water (n=10)	0.2	0.08	1.89	3.61	5.54	2.25	0.006	0.19
CWQG	N/D	N/D	(25-150)	(variable[1])	30	5	1	(1-7)
CCC[2] (Chronic)	11[3]	N/D	52	1.45	120	150	0.25	2.5
CMC[4] (Acute)	16[3]	N/D	470	2.37-107,860[5]	120	340	2	65

[1] The CWQG for Cu is related to water hardness (as $CaCO_3$). Normally ranging between 2 to 4 μg/L. No fact sheet created.

[2] Criterion Continuous Concentrations (U.S. Environmental Protection Agency, 2009).

[3] Recommended values for chromium VI.

[4] Criterion Maximum Concentrations (U.S. Environmental Protection Agency, 2009).

[5] "Species Mean Acute Values (SMAVs) ranged from 2.37 μg/L for the most sensitive species '*Daphnia pulicaria'*, to 107,860 μg/L for the least sensitive species '*Notemigonus crysoleucas'* (U.S. Environmental Protection Agency, 2007).

Copper has a wide range of acute values since the criterion maximum concentration (CMC) of copper depends on species sensitivity (U.S. Environmental Protection Agency, 2007). However, the concentration of dissolved copper (from pore water and leaching from sediment) in overlying water is relatively high in comparison to CCC presented in Table 4.10. The main reason is the presence of organic matter (i.e. dissolved or passed through a 0.45 μm filter paper) in water samples taken from the reactor. According to the literature (Sundaray et al., 2011; Pagnanelli et al., 2004), the main Cu concentration exists in the organic fraction and consequently can affect the dissolved concentration of Cu in water samples. Moreover, the average concentration of Cu in river samples was naturally high (i.e. more than 10 μg/L).

Water turbidity was measured at the beginning of the experiment, which was 2.8 NTU. Depending on the texture of the sediment samples, it took approximately between 2 days and 7 days to return the water turbidity in the reactor to the original level.

The reasons of low leachability of metals into the water column after employing the resuspension method can be classified into 2 parts. 1) pH, which increased during the resuspension and prevented remobilizing of metals in aqueous phase. If anoxic sediment samples had been used in this study, the presence of sulfide complexes could affect the mobility of metals during the resuspension. Aeration could enhance redox potential and by oxidation of sulfide, pH could drop during the resuspension of anoxic sediment (Eggleton and Thomas, 2004). 2) Duration of resuspension was another factor, which was quite short in these experiments. Cantwell et al. (2008) illustrated that even in sulfidic sediment, low levels of metals are released to the aqueous phase during the short-term resuspension, which was 6 hours with five dynes per square centimeter pressure. Despite the majority of studies that implied the adverse effects of resuspension in anoxic sediment on remobilization of heavy metals in overlying water, some research has shown that even for an anoxic sediment, where redox potential and pH do not change drastically during a short-term resuspension, the release of metals is negligible (Forstner et al., 1989; Eggleton and Thomas, 2004).

4.4 Conclusions

Resuspension of contaminated sediments was successful in reducing the concentration of selected heavy metals in sediment samples from a harbour in the province of Quebec in Canada. The main goal of this study was to evaluate the feasibility of applying this technique as an alternative for common remediation techniques in a shallow harbour area. The laboratory scale experiments of resuspension technique showed that the concentrations of heavy metals in sediment samples decreased below PEL in almost all sediment samples. Removal efficiency was more than 21% on average for all samples with a maximum of 25.9% for Zn and a minimum of 17.6% for Co, which showed the capability of this technique to reduce the concentration of pollutants. The results of SET indicated that SPM with high EF values not only led to higher removal efficiency of metals, but also contained higher concentration of contaminants (i.e. Cd and Pb) in labile fractions. Therefore, the risk of metal availability could be reduced by applying the resuspension method.

The water quality after resuspension also was assessed. Except for copper, the leaching of the other selected heavy metals was below the CCC (i.e. chronic effects level). The dissolved concentration of copper was slightly above CCC and drastically below the CMC (i.e. acute effects level).

Unlike the common in situ techniques for remediation of contaminated sediment, this method could sufficiently reduce the total concentration of contaminants. Conventional in situ methods for remediation of contaminated sediments not only cannot decrease the total concentration of pollutants, but also they are not applicable in these cases since they decrease further the depth of the water column. Selective removal of the highly contaminated sediments is difficult by dredging and thus large quantities of contaminated sediment are removed and must be managed.

Sediment risk management is often based on bulk total concentration of pollutants. Therefore, sediment removal is risky and can be destructive or even ineffective for risk reduction. The total concentration of copper and zinc in this study were high enough for classification as contaminants based on the SQG, although the SET showed they were environmentally unavailable and could not pose any threat to the aquatic ecosystem under stable conditions. Conversely, total concentrations of cadmium and lead were below PEL (except Pb in station one) and it seemed that there were not counted as contaminants. However, SET results confirmed that a significant percentage of their concentrations existed in labile fractions and could be environmentally available. For areas like harbours with shallowness issues and contaminated sediment, even dredging the contaminated area could release serious toxic substances in ecosystem. The proposed technique in this study could reduce the risk of unexpected resuspension caused by nature or/and anthropogenic activities. Moreover, potential dredging in these areas (as it is unavoidable) could be performed safer and more cost-effective. Like any other technique for managing the contaminated sediments, this method also has its own advantages and disadvantages. Advantages are listed as follows:

- The resuspension method as an *in situ* method could sufficiently reduce the level of contaminants with removal of a small portion of sediments that are highly contaminated. As a result, costs for dewatering, transportation and tipping fees for handling the contaminated disposal materials in landfill can be reduced.

- No chemical substances were employed. Subsequently, less destruction can be caused in aquatic ecosystem.
- If the sediments level needs to be reduced further after the resuspension operation, open water disposal of the remaining sediments would be allowed as the levels of contaminants could meet the standard levels and no risk would be posed to the receiving environment.

Future studies of the resuspension technique are needed to investigate the following:

- Applying the resuspension technique for anoxic sediment samples and/or in the presence of seawater could change the results.
- The resuspension technique potentially could have an adverse effect on sensitive species. The intensity and duration of resuspension should be modified according to the characteristics of water and sediment as well as the site's ecosystem.

This laboratory-scale experiment was the first step in providing beneficial information to address concerns about shallow harbours with contaminated sediments. Pilot-scale study on sediments with various physicochemical characteristics should be considered for scale-up of this technique.

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Chapter 5

In Chapter 4, the resuspension method was introduced and evaluated for remediation of contaminated sediment in a shallow aquatic environment and a viable option for reducing the level of contamination prior to dredging or any method of sediment management. In this chapter, the details of removal mechanism through extracting SPM are explained. The results of experiments released in this chapter, indicate the capability of the resuspension technique for reducing the level of contamination by removing a small portion of sediment instead of dredging the contaminated spots.

5 Effect of the Resuspension Technique on Distribution of the Heavy Metals in Sediment and Suspended Particulate Matter

Mehdi Pourabadehei, Catherine N. Mulligan

Department of Building, Civil and Environmental Engineering, Concordia University, 1455 de Maisonneuve Blvd. W., Montreal, Qc, Canada, H3G 1M8

Abstract

Harbour areas play important roles in the economy worldwide. Human activities however in those areas generate contamination, where they mostly accumulate in the sediments. On the other hand, harbour areas have been facing deposition of significant amounts of sediment each year. As a consequence, shallowness and accumulation of contaminants in sediment become challenging issues in harbours. Among the various management options for remediation of contaminated sediments in harbours, resuspension technique was introduced as a new approach to address those issues. The concept of the resuspension method is that finer sediments have a greater tendency to adsorb the contamination. Therefore, removing the finer sediments instead of dredging the whole contaminated area is the main goal of the resuspension technique. The objective of this paper was to evaluate the effect of the resuspension method on reducing the concentration of contamination and distribution of heavy metals in the sediment and suspended particulate matter. The resuspension method was successful in reducing the concentration of seven selected heavy metals (Cr, Ni, Cu, Zn, As, Cd and Pb) by removing just 4% of contaminated sediment. The contamination intensity in the sediment, presented by the geoaccumulation index, was reduced for Cd and Pb as the main contaminants by 26 and 28 percent and for the rest of the selected heavy metals returned to the non-polluted level. The results of the sequential extraction tests and enrichment factor implied that the resuspension technique is capable of decreasing the risk of the heavy metal availability.

Keywords: Resuspension, contaminated sediment, harbour, heavy metals, principal component analysis.

5.1 Introduction

Activities at harbour areas, particularly on large rivers, have been known to be harmful to the aquatic environments (Buruaem et al., 2012). Construction of the breakwaters in those areas can affect sediment transport. Subsequently, harbour areas have been facing deposition of significant amounts of sediment each year. Additionally, generation of waste and the discharge of contaminants into the water body are the main threats to the aquatic ecosystem (NRC, 1997). Sewage and wastewater, petroleum and compounds released by antifouling paints that are received from land and river can be adsorbed by up to 99 percent by the sediment (Salomons and Stigliani, 1995; Huang et al., 2012). Therefore, shallowness and contaminated sediments at harbour areas become challenging issues.

Among the various pollutants, heavy metals adsorbed by sediments are of particular concern due to their mobility and toxicity in the aquatic ecosystem. Binding of heavy metals to the contaminated sediment may not be permanent and can release those inorganic pollutants. Contaminated sediments with heavy metals are not only a short-term threat to biodiversity but they also can serve as long-term exposure sources to ecosystems (Ghosh et al., 2011).

Because of the concentration of pollutants, *ex situ* remediation after dredging is the main viable option. On the other hand, *in situ* techniques are mainly used to reduce the mobility of the contaminants. Dredging the contaminated sediment can increase the risk of mobility and availability of heavy metals in the harbours and impacts on the disposal sites that receive the dredged sediment (USEPA, 1991).

Capping with or without reactive amendments are the most common in situ methods employed in contaminated sediment cases. However, capping is not applicable since shallowness is an issue in the harbours. Additionally, both capping and dredging may have an adverse effect on existing benthic ecosystems (Ghosh et al., 2011). Therefore, developing new techniques with more flexibility for managing contaminated sediment and minimal harm to the surrounding environment is highly desirable.

In order to address this issue in shallow harbour areas, the resuspension technique was introduced as a new approach to remediate contaminated sediments. The concept of the resuspension method is that finer sediments (i.e. clay and fine silt) have a greater tendency to adsorb the contamination (Mulligan et al., 2009). Due to the high specific surface adsorption and ionic attraction, finer sediments tend to have a relatively higher concentration of contaminants (USEPA, 1991). Suspended sediment and the organic components of sediment can also scavenge organic and inorganic contaminants (Fukue et al., 2007). Therefore, removing the finer sediments without dredging the whole contaminated area is the main goal of the resuspension technique.

Fukue et al. (2012) applied the resuspension approach for evaluating the feasibility of reducing the level of organic matter that led to hydrogen sulfide production in Fukuyama city harbor, Japan. However, in this study the resuspension process was modified for removing inorganic pollutants (i.e. heavy metals). Briefly in the resuspension process, finer sediments are targeted for removal by a suspension mechanism. Through a powerful air jet, in a confined water column, sediments are forced to resuspend over a period of the time and then they will settle based on size. The finer suspended solids containing higher concentrations of heavy metals can be removed from the aquatic ecosystem by pumping and filtration.

