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**The Hong Kong Polytechnic University**

**Department of Civil and Structural Engineering**

**The Study of Sediment Quality and Ecological Recovery  
in Victoria Harbour**

**TANG Wing Yee, Chloe**

**A thesis submitted in partial fulfillment of the requirements for  
the Degree of Master of Philosophy**

**November 2006**



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TANG Wing Yee, Chloe

## **Abstract**

Victoria Harbour has received a substantial loading of pollutants from industrial and municipal wastewater since the 1950s. Contaminant inputs have declined drastically during the last two decades as a result of better source control and improved treatment processes. This study aims to examine the distribution, sources and geochemical behaviour of trace metals in Victoria Harbour sediments, in order to facilitate more effective management or restoration alternatives.

Core and grab sediments were collected to study the concentrations of trace metals (Cu, Pb and Zn), Pb isotopic ratio, particle size and total organic content (TOC). Serious metals contamination was observed in the central part of Victoria Harbour. Proximity to urbanized and industrial areas, and harbour hydrodynamics were found to be the main factors controlling spatial distribution of metals in sediments. Sediment cores revealed a substantial increase of trace metals during the 1950s to 1980s, corresponding with the period of rapid urban and industrial development in Hong Kong. There was a major improvement of metals contamination from the late 1980s due to the relocation of industrial activities and set-up of the Chemical Waste Treatment Centre in the territory. Nevertheless, metals were still elevated in uppermost sediments, which may act as a secondary source of pollution. Anthropogenic sources of Pb were verified by a lower Pb isotopic composition in

sediment samples, probably originating from leaded gasoline and other anthropogenic sources, such as industrial and ship repairing activities.

The geochemical behaviour of metals (Fe, Mn, Cu, Pb and Zn) in surface sediments was investigated using a single extraction method with cold HCl and a modified 5-step Tessier's sequential extraction technique. The harbour sediments, especially at the central part, were characterized by strongly reducing conditions and high amounts of acid volatile sulfide (AVS). Copper was predominantly associated with organic matter, carbonate/specifically adsorbed, and to a lesser extent sulfide phases; Zinc was mainly in the carbonate/specifically adsorbed, oxides phases, and possibly sulfide phases, while Pb was mainly found in the carbonate/specifically adsorbed phase in harbour sediments. Hence, the bioavailability order of trace metals was  $Pb > Zn > Cu$ . A major temporal change (October 2005 and April 2006) of redox conditions in sediments as a result of sediment resuspension was observed in the central part of the harbour. Sediments in October were characterized by less reducing conditions, which led to subsequent increases of Cu in the carbonate/specifically adsorbed phase and Zn in the oxide phase. Such changes of metal partitioning in harbour sediments may release metals to the water column and lead to a greater environmental risk to marine organisms.

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## Table of Content

<b>Certificate of originality .....</b>	<b>I</b>
<b>Abstract.....</b>	<b>II</b>
<b>Table of Content.....</b>	<b>V</b>
<b>List of Tables .....</b>	<b>VII</b>
<b>List of Figures.....</b>	<b>IX</b>
Chapter 1 Introduction .....	1
1.1. Background .....	1
1.2. Objectives of the present study .....	3
1.3. Scope of work .....	4
1.4. Organization of the thesis .....	4
Chapter 2 Literature Review .....	6
2.1. Sediments and trace metals .....	6
2.1.1. Sediments .....	6
2.1.2. Trace metals .....	7
2.2. Potential sources of metals in the aquatic environment.....	8
2.2.1. Natural sources.....	8
2.2.2. Anthropogenic sources.....	9
2.3. Heavy metals in urban harbours.....	13
2.4. Partitioning of metals in sediments.....	14
2.4.1. Oxic sediments .....	16
2.4.2. Anoxic sediments.....	18
2.4.3. Remobilization of metals from polluted coastal sediments .....	20
2.5. Methods for sediment quality assessment.....	22
2.5.1. Chemical analysis .....	22
2.5.1.1. Total acid digestion and sediment quality guideline of sediment.....	22
2.5.1.2. Sequential extraction of the sediment .....	25
2.5.1.3. Cold HCl extraction of the sediment (AVS/SEM analysis).....	32
2.6. Identification of trace metal contamination and sources in sediments .....	37
2.6.1. Trace metal normalization for the particle size effect.....	37
2.6.2. Study of the temporal metal distribution using <sup>210</sup> Pb dated sediment cores .....	39
2.6.3. Statistical analysis of metal concentrations .....	41
2.6.4. Study of Pb sources using Pb isotopic ratio.....	41
Chapter 3 Study Area and Methodology .....	44
3.1. The study area – Victoria Harbour.....	44
3.2. Sample collection and preparation.....	54
3.3. Sample analysis.....	56