The objective of this paper was to determine the effect of the resuspension method on distribution of heavy metals in the sediment and the subsequent suspended particulate matter (SPM). Moreover, the risk of mobility and availability of seven heavy metals in the sediment of a harbour area was assessed. The feasibility of the resuspension method as a new technique for remediation of contaminated sediment also was evaluated.

5.2 Materials and methods

5.2.1 Study area

A harbour in the province of Quebec, Canada, was selected for this study, which is located on the north bank of the St. Lawrence River. The area of the harbour was approximately 15,000 m^2. Two floating and one solid breakwaters protected the harbour from the waves. Consequently, there was a quasi-steady flow around the passageways and dock area, which led to deposition of sediments (Figure 5.1). The boat maintenance area was located at the northern west of harbour and mainly used for repairing and repainting in the summer and storing the boats in the winter.

Figure 5.1 Study area with the selected stations, which were potential locations for dredging.

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 14 years since dredging was employed in this harbour. The water depth varies between 0.6 meter (around the dock area) and 3 meters (around the floating breakwater). However, prior to dredging or any other management method, the quality of sediments was assessed to evaluate management options. Nine different stations along the passageways and the dock area, which are the most relevant places for dredging, were chosen for analysis. These stations are shown on the map in Figure 5.1.

5.2.2 Sampling

A set of surface sediment samples was obtained at the selected stations (Figure 5.1) based on the sediment-sampling guide for dredging and marine engineering projects in the St. Lawrence River (Environment Canada, 2002). The samples were taken with a Birge-Ekman grab sampler from the surface of the sediments to a vertical distance to a maximum depth of 10-centimeter. Each sample was about 1±0.2 kilogram. The sampler consists of a stainless steel box with a pair of jaws and free-moving hinged flaps (Gouws and Coetzee, 1997). The jaws can trap sediments as soon as they reach the river bottom and keep the sediments in the stainless steel box to prevent washout during retrieval. Sediment samples were transferred and kept in the airtight polyethylene bottles and placed in an ice-cooled box. They were transferred to the freezer at the Environmental Engineering laboratory at Concordia University and were used for subsequent experiments.

All plastic- and glass-ware used during the experiment process was new or soaked in 5% (v/v) nitric acid and 2.5% (v/v) hydrochloric acid (trace metal grad) for at least 8 hours followed by two rinses with deionized water (Milli-Q 18 μΩ cm) prior to use. For quality control, all sediment samples were analyzed using a control and duplicates.

5.2.3 Experimental design

The setup for resuspension of sediment contained three parts. The first part is resuspension/aeration, which was performed by an air jet connected to the central compressing air system in the laboratory. The central air compressor provided up to 400 kPa. However, the velocity of the air injected to the water was around 10 meters per second, which could create a strong turbulence in a reactor. The head of the air injector was submerged in the water and located 5 cm above the sediment in the reactor. The reactor was a vertical plexiglass cylinder with 20 and 60-centimeter in diameter and height, respectively (Figure 5.2). Sediment sample was homogenized and deposited into the reactor followed by adding the tap water. The ratio of the sediment sample to tap water was 1:10 (vol./vol.) in the reactor. Tap water was used in all experiments since it has relatively similar characteristics to the river freshwater samples. Sediments were suspended in the reactor during air injection, which took two hours for each sample. The injected air contributed to the increase in the volume of the water/sediment by approximately 30% in each sample.

For the second part, aeration was stopped after two hours and the coarser sediments started to settle. In about 15 minutes, the sand and coarse silt fraction almost completely settled. Then, by using a pump with a maximum flow rate of 22 liters per minute, 30% of the slurry in the reactor containing the water and suspended particulate matter (SPM) and some insoluble organic matter was removed and conveyed to the filter system (Figure 5.3). The suction pipe for pumping was located at the middle of the water column depth and it took less than a minute to remove 30% of the slurry from the reactor. The filter system was comprised of two layers of a non-woven geotextile (Titan TE-GTP 250) with an apparent opening size of 90 microns. The volume of the water/SPM removed by the pump in this research was 10 to 15 percent of the suspended solid.

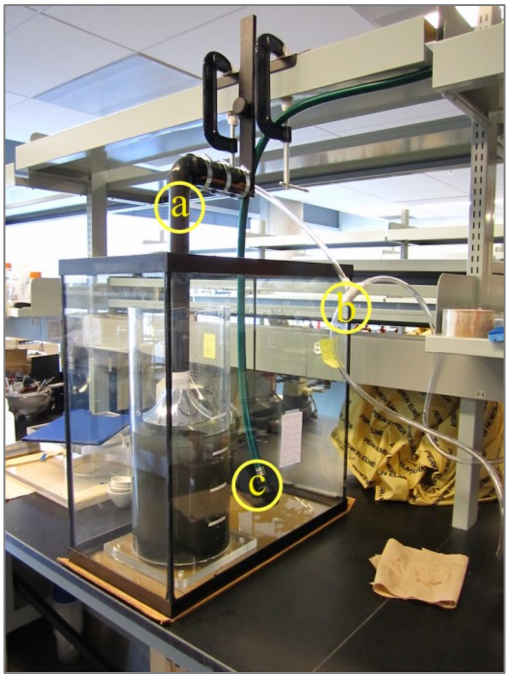


Figure 5.2 Reactor with air injection system (a) connected to the air compressor (b), suction pipe for delivery the SPM to the filter system (c).

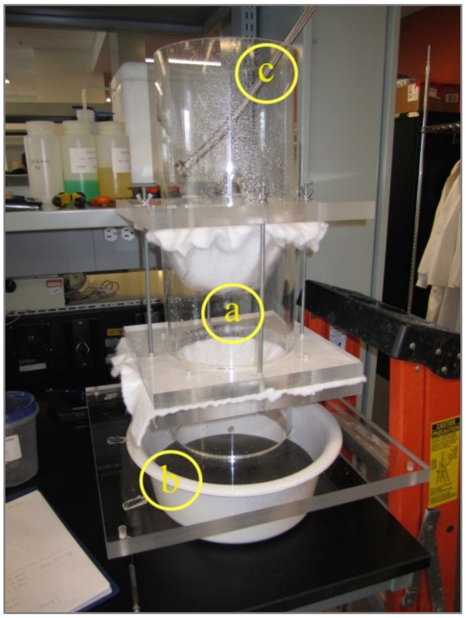


Figure 5.3 Multi-layer filtration system (a) and reservoir (b) to settle SPMs with delivery pipe (c) at the top.

It should be noted that surface sediments, in some stations, contained a significant amount of natural organic matter (NOM) such as algae (up to a quarter of their weight). NOM was not removed prior to the resuspension test since naturally they are a part of the surface sediment on the site. A sample of sediment was obtained for each experiment (about 20 g) from the reactor before and after the test and analyzed. SPM sample was also taken from the reservoir 48 hours after filtration when all the SPM settled in the reservoir for each experiment. Filtration chiefly trapped the tiny pieces of NOM and likely the SPM larger than 90 microns that was pumped into the filtration system. A schematic of the whole resuspension procedure is presented in Figure 5.4.

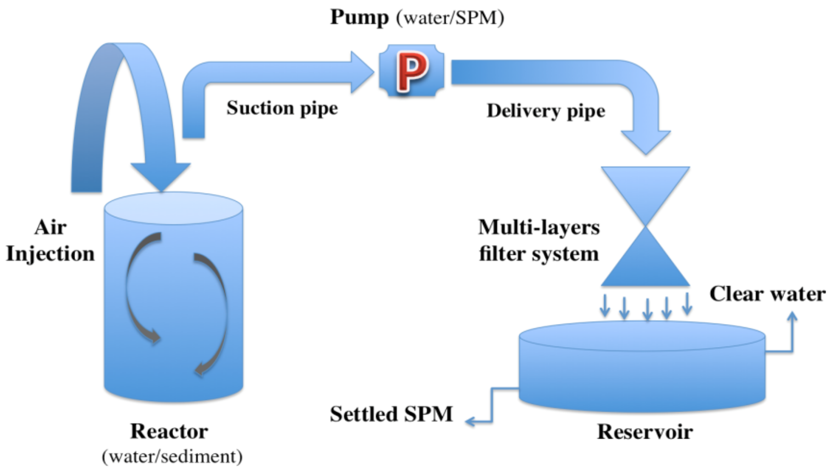


Figure 5.4 Schematic of the resuspension procedure.

5.2.4 Sediment characterization

Among the 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 a laser scattering analyzer (HORIBA, LA-950V2). D_{50} (50% of the particles are less than this size) and the percentage of clay, silt and sand for each sample were determined.

The pH, oxidation-reduction potential (ORP) and dissolved oxygen (DO) were measured by a multiparameter meter (HANNA HI 9828). They are common parameters measured for water quality purposes. Loss on ignition (LOI) was another parameter chosen to estimate organic and carbonate content in the sediment. According to ASTM D2974-00 (American Society for Testing and Material, 2000), oven dried sediment samples (105^{o} C) were placed in a furnace at 550^{o} C for 4 hours. After the sediments were cooled down in a desiccator and their weights (w) were measured, loss on ignition (%) in each sample was calculated based on the following equation:

$$LOI\ \% = ((W_{105^{o}C} - W_{550^{o}C})/W_{105^{o}C}) \times 100 \qquad [5.1]$$

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 (i.e. sediment), acid digestion was required. The EPA 3050B method was the protocol used to digest the sediment samples and prepare them for analysis by in ICP-MS. For digestion, 1 or 2 grams of wet sample or 1 gram of the dried sample were digested with repeated additions of nitric acid (HNO_3, 70%-trace metal grade), hydrogen peroxide (H_2O_2, 30%) and hydrochloric acid (HCl, 35%) at the end digestion [USEPA, 1996]. The digested samples were kept in the fridge at approximately 4° C until analysis.

5.2.5 Sequential extraction procedure

A sequential extraction test (SE) was employed on the basis of Yong et al. (1993). Heavy metal ions in sediments are partitioned between different fractions. Determining the concentration of metals in each fraction can provide detailed information about their physicochemical availability and mobilization (Filgueiras et al., 2002). The most available metals were found in the water soluble and exchangeable fractions by adding 8 ml of 1 M $MgCl_2$, 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, with 5 hours shaking at room temperature. Metals bound to Fe-Mn oxides and hydroxides were removed by adding 20 ml of 0.04 M $NH_2OH.HCl$ 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 HNO_3 and 5 ml of 30% H_2O_2 (pH 2) were added at 85° C for 2 hours, followed by 3 ml of 30% H_2O_2 (pH 2) at 85°C for 3 hours. Finally 5 ml of 3.2 M ammonium acetate in 20% (v/v) HNO_3 was added and then diluted to 20 ml at room temperature 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 HNO_3 + 750 ml deionized water) for 3 hours at 96° C. After each extraction step the suspensions were centrifuged with 1478 x g for 20 minutes (Thermo IEC HN-SII-58012). The supernatant was then filtered through a 0.45µm polytetrafluoroethylene (PTFE) syringe filter to remove any remaining particles, before analysis by ICP-MS. Those samples that contain high amounts of a metal concentration were diluted.

5.2.6 Geoaccumulation index and enrichment factor analysis

The index of geoaccumulation (I_{geo}) is a criterion to assess the intensity of heavy metal contamination. This index was originally presented by Muller (1979) as follows:

$$I_{geo} = log_2(C_m/(1.5 \times B_m)) \qquad [5.2]$$

where, C_m is the metal concentration detected in sediment samples and B_m is the background value of that metal in the site. The factor 1.5 corresponds to possible variation of crustal contribution in sediment mainly by weathering or bank erosion in the rivers.

Table 5.1 presents a qualitative scale of contamination intensity for sediment samples with 7 classes. The classes of zero and one, as it is noticeable from equation [5.2], show the background/unpolluted levels. For those samples with I_{geo} values above unity, early signs of contamination are expected. It is worth mentioning that, for classifying the sediment samples by this index, the worst pollutant is actually considered. In other words, if a sample showed a higher index for a single metal, it would be ranked based on that element (Buruaem et al., 2012).

Table 5.1 scale of contamination intensity for geoaccumulation index values -I_{geo} (Buruaem et al., 2012).

I_{geo}	Class	Contamination intensity
>5	6	Very strongly polluted
4-5	5	Strongly polluted
3-4	4	Moderately to strongly polluted
2-3	3	Moderately polluted
1-2	2	Unpolluted to moderately polluted
0-1	1	Unpolluted
<0	0	Background levels

The enrichment factor (EF) is another parameter, which has been widely used to estimate the anthropogenic impact on sediment based on the use of a normalization element (Al or Fe) to make easier the variations produced by heterogeneous sediments (Adamo et al., 2005). The EF of heavy metals in this study are calculated using the following equation:

$$EF = (M/Fe)_S/(M/Fe)_R \qquad [5.3]$$

Where, $(M/Fe)_S$ and $(M/Fe)_R$ are the ratio of each heavy metal to Fe (as a normalization element) in the sample and reference samples, respectively. Background values of heavy metals (as a reference) were measured and compared to levels reported by Environment Canada (Table 5.2).

Table 5.2 Total concentrations of selected major and trace metals in the St. Lawrence River (mg/kg) (Environment Canada, 2007).

Natural levels	Cr	Ni	Cu	Zn	As	Cd	Pb	Fe
Pre-industrial sediment	60	29	19	86	6.6	0.2	13	30,000
Postglacial clay	150	75	54	150	8	0.2	16	56,000

5.3 Results and discussion

5.3.1 Physicochemical characteristics of sediment samples

The general characteristics of sediment samples in selected stations were determined. According to Table 5.3, the pH was neutral at almost all stations. As expected, the surface samples contain significant organic materials as the loss on ignition (LOI) implies. The presence of organic materials in those stations located at the stationary parts of the harbour was more noticeable. The percentage of dissolved oxygen (DO) and the amount of oxidation-reduction potential (ORP) indicated that the surface sediments were not anoxic before the test.

Table 5.3 Physiochemical characteristics of sediment samples before the test.

St. No.	pH	ORP (mV)	DO (%)	LOI (%)
S 1	7.0	20.3	30.4	4.4
S 2	7.7	87.4	27.9	12.8
S 3	8.0	124.4	86.7	12.4
S 4	6.9	86.9	38.2	11.4
S 5	6.9	-61.3	27.5	10.7
S 6	6.6	33.7	0.0	12.5
S 7	7.0	116.0	23.2	7.6
S 8	7.0	99.4	52.3	11.1
S 9	7.1	60.7	12.1	7.9

5.3.2 Particle size analysis

Analysis of the particle size distribution was performed for the bulk sediment samples and the suspended particulate matter (SPM- those particles remain suspended at least for 15 minutes in stationary water after resuspension). It is essential to estimate the amount of the sediment that was actually removed through the resuspension test. Quality and quantity of removed SPM can have a significant effect on the resuspension efficiency. Lower amounts of sediment with higher contamination removal is desirable.

Particle size distribution showed the texture of the samples before the test was very fine with a D_{50} around 1.3 microns on average (Table 5.4). However, S1 had the coarsest texture and lowest organic contents. The texture of this area was completely different from the rest of the stations. S1 is the area that usually receives the runoffs from land particularly from the maintenance area and this can be the reason for the presence of a significant percentage of sand (i.e. 17.5%).

Clay and colloids ($D < 2$ μm) were the dominant particles found in SPMs. SPMs were the part of the bulk sediment, which were suspended during the test and removed afterward. As it is expected, the texture was finer than the sediment samples. However, it is important to know how much sediment was removed through the resuspension procedure. The first step is to estimate how many percent of sediment was SPM and at the second step how much SPM was actually removed. To answer these questions, the distributions of the particle size in the sediment samples and SPM are presented in Figure 5.5 and Figure 5.6.

Table 5.4 Particle size analysis for sediment samples before the test and SPMs.

St. No.	Sediment -Before the test				SPM			
	D_{50}	Clay[1]	Silt[2]	Sand[3]	D_{50}	Clay	Silt %	Sand
S1	6.18	41	41.5	17.5	0.24	94.6	5.4	0
S2	0.49	62.8	35.1	2.1	0.23	91.6	8.4	0
S3	0.47	67	32	1	0.28	86.3	13.7	0
S4	1.51	66.7	30.8	2.5	0.22	91.7	8.3	0
S5	0.48	66.9	32	1.1	0.22	93.8	6.2	0
S6	0.43	75.3	23.5	1.2	0.37	78.8	21.2	0

St. No.	Sediment -Before the test				SPM			
	D_{50}	Clay[1]	Silt[2]	Sand[3]	D_{50}	Clay	Silt %	Sand
S7	1.59	65.5	30.1	4.4	0.22	89.7	10.3	0
S8	0.44	70	25.4	4.6	0.36	86.4	13.6	0
S9	0.37	80.8	19.2	0	0.29	88.3	11.7	0

[1] Caly: < 2 µm
[2] Silt: 2 – 62.5 µm
[3] Sand: 62.5 – 2000 µm (American Society for Testing and Material, 2006)

S1 and S8 were chosen as a representative of all sediment samples to show the particle size frequency and cumulative percent. As it is mentioned earlier, S1 had a coarser texture than the rest of samples and since the SPMs almost had the same texture, the cumulative percent curve has a different shape and distance to the SPM curve, unlike the S8 sample. On the other hand, the frequency of particles in SPM in both samples has the highest amount between 0.1 to 1 micrometers that is in the colloidal range. Also, most of the particles in sediment samples were found between D_{10} and D_{90} (0.3 and 40 microns on average respectively), which are 10 percent and 90 percent of the particles finer than those sizes, respectively. Therefore, to estimate the percent of SPM in the sediment samples, the size index (SI) was used as follows:

$$Size\ Index(\%) = ((D_{90} - D_{10})_{SPM}/(D_{90} - D_{10})_{Sed-B}) \times 100 \qquad [5.4]$$

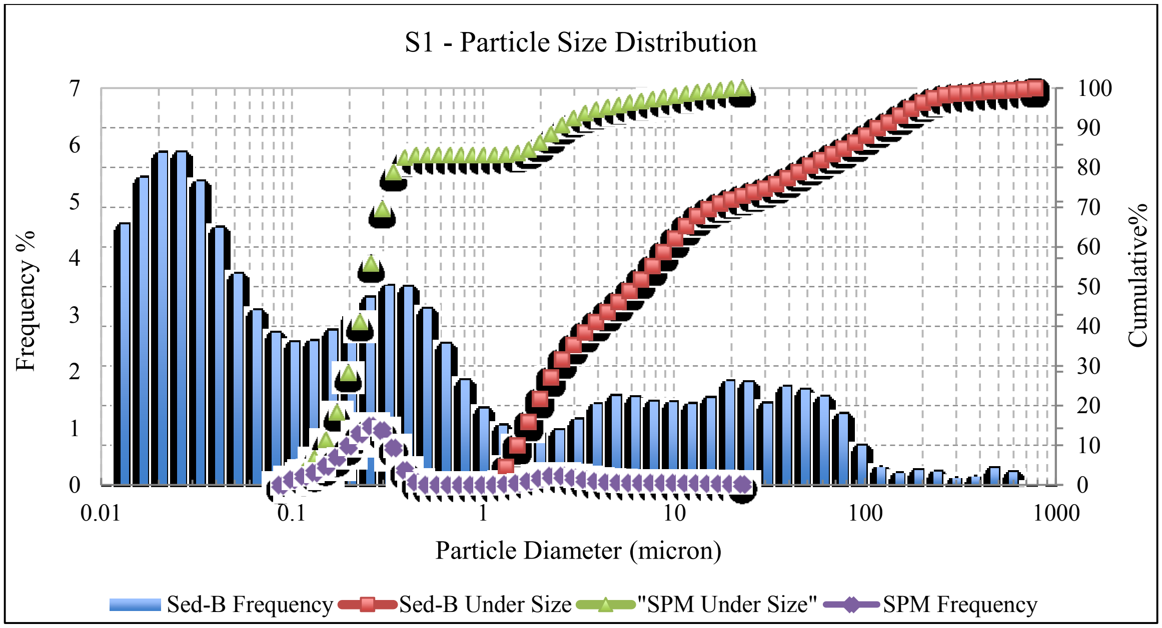


Figure 5.5 Distribution of particle size in S1 with frequency % and cumulative curves for the bulk sediment before the test (Sed-B) and SPM.

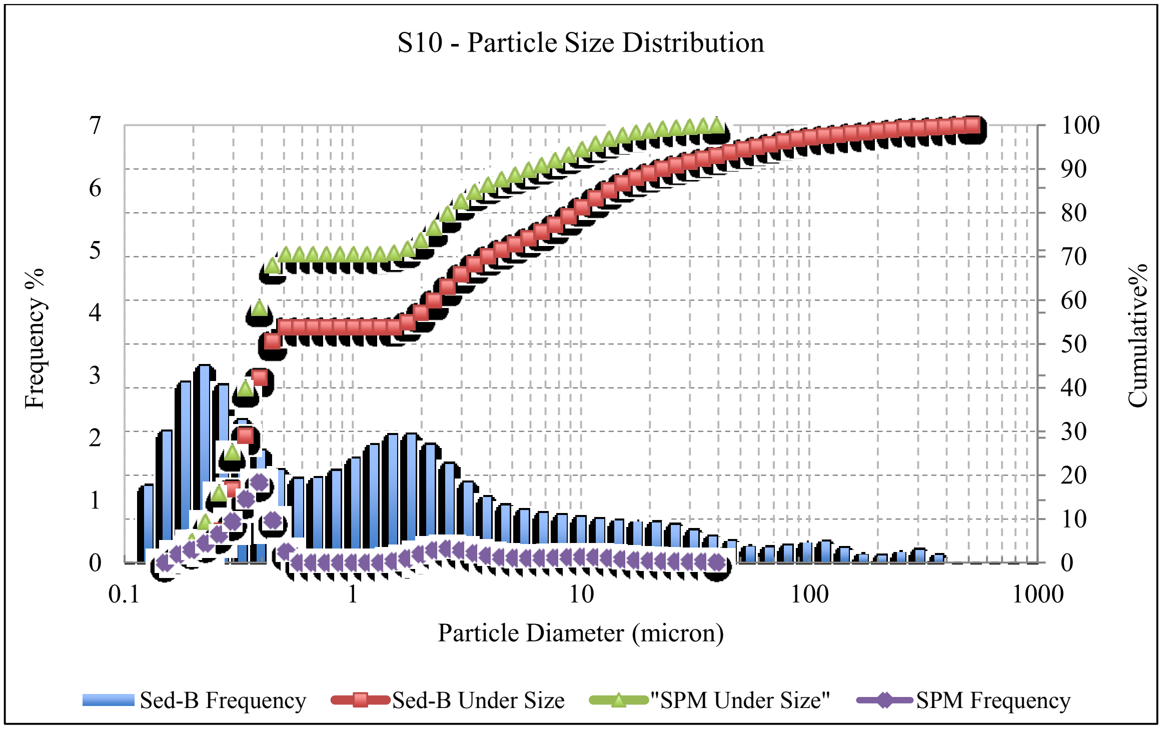


Figure 5.6 Distribution of particle size in S8 with frequency and cumulative percent curves for the bulk sediment before the test (Sed-B) and SPM.

Table 5.5 shows the D_{10} and D_{90} of sediment and SPM and also the size index of each sample. For those stations that had a coarser texture, a lower percentage of the size index was calculated (e.g. S1). The average of the size index was about 26 percent. It means that approximately a quarter of the sediment samples consisted of SPM. On the other hand, during the resuspension test, 10 to 15 percent of suspended solids were removed as it mentioned earlier. Therefore, in the worst-case scenario 15 percent of the SPM, which was about 26% of the bulk sediment sample, were removed in each test. Consequently, 4 percent (15% × 26%) of the sediment was actually removed through this technique (if linear distribution of particle size has been assumed). This is the approximate amount in order to show the sediment quality improvement in this method. Handling 4% of contaminated sediment is much easier than the whole dredged sediment from the contaminated area.

Table 5.5 Particle diameter of D_{10} and D_{90} for SPMs and bulk sediment samples (micron) with Size Index (%).

	SPMs		Sed-B		Size Index
St. No.	D_{10}	D_{90}	D_{10}	D_{90}	%
S 1	0.14	2.49	1.51	117.31	2.0
S2	0.14	2.59	0.35	21.85	11.4
S3	0.17	6.55	0.32	13.08	50.0
S4	0.14	3.26	0.35	23.14	13.7
S5	0.14	2.69	0.32	15.53	16.8
S6	0.20	7.58	0.32	16.69	45.0
S7	0.13	4.13	0.31	13.18	31.0
S8	0.23	6.04	0.27	22.89	25.7
S9	0.18	4.57	0.24	10.28	43.7
Mean	0.16	4.43	0.44	28.22	26.59

5.3.3 Total concentration of heavy metals

The total concentration of heavy metals was measured for sediment samples before and after the test taken from the reactor and also for SPM from the reservoir (Table 5.6). The resuspension method was successful in reducing the concentration of heavy metals by 24% on average. The maximum reduction was recorded for Zn (31%) and the minimum was for Cd (19%). In order to validate the results of the total concentration of metals in sediment samples, a mass balance was performed for each test. Resuspension was capable of removing a part of sediment from the aquatic environment, which contains more contamination than the rest of sediment. Precisely, by applying the resuspension technique almost 4 percent of sediment was removed that carried about 34% more contamination than the rest of sediment in the reactor. As a result, the concentrations of the contaminants decreased without removing all sediment. Moreover, costly operations such as dredging, dewatering, transportation and discarding the contaminated sediment could be avoided.

5.3.4 Enrichment factor (EF)

Beside the different guidelines for assessing the quality of sediment, enrichment factor (EF) can estimate the level of contamination that mostly occurred by anthropogenic activities. To calculate the EF values, the natural level (NL) of heavy metals concentration should be identified. Results from X-ray diffraction (XRD) for some sediment samples, implied that the mineral fractions and physical properties (i.e. particle size distribution) of sediments in the harbour is relatively similar to postglacial clays in St. Lawrence River rather than pre-industrial sediments. Figure 5.7 shows the mineral fraction of S8 as an example of sediment in the harbour. These clays typically were deposited earlier in a marine context. However bottom and bank erosion and deposition in the inner part of the river contributes significantly to the supply of fine particles in recent sediments (Pelletier and Lepage, 2002). Therefore, the natural levels of heavy metals in postglacial clays were employed as a reference concentration (Table 5.2).

The results of EF values for sediment before the test are presented in Figure 5.8. The concentrations of Fe were measured in five stations and the average was used to calculate the iron ratio in equation 3. According to the literature, the range of EF values of 0.5 to 1.5 is considered as the contribution of heavy metals from crustal such as weathering. EF values between 1.5 and 4 indicate the contribution of both crustal and non-crustal (e.g. natural processes or/and anthropogenic activities) and for those EF values above 4, heavy metals in the sediment samples are mostly provided by anthropogenic influences (Zhang and Liu, 2002; Yuan et al., 2012).

Table 5.6 Total concentration of heavy metals (mg/kg) in sediment before and after the test as well as SPMs.

St. No.	Cr	Ni	Cu	Zn	As	Cd	Pb
S1-B	37	22	219	204	6.1	0.5	134
S2-B	60	47	159	303	7.0	0.8	51
S3-B	74	64	138	563	6.6	0.8	77
S4-B	71	39	137	372	9.4	0.9	69
S5-B	72	46	59	305	8.4	0.9	37
S6-B	67	43	70	266	6.4	0.8	33
S7-B	62	38	47	205	6.0	0.8	33
S8-B	99	46	67	334	18	1.1	55
S9-B	74	39	75	201	11	0.8	34
Mean	**68**	**43**	**108**	**306**	**8.8**	**0.8**	**58**
SD	16	11	58	114	4.0	0.2	33
S1-A	24	14	160	110	5.7	0.3	65
S2-A	60	47	159	303	7.0	0.8	51
S3-A	72	37	108	331	7.4	0.9	73
S4-A	41	20	89	157	4.4	0.5	41
S5-A	60	37	65	224	6.4	0.8	35
S6-A	36	22	29	137	3.7	0.4	19
S7-A	60	37	40	199	5.4	0.8	32
S8-A	79	49	61	240	10	0.8	45
S9-A	59	36	42	195	6.7	0.8	41
Mean	**55**	**33**	**84**	**211**	**6.3**	**0.7**	**45**
SD	18	12	50	73	1.9	0.2	17
SPM 1	79	54	208	359	10	1.0	119
SPM 2	72	46	84	272	5.5	0.6	39
SPM 3	77	44	109	379	7.3	0.8	66
SPM 4	73	48	144	342	8.4	0.8	62
SPM 5	76	50	95	237	6.5	0.7	34
SPM 6	73	38	79	158	25	0.7	15
SPM 7	75	50	110	340	5.7	0.6	38
SPM 8	67	60	132	310	8.5	0.6	38
SPM 9	72	47	92	234	8.1	0.7	52
Mean	**74**	**49**	**117**	**292**	**9.6**	**0.7**	**51**
SD*	3.4	6.1	40	72	6.2	0.1	29

*SD: signifies standard deviation

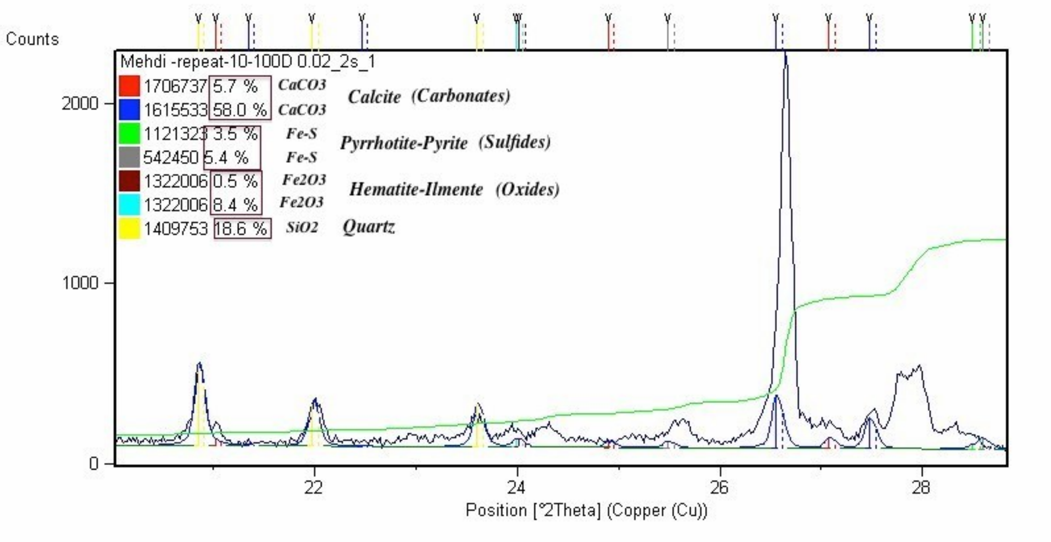


Figure 5.7 XRD results for mineral fractions of sediment sample from station 8.

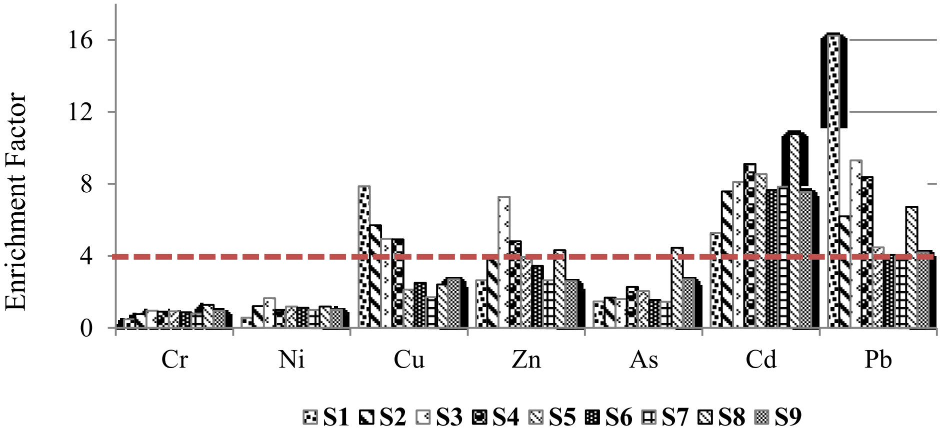


Figure 5.8 Enrichment factor of metals in sediment samples before the resuspension test.

Therefore, based on the EF values, Cd and Pb are the main contaminants in this study followed by Cu and Zn. The first four stations were more contaminated than the other stations. These stations received the runoffs from the maintenance area, which mainly contain the components of antifouling paint. Antifouling paint is usually applied on the hull of the boats to prevent the growth and colonization of river microorganisms (Yebra et al., 2004; Braithwaite et al., 2007). Copper, zinc, lead and cadmium are the most common components of many antifouling paint formulations (Simpson et al., 2013). Sanding the old paints prior to repainting boats on the maintenance area is most likely the origin of a significant amount of heavy metals to the river from runoff and eventual adsorption by the sediments.

5.3.5 Geoaccumulation index (I_{geo})

The results of I_{geo} for sediment before the resuspension are presented in Figure 5.9. According to Figure 5.9 and Table 5.1, Cr, Ni and As were not considered as contaminants. Their EF values also endorsed this fact. However, Cu and Zn at stations 1 and 3 were categorized as 'unpolluted to moderately polluted', which is class 2. Cd in all stations except for 1 and Pb in four stations were found in class 2. Lead was the only element that in station 1 was detected as moderately contaminated. In general, Station 1 was the most contaminated sediment mostly polluted by Pb and Cu. On the other hand, station 6 was the least contaminated station slightly polluted by Cd. Considering EF and I_{geo} values, Cd and Pb were the main contaminants.

The effect of the resuspension method is presented in Figure 5.10. The resuspension could improve the I_{geo} for most of the elements including Cd and Pb. No elements were categorized as moderately contaminated (Class 3) after the test. Furthermore, the I_{geo} values of Cd and Pb in sediment after the test decreased and for some stations returned to the non-polluted level. Precisely, the I_{geo} values of Cd and Pb were 1.45 and 1.12 before the resuspension test and they were reduced to 1.07 and 0.8 after the test on average (26 and 28 percent improvement were achieved, respectively).

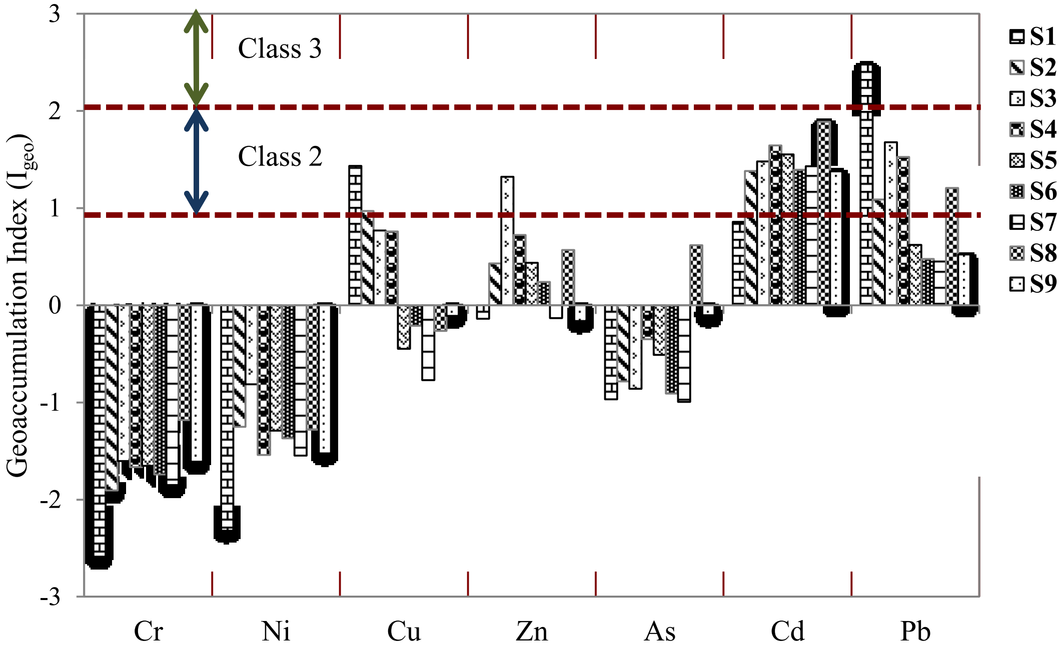


Figure 5.9 Geoaccumulation Index of sediment samples before the resuspension test.

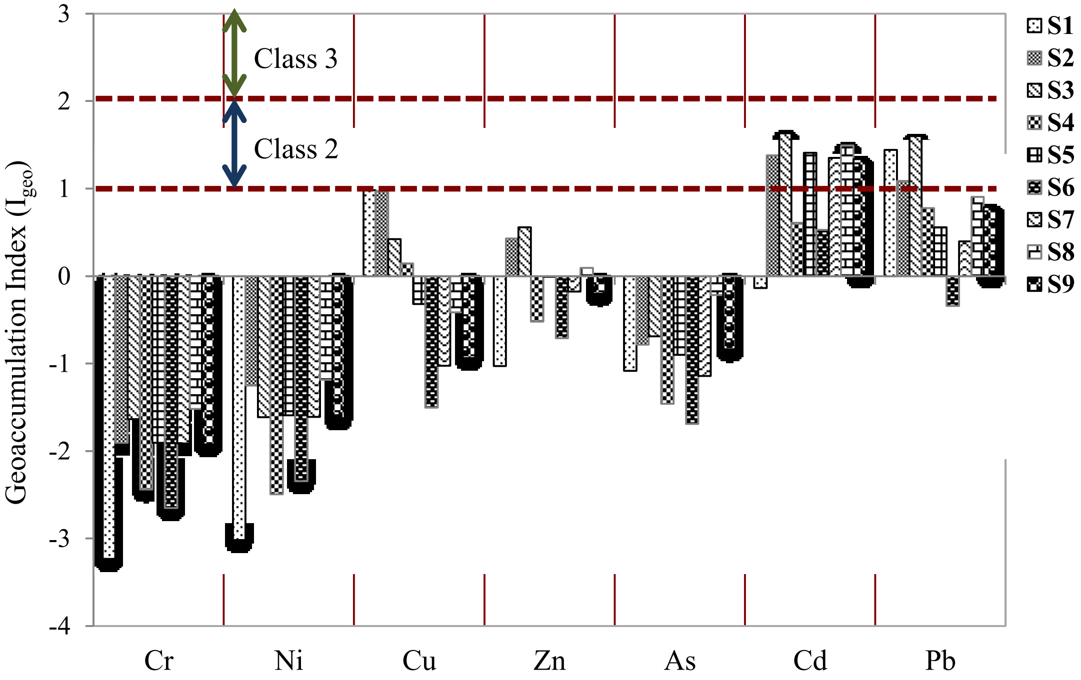


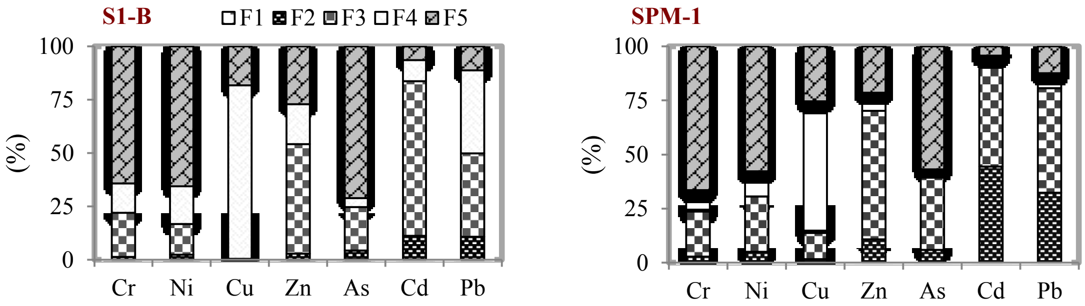
Figure 5.10 Geoaccumulation Index of sediment samples after the resuspension test.

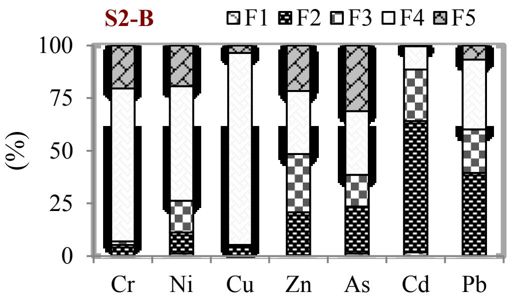
In spite of the information from EF and I_{geo}, detailed information about the heavy metals origin and mode of occurrence was still required to have a better understanding of the distribution in the sediment fractions and their availability and mobilization in the samples (Filgueiras et al., 2002).

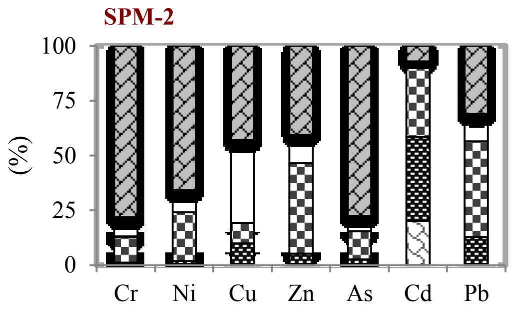
5.3.6 Sequential extraction analysis

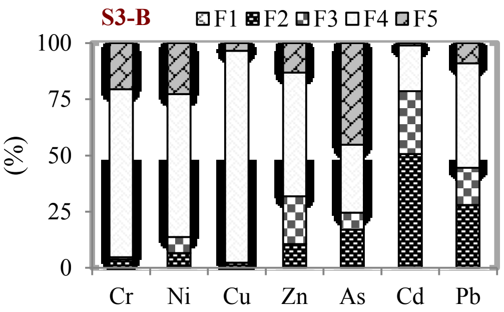
Sequential extraction (SE) was employed to determine the heavy metal fractionation in sediment samples before the resuspension as well as in the SPMs. It is vital to understand how the resuspension technique can affect the mobility and availability of the heavy metals in sediment. Therefore, knowledge on the distribution of the heavy metals in the SPM fractions was desirable. Regardless of the efficiency of this technique to reduce the total concentration of metals in sediment, the mechanism of metal removal through SPM should be considered. In other words, the fractionation of metals, which were removed by SPM can be helpful to examine the capability of this technique for remediation of different heavy metals with different bonds to the sediment.

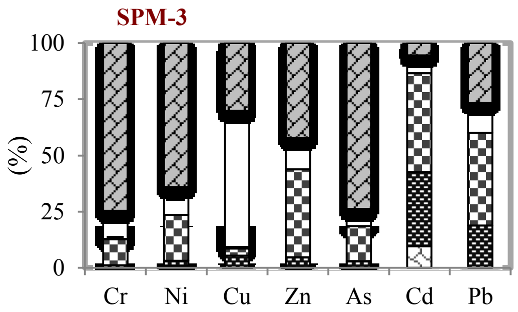
Figure 5.11 presents the results of SE for sediment samples before the resuspension and for SPMs. Five distinct fractions were determined and are presented. Exchangeable fractions (F1) can be used to assess the risk of bioavailability of heavy metals in an aquatic ecosystem. Metals exist in the acid-soluble (F2) and reducible fractions (F3) are representative of the potentially mobile components under changing conditions. Organic and residual fractions (F4 and F5, respectively) are the ones related to metals with more stable forms. They usually have less influence on the ecosystem due to their unavailability (Filgueiras et al., 2002).

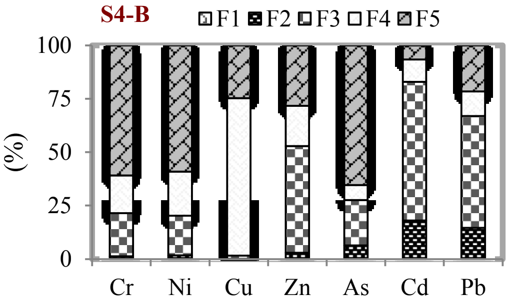


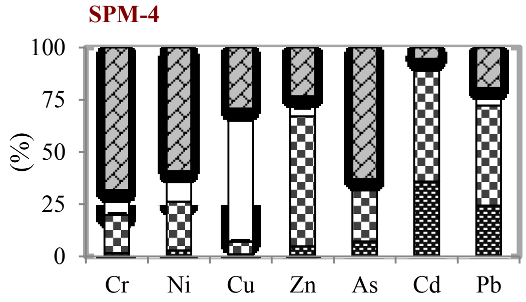

S2-B
F1 F2 F3 F4 F5
100
75
50
25
0
(%)
Cr Ni Cu Zn As Cd Pb

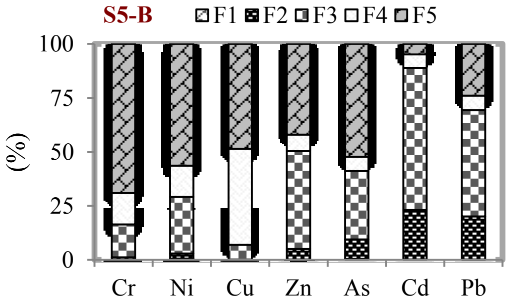

SPM-2
100
75
50
25
0
(%)
Cr Ni Cu Zn As Cd Pb

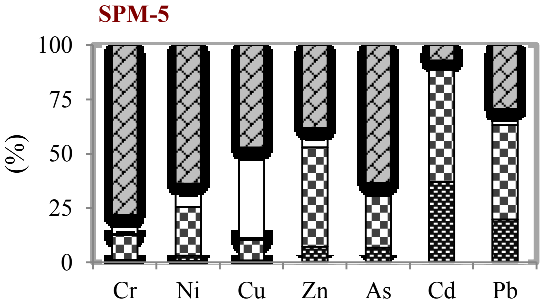

S3-B
F1 F2 F3 F4 F5
100
75
50
25
0
(%)
Cr Ni Cu Zn As Cd Pb


SPM-3
100
75
50
25
0
(%)
Cr Ni Cu Zn As Cd Pb


S4-B
F1 F2 F3 F4 F5
100
75
50
25
0
(%)
Cr Ni Cu Zn As Cd Pb


SPM-4
100
75
50
25
0
(%)
Cr Ni Cu Zn As Cd Pb


S5-B
F1 F2 F3 F4 F5
100
75
50
25
0
(%)
Cr Ni Cu Zn As Cd Pb


SPM-5
100
75
50
25
0
(%)
Cr Ni Cu Zn As Cd Pb

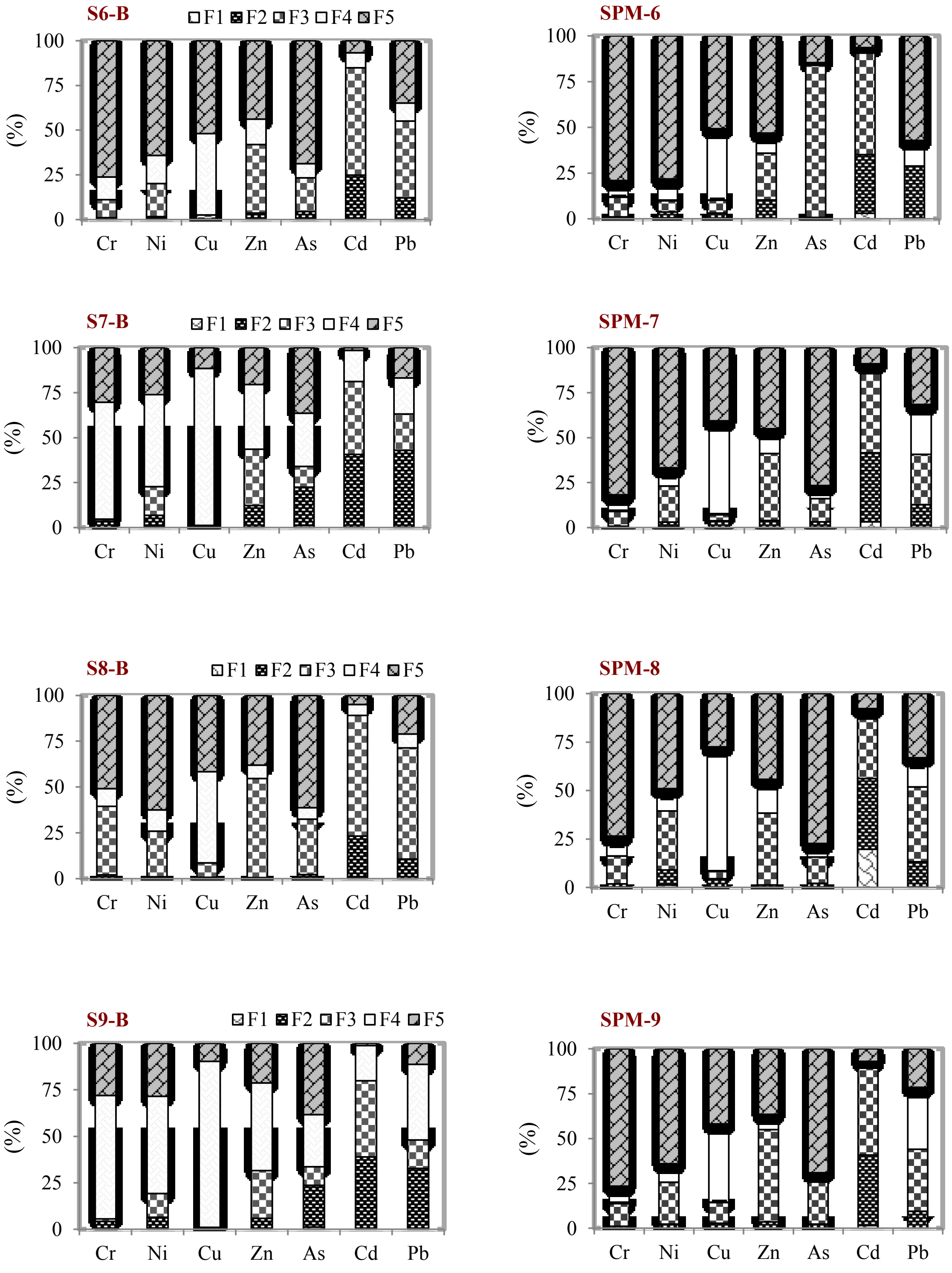


Figure 5.11 SE results for sediment samples before the test (S-B) and SPMs. F1 to F5 are representative of the fraction 1 to fraction 5, respectively.

To assess the potential mobility and availability of heavy metals in the sediment, the risk assessment code (RAC) was used, which was established by Perin et al. (1985). The RAC was defined based on the total of the exchangeable and carbonate-bound fractions (F1+F2 %) (Perin et al., 1985). Table 5.7 presents the classification of RAC. According to the results of SE and Table 5.7, RAC for sediment samples before the test and SPMs are shown in Figure 5.12 and Figure 5.13.

Table 5.7 Classification of risk assessment code (RAC).

RAC	F1+F2 (%)
No risk	< 1
Low risk	1 – 10
Medium risk	11 – 30
High risk	31 – 50
Very high risk	> 50

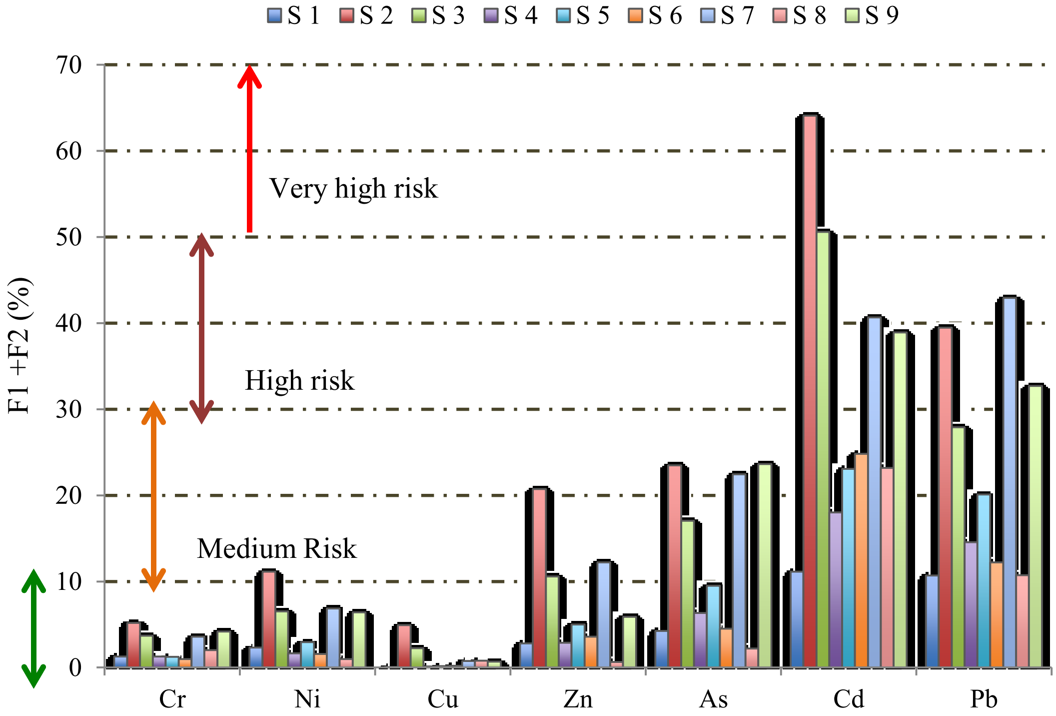


Figure 5.12 Risk assessment code for sediment before the resuspension.

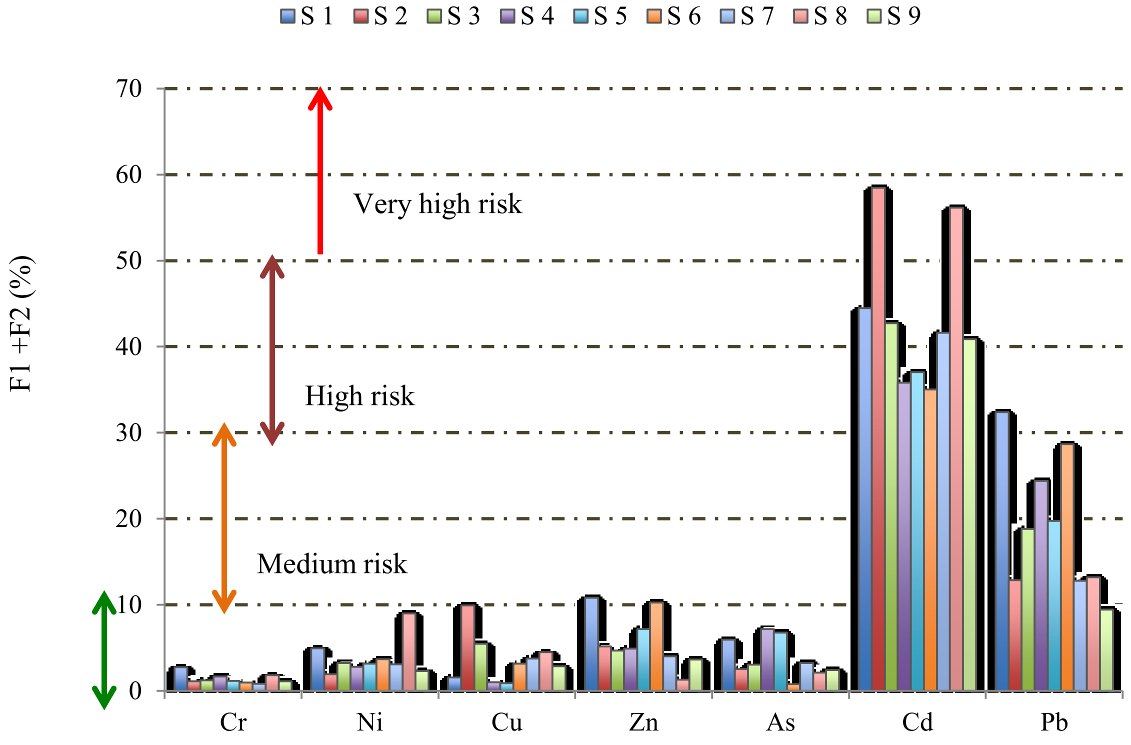


Figure 5.13 Risk assessment code for SPMs.

In Figure 5.12, Cd and Pb were the most potentially available metals. The availability of sediment samples followed this order: Cd > Pb >> As > Zn > Ni > Cr > Cu. In other words, the availability of all metals excluding Cd and Pb on average was about 5.6% and for Cd and Pb on average was 28.1% (i.e. 5 times more available than the rest of heavy metals). Moreover, unlike the other heavy metals, Cd and Pb were mostly located in the medium to very high-risk areas.

On the other hand, in Figure 5.13 except for Cd and Pb, the RAC of all heavy metals were in the green area (low-risk) in SPM. Conversely, the RAC values for Cd and Pb increased in comparison with sediment before the test. Precisely, the RAC value in SPM on average for Cd and Pb was 31.4% and for the rest of selected metals was 3.7% (almost 8.5 times).

Generally speaking, the majority of heavy metal concentrations in SPM were in the residual fraction (almost 45% on average of all selected metals). However, for those metals existing in the less stable fractions in the sediment (i.e. Cd and Pb), they were more available in the SPM. Conversely, for those metals more strongly bound to the sediment matrix, they were found in more stable fractions and became even less environmentally available in SPM. Cd and Pb were mostly found in F2 and Zn in F3. Therefore, removing the contaminants through the SPM removal in this technique removed more environmentally available heavy metals with high RAC (i.e. Cd and Pb). As a result, less risk would be posed to the aquatic ecosystem.

5.3.7 Principal Component analysis (PCA)

Principal component analysis (PCA) is the most common type of multivariate analysis, which has been widely used in environmental studies (Abollino et al., 2002; Liu et al., 2003; Lucho-Constantino et al., 2005; Rognerud and Fjeld, 2001; Sundaray et al., 2011). The purpose of applying PCA is to reduce the number of influential variables into a few new components. The new principal components explain the major part of the variance of the data set (normally more than 75% of the cumulative of the variance). In other words, the variance of a linear combination of the variables would be maximized during the process of PCA. The main challenging and critical part of the PCA procedure is to assign source identity to each one of the principal component (PC). It helps to better understand the principal factors that actually affect in the study and enable a better interpretation and judgment.

In this study, PCA was employed in order to assess the dynamics of heavy metals and identify the role of the fractionation of those elements in the resuspension process. In other words, the importance of the weakly or strongly bound heavy metals into the sediment matrix was re-evaluated by this statistical tool.

The variables employed in this study in the PCA process were: 1) the availability of all the selected heavy metals (F1+F2%). They presented the weakly bound elements to the sediment matrix, which probably recently adsorbed by the sediment. Sundaray et al. (2011) termed this group of variables as ‘anthropogenic factor’ since they found the majority portion of the metals associated with available fractions were contributed by anthropogenic activities. 2) The concentration of the metals contributed to F3 (%). This group of variables showed the importance of Fe-Mn oxides and hydroxides in retaining the metals and its role in this study. 3) The concentration of the metals contributed to the most stable fractions (F4+F5)%. This set of variables presented those metals with strong bounds to the sediment matrix, which were either the aged pollutants or the metals originating from crustal contribution. 4) Contamination intensity of all selected metals (I_{geo}) was another group of variables. They presented the difference of concentration of the elements in the sediment and their natural levels. 5) Texture analysis (percentage of clay, silt and sand) as well as the loss of ignition, as a representative of organic and carbonate in the sediment samples, were the last group of variables. In total, 32 unit-less variables were employed with 9 subjects for each variable, which were the representatives of the 9 stations in the harbour for surface sediment before the resuspension.

SPSS statistical desktop 23.0 was employed for PCA. Kaiser-Mayer-Olkin and Bartlett's test was used for evaluate the suitability of the data set for PCA. Also, oblimin rotation with Kaiser normalization was chosen for identifying the new axes and eventually the new components. Those components with the eigenvalues greater than one were considered and then the most relevant PCs with highest eigenvalues and the cumulative variance greater than 75% were introduced as the principal components (Kaiser, 1960).

Table 5.8 presents the three selected PCs and the contributed variables as well as their eigenvalues and the total variances explained. The data set presented in Table 5.8, was sorted by the contribution of more significant variables (<0.3 loading factor).

According to Table 5.8, three principal components were detected with significant amounts of the eigenvalues that together described more than 81% of the variance of the data set. It is worth mentioning that more than 42% of the variance has been explained by the first component. The main loading factors (i.e. eigenvectors or weights) in each component were highlighted in Table 5.8.

Table 5.8 Principal components for the sediment samples before the test's data set as well as their variables. A: Availability (F1+F2)%, F3: Fraction 3 (Fe-Mn oxides/hydroxides), NA: Non-availability (F4+F5)%, I_{geo}: Contamination intensity.

Variables	Component		
	1	2	3
Ni (A)	**.987**		
Cd (A)	**.956**		
Cd (F3)	-.954		-.332
Zn (A)	**.951**		
As (A)	**.927**		.320
Pb (A)	**.920**		
Cr (A)	**.918**		
Zn (F3)	-.877		-.560

Pb (F3)	-.863		-.642
Cr (F3)	-.843		-.585
Cu (A)	.815		
Cr (NA)	.790		.607
Clay		**.941**	
Cr (I_{geo})		.934	-.315
Sand	-.376	**-.907**	
Cd (I_{geo})		.828	-.501
Silt		**-.827**	
Ni (I_{geo})	.405	.783	
Pb (I_{geo})		-.736	
Cu (I_{geo})		-.691	
LOI		.650	
As (I_{geo})	-.402	.503	-.472
Zn (I_{geo})		.338	
Cd (NA)			**.934**
Ni (NA)		-.314	**.903**
Pb (NA)	.332		**.877**
Cu (NA)		-.447	**.874**
Ni (F3)	-.570		-.854
As (F3)	-.700		-.826
Cu (F3)	-.562	.414	-.790
Zn (NA)	.533	.406	.745
As (NA)	-.374		.645
Eigenvalues	13.6	8.4	4.1
% of variance	42.4	26.2	12.9

Strong weights of the metal availability in the first component clearly indicated that this component could be termed as a "weakly bound factor". The second component chiefly belonged to the textural factor since the weights of the clay, silt and sand were noticeable. This shows the importance of particle size analysis as it has a key role in assessment of the contamination sites and then choosing the proper management strategy for remediation. The third and last component described the non-available heavy metals in the sediment samples. In other words, the third component presents the importance of the elements, which were bound to the most stable fractions in the sediment matrix over time. To conclude, the risk of mobility and availability of the metals were approximately 2 and 3 times more than the second and the third components in the sediment samples, respectively. Consequently, an appropriate technical method for contaminated sediment management in the harbour should address firstly the metal availability issue and then dealing with those contaminants with strong bounds to the sediment. So, was the resuspension method a proper strategy to satisfy the harbour's needs? To answer that, SPM data set was analyzed by PCA.

In order to evaluate the main component in SPM, the same procedure was followed and the results present in results present in

Table 5.9. It is worth highlighting that 18 variables were used for SPM data analysis including the main contaminants (Cu, Zn, Cd and Pb) since it provided more meaningful components with more explanation of the total variance.

Based on the results in

Table 5.9, the concentrations of Pb and Zn in F3 and texture of the SPM had a significant weight in the first component. In other words, the role of Fe-Mn hydroxide (F3) and clay as the key scavengers of heavy metals were dominant in the first component.

Table 5.9 Structure matrix, which presents the contribution of variables in each component for the SPM data set. A: Availability (F1+F2)%, F3: Fraction 3 (Fe-Mn oxides/hydroxides), NA: Non-availability (F4+F5)%, and I_{geo}: Contamination intensity.

Variables	Component		
	1	2	3
Pb (NA)	-.945		
Pb (I_{geo})	.932		
Pb (F3)	**.908**		
Zn (F3)	**.878**		
Clay	**.864**		
Silt	**-.864**		
Zn (NA)	-.842	.408	.388
Cu (I_{geo})	.796		
Zn (I_{geo})	.774		.491
Cd (I_{geo})	.665	-.569	
Cd (F3)		-.903	
Cd (A)		**.880**	
Cu (A)		**.837**	
Pb (A)		**-.786**	-.347
Zn (A)		**-.655**	-.652
Cd (NA)			**.938**
Cu (F3)			-.905
Cu (NA)		-.451	**.809**
Eigenvalues	7.6	4.6	3.0
% of variance	42.2	25.5	16.5

The second component explained the importance of SPM for removing the available contaminants from the aquatic environment. This factor was the first component in the sediment samples before the test. Since the variables in each component should have a correlation to each other, it might be true if we consider that those contaminants (Zn-Pb and Cu-Cd) have the same origin (Lucho-Constantino et al., 2005).

The last component explained the influence of the concentration of the Cu and Cd in stable fractions with 16.5% of the variance explained. It seems that the available (F1+F2) and potentially mobile concentrations of heavy metals under changing conditions (F3) in SPM have a dominant role according to the first and second components. To conclude, removing the SPM through the resuspension method not only satisfied the reduction of the mobility and availability risk of heavy metals (second component), but also was efficient for reducing those concentrations of elements existing in the most stable fractions. Subsequently, the resuspension could reduce the short term and long term risk in the aquatic ecosystem without applying chemical additives.

5.4 Conclusions

A series of experimental tests was performed to evaluate the capability of the resuspension technique as a new alternative for remediation of contaminated sediment in harbours. Additionally, the effect of this technique on the distribution of heavy metals in sediment and SPM's fractions were considered. Sediment samples were taken from a harbour in the province of Quebec in Canada.

The resuspension method was successful in reducing the concentration of seven selected heavy metals by 24%. The results of enrichment factor and geoaccumulation index implied that cadmium and lead are the main contaminants followed by zinc and copper. The resuspension method improved the quality of sediment based of geoaccumulation results after the process. A sequential extraction test also was applied to estimate the mobility and availability of the selected heavy metals. The sequential extraction results were the basis for establishing the risk assessment code and eventually assessing the risk of metal mobility. Cadmium and lead levels were in the medium to very high-risk zones unlike the other metals. Moreover, metals with more availability were found in more labile fractions in SPMs and those metals with more stable bonds to sediment matrix were detected in more stable fractions in SPMs. Removing the contaminants through the SPM removal in this technique removed more environmentally available heavy metals, with a high RAC and subsequently decreased the risk posed to the aquatic environment.

Moreover, removing 4 percent of the total contaminated sediment from the harbour area can lead to lower transportation costs and handling of the sediment.

Acknowledgments

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5.5 **Appendix:** Principal component analysis for surface and core samples

The purpose of this appendix is to present the results of the PCA for both surface and core sediment samples (sediment before the resuspension test) in 15 locations across the harbour (Figure 3.1a). PCA was performed based on the data sets adopted from Chapter 3 and Chapter 5 (this Chapter) comprised of 17 subjects (surface and core sediment samples) and 32 variables. Surface samples from stations 1, 2, 3, 4, 8, 10, 12, 13 and 15 were employed along with core sediment samples from stations 1, 2, 3, 4, 5, 6, 13 and 15. Similar to variables used in this Chapter, 32 unit-less variables were used in PCA. The details of the procedure and applied technique were described in Chapters 3 (section 3.3.6) and 5 (section 5.3.7). Table 5.10 presents the results of the rotated component loading score for described data set. Eigenvalues, percentage of variance and cumulative percent are also presented in this table.

Table 5.10 Principal components for the sediment samples (surface and core) before the test's data set as well as their variables. A: Availability (F1+F2)%, F3: Fraction 3 (Fe-Mn oxides/hydroxides), NA: Non-availability (F4+F5)%, I_{geo}: Contamination intensity.

Variable	PC1	PC2	PC3	PC4
Ni (A)	**.973**			
Cd (A)	**.941**		-.340	
Zn (A)	**.936**			
As (A)	**.934**			
Pb (F3)	-.913			-.464
Cd (F3)	-.887		.411	-.324
Zn (F3)	-.886			-.424

Cu (A)	**.798**			
Pb (A)	**.796**			
Cr (F3)	-.774	.343	.607	
Cr (NA)	.707	-.393	-.635	
As (F3)	-.685	.349	.411	-.561
Cr (A)	.602	.469		
Zn (NA)	.591		-.362	.569
Pb (NA)	.569			.562
Cr (I_{geo})		**.932**		-.321
Cd (I_{geo})		**.861**		
Ni (I_{geo})	.399	**.819**		
Zn (I_{geo})		**.790**		
As (I_{geo})	-.372	**.767**	.362	-.338
LOI		.684	.615	
As (NA)		-.565		.501
Clay			**-.938**	
Silt			**.901**	
Sand	-.357		**.883**	
Pb (I_{geo})	-.324	.319	.455	.301
Ni (F3)	-.399			**-.893**
Ni (NA)				**.875**
Cu (NA)		-.540		**.814**
Cu (F3)	-.562	.399		**-.766**
Cd (NA)		-.410		**.700**
Cu (I_{geo})				.423
Eigenvalue	12.0	6.8	4.1	2.4
% of Variance	37.5	21.2	12.7	7.5
Cumulative %	37.5	58.7	71.4	78.9

The results of Table 5.10 are slightly different than similar analysis in Chapters 3 and 5. Precisely, unlike the other PCAs for surface and core samples separately, the analysis of the combined data set indicated that 4 main components explained 78.9% of the variances. The main factor (PC1), similar to the results of the surface samples in this Chapter, implies the significance of metal availability. As it is cited earlier, Sundaray et al. (2011) entitled this group of variables as anthropogenic factor. Cd, Pb and Zn as the main contaminants along with other selected heavy metals were found in this group. It should be noted that the concentration of Cd, Pb and Zn in Fe-Mn oxide/hydroxide fraction also showed a significant loading score in PC1. This fraction, in core sample particularly, contains the contaminants that moved from labile fractions to F3 over time. Therefore, anthropogenic activities at least in the last 14 years (since dredging was employed in the study area) could be the most influential factor in making a proper decision for managing the contaminated sediment.

Intensity of contamination of heavy metals in sediment is the second principal component. Unlike the results of PCA in this Chapter, the second PC in Table 5.10 clearly contains the variables representative of I_{geo}. This factor was recognized for core samples in Chapter 3 as the most significance component. Determining the contamination intensity of metal in sediment is a key achievement for identifying the actual contaminants and consequently selecting a proper management option.

The third PC indicated the role of textural factor (particle size analysis) in the data set. Although this group of variables explained 12.7% of the variance, they have a crucial function for adsorbing and transporting the contaminants. Clay and colloid, as the dominant particles in the sediment samples, carried higher concentrations of pollutants with respect to the rest of sediment grains, according to the enrichment factor results. Subsequently, the textural factor can be an influential factor for selecting remediation options.

The last significant component is the contribution of non-available metals' fraction in explaining of the variance (7.5%). This component can be termed as the lithogenic factor on contribution of metal in sediment fractions. Metals that are contributed by this factor cannot pose any threat to aquatic ecosystem. In this study, Cr, Ni and As (almost in all samples) are the metals mainly found in the most stable fraction and their total concentrations were about their natural levels.

Chapter 6

6 Conclusions, contributions and future work

6.1 Summary of conclusions

The main focus of this study was to address the particular issue of some harbours, which was the combination of shallowness and contaminated sediment with heavy metals. Dredging the sediment, as an unavoidable operation in shallow aquatic areas, causes an increment of oxygen demand and turbidity levels, and increases the risk of remobilization of heavy metals into overlying water. An appropriate management strategy for contaminated sediment is required prior to dredging in order to reduce the concentration of contaminants and the risk potentially posed to the aquatic ecosystem.

At the first step to achieve the goal, influential parameters for the proper management option were identified by assessing different physicochemical characteristics of contaminated sediment in a harbour in the province of Quebec, Canada. The harbour (study area) was located on the north bank of the St. Lawrence River, with the area of approximately 15,000 m^2. Two sets of sediment samples (surface and core sediment) were obtained at 15 selected stations across the harbour. The texture of sediment samples was pretty fine (with D_{50} about a micron) and they contained NOM. However, the results of redox potential and dissolved oxygen indicated that the sediment were oxic under the oxygenated water in the site.

The quality of sediments was assessed through the Canadian sediment quality guidelines, provided by Environment Canada and MDDEP. Although the total concentration of metals suggested that Cr, Cu and Zn were the main elements exceeding the OEL and PEL, the results of the EI and I_{goe} clearly indicated that Cd and Pb were the main contaminants that exceeded their natural levels, followed by Zn and Cu. Moreover, analysis of metal fractionation showed that the potential mobility and availability of Cd and Pb were about 5 times more than the rest of selected metals (i.e. Cr, Ni, Cu, Zn and As). The risk assessment code also suggested that Cd in surface sediment was located at a high to very high-risk zone (for stations in the vicinity of the maintenance area) and Pb in the core sediment was found at medium to high-risk zone (at the same locations). It is worth mentioning that Cd and Pb in both surface and core samples showed a high level of availability with respect to the rest of the selected metals.

The main influential factors in selecting an appropriate and balanced management option were identified by employing multivariate statistical analysis (i.e. principal component analysis and cluster analysis). Analysis of a data set, generated by 17 samples (9 surface and 8 core sediment samples) from different locations across the harbour, demonstrated that the anthropogenic factor (availability of metals) is the most influential parameter in proposing a sustainable management strategy for this specific case. Also, intensity of contamination in the sediment and textural factor were recognized as the other main factors in this regard. Cluster analysis, however, was employed for grouping the stations in the harbour based upon similarities of their contamination intensity. Locations near the maintenance area (i.e. 1, 2, 3, and 4) were categorized as the most contaminated areas. Also, stations 6, 9 and 15 were non-contaminated areas, which implied that the sources of pollution were from the area in the vicinity of the harbour (i.e. antifouling paint particles or/and petroleum and its derivatives from motorboats) rather than the industrial regions upstream of the river.

A resuspension technique was introduced as a balanced and sustainable management option in shallow harbour areas, for the contaminated sediments. A series of laboratory-scale experiments were designed and conducted in order to address the harbours' issues. The resuspension method successfully reduced the total concentration of contaminants in almost all samples below the probable effect level (PEL) with no significant change in the quality of the overlying water. pH of the overlying water slightly increased over the 2 hours of resuspension, although it gradually returned to its original level 48 hours after the test. Dissolved oxygen and redox potential noticeably improved during the test as well, which helped to enhance the quality of water after the resuspension.

Removal efficiency of heavy metals from the surface sediment samples on average was positive for all heavy metals (with a minimum 17.6% for Co and a maximum for 25.9% for Zn), which endorsed the capability of this technique to reduce the concentration of pollutants.

However, analysis of the removal efficiency (RE) and enrichment factor (EF) results suggested that RE could be drastically enhanced for metals in the sediment with higher EF values.

Suspended particulate matter (SPM) was the targeted sediment, which were suspended and removed over the resuspension test. They carried 34% more concentration of contaminants than the bulk sediment on average for all selected heavy metals. Over the resuspension test in this study, just 4% of the sediment was removed from the reactor. In other words, by removing just 4% of the targeted contaminated sediment through this technique, the contamination intensity in the sediment, presented by geoaccumulation index, was reduced for Cd and Pb as the main contaminants by 26 and 28 percent and for the rest of the selected heavy metals returned to the non-polluted level.

For selected surface sediments, the majority of heavy metal concentrations in the SPM were in the residual fraction (almost 45% on average of all selected metals). However, for those metals existing in the less stable fractions in the sediment (i.e. Cd and Pb), they were more available in the SPM. Conversely, for those metals more strongly bound to the sediment matrix, they were found in more stable fractions and became even less environmentally available in SPM. Cd and Pb were mostly found in F2 and Zn in F3. Therefore, removing the contaminants through the SPM removal in this technique removed more environmentally available heavy metals with high RAC (i.e. Cd and Pb). As a result, less risk would be posed to the aquatic ecosystem.

Removing the SPM through the resuspension method not only satisfied the reduction of the mobility and availability risk of heavy metals (as the most influential factor in managing the sediment in this study), but also was efficient for reducing those concentrations of elements existing in the most stable fractions. Subsequently, this method is able to reduce the short term and long term risk in the aquatic ecosystem without applying chemical additives.

6.2 Contributions

This study, for the first time, evaluated the feasibility of the resuspension technique as a new approach for remediation of contaminated sediment with heavy metals. This technique, in some particular cases, is the only viable option for reducing the risk of remobilization of contaminants in harbours due to an undesirable resuspension event. Unlike the common in situ techniques, this method could successfully reduce the total concentration of contaminants in almost all samples below the probable effect level (PEL) with no significant change in the quality of overlying water.

The resuspension method can be employed in a shallow contaminated aquatic environment, where the common *in situ* techniques are not applicable. *Ex situ* remediation techniques also require dredging the contaminated sediments, which can increase the risk of mobility and availability of heavy metals in the harbours and impacts on the disposal sites that receive the dredged sediment. Moreover, no chemical additives were employed in this method.

The resuspension technique is designed to remove a small percentage of sediment (i.e. 4% in this study), containing the largest concentration of contaminants. Risk of mobility and availability of heavy metals in future dredging operations can be reduced and handling fees for disposal of contaminated sediments in landfills can be minimized. Considering this fact that open water disposal of highly contaminated sediments is not allowed in many countries, this method could be a solution to reduce dewatering, transport and landfill tipping fees for contaminated sediment, which are the major costs in sediment management. Moreover, the threat of uncontrolled resuspension of contaminated sediment, by the natural or anthropogenic events at the site, posed to the aquatic environment can be drastically reduced.

6.3 Recommendations for future work

The following are the author's suggestions for expanding this research.

- This study was performed under the laboratory-scale experiments, although the samples were with sediment from the site (St. Lawrence River). Scaling up of the equipment for performing the pilot test is recommended. Pilot tests have particular challenges, which cannot be foreseen in laboratory-scale experiments. Moreover, a pilot test could assist in commercializing this technology.
- Sediments from the harbour in St. Lawrence River were not highly contaminated. Conducting the resuspension method on more contaminated sediments may show stronger performance and provide a more significant distribution of contaminants between bulk sediment and SPM.

- This technique is capable of remediating the sediment polluted with both organic and inorganic contaminants. Applying the resuspension on contaminated sediments containing both types of pollutants is recommended for expanding this research. Moreover, employing well-graded sediment (sediment with a wider range of particle sizes) is suggested.
- This research was conducted for oxic sediment under oxygenated water, since the samples were obtained from a shallow harbour with an over saturated oxygen condition. However, the capability of this technique should be evaluated under anoxic conditions as well. Also, seawater with the certain amount of salinity can be used to assess the quantity of remobilized heavy metals into the aqueous phase. Perhaps, air jets can be replaced by water jets to control the level of oxidation, in that case.
- Intensity and duration of resuspension/aeration are the key elements in this method. These parameters also need to be adjusted based on the physicochemical characteristics of the sediment and water for each case accordingly.

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