3.3.1. Determination of trace and major element concentrations .....	56
3.3.2. Sequential extraction of trace metals in sediments .....	57
3.3.3. Cold HCl extraction of AVS in sediments .....	60
3.3.4. Lead isotopic composition analyses using ICP-MS.....	61
3.3.5. <sup>210</sup> Pb dating analyses along sediment cores .....	62
3.3.6. Other parameters (including particle sizes, TOC and PO <sub>4</sub> analyses in sediments) .....	62
3.4. Preliminary laboratory bioaccumulation test .....	63
3.5. Statistical analyses .....	64
 Chapter 4 Spatial and temporal distribution of trace metals in sediments of Victoria Harbour, Hong Kong .....	66
4.1. Physical properties of harbour sediments .....	66
4.2. Spatial distribution of trace metals in harbour sediments .....	69
4.3. Temporal distribution of trace metals in harbour sediments .....	76
4.4. Potential sources of trace metals in the harbour .....	83
4.5. Pb isotopic composition of harbour sediments .....	87
 Chapter 5 Geochemical behaviour of trace metals in surface sediments of Victoria Harbour, Hong Kong .....	91
5.1. Physiochemical properties of surface sediments .....	91
5.2. Non-residual form of metals in sediments .....	95
5.3. Cold HCl extraction of harbour sediments .....	99
5.4. Five-step sequential extraction of harbour sediments.....	108
5.5. Environmental implications of metal enrichment in harbour sediments .....	116
5.6. Biological uptake of trace metals in harbour sediments .....	119
 Chapter 6 Conclusions and Recommendations.....	122
6.1. Conclusions.....	122
6.2. Recommendations.....	125
6.3. Future Research .....	126
 References .....	129
 Publication List .....	161
 Appendix I Analytical results of the study of Victoria Harbour sediments.....	162
 Appendix II Analytical procedures in the present study.....	189



## List of Tables

Table 2.1. Some industrial activities which may introduce metals to the environment (modified from Siegel, 2002).....	11
Table 2.2. Solubility relationships for different metal sulfides (Stumm and Morgan, 1996) .....	20
Table 2.3. Sediment quality guidelines for trace metals (mg/kg, dry wt.).....	25
Table 2.4. Examples of sequential extraction schemes.....	27
Table 2.5. Examples of acid volatile sulfide (AVS) extraction method .....	36
Table 4.1. Sampling locations, physical parameters of waters, redox potential and TOC of surface sediments in Victoria Harbour .....	67
Table 4.2. Grain size distribution in selected sediment samples from location B1 to B5 in Victoria Harbour .....	68
Table 4.3. Concentrations of Cu, Pb and Zn in surface sediments of Victoria Harbour collected at different sampling periods .....	70
Table 4.4. Mean ( $\pm$ S.D.) of the total metal concentrations (mg/kg, dry weight) in surface sediments of Victoria Harbour (n=8) .....	71
Table 4.5. Metal concentrations in sediments of other polluted harbours (mg/kg, dry weight) .....	75
Table 4.6. Result of the principle component analysis on total metal concentrations in B1 to B5 sediment cores (n=116) .....	85
Table 4.7. Cu/Zn ratios in B1 to B5 surface sediments of Victoria Harbour and ratios in different anthropogenic sources in Hong Kong .....	87
Table 4.8. Mean ( $\pm$ S.D.) and range of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in sediment cores, B1 to B5, of Victoria Harbour .....	88
Table 5.1. Physical parameters of bottom waters and surface sediments in Victoria Harbour .....	93

Table 5.2. Chemical parameters of surface sediments in Victoria Harbour (in mg/kg except TOC).....	95
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Table 5.3. Concentrations of AVS and SEM in surface sediments of Victoria Harbour collected in October 2005 and April 2006.....	104
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## List of Figures

Figure 2.1. A hypothetical porewater profiles predicted by the successive utilization of inorganic compounds during the degradation of sedimentary organic matter (modified from Burdige, 1993).....	15
Figure 2.2. A schematic representation of the sulfate reduction reaction in anoxic sediments (Berner, 1972) .....	18
Figure 3.1. Map showing the location of Hong Kong .....	44
Figure 3.2. Location of major sewage outfalls along Victoria Harbour (from Sin et al., 1995) .....	47
Figure 3.3. Major stormwater outfalls in Victoria Harbour (modified from Sin et al., 1995) .....	49
Figure 3.4. The sampling locations, B1 – B5, in Victoria Harbour .....	55
Figure 4.1. Spatial distribution of average Cu concentrations in surface sediments of Victoria Harbour collected in the four sampling periods (mg/kg, dry weight)..	71
Figure 4.2. Spatial distribution of average Zn concentrations in surface sediments of Victoria Harbour collected in the four sampling periods (mg/kg, dry weight)..	72
Figure 4.3. Spatial distribution of average Pb concentrations in surface sediments of Victoria Harbour collected in the four sampling periods (mg/kg, dry weight)..	72
Figure 4.4. Results of $^{210}\text{Pb}$ dating in sediment cores B2, B4 and B5 of Victoria Harbour .....	77
Figure 4.5. Temporal distribution of Cu, Zn and Pb in core sediments, B1 to B5, of Victoria Harbour (Core B4 with the estimated date) .....	78
Figure 4.6. $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and Pb concentrations (mg/kg) in dated sediment core B4 of Victoria Harbour .....	89
Figure 4.7. Relationship between $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ in sediments of Victoria Harbour and those from known sources in Hong Kong.....	90

Figure 5.1. Relative percentages of metal speciation in surface sediments of Victoria Harbour collected in October 2005 (Step 1: exchangeable; Step 2: carbonate and adsorbed; Step 3: reducible; Step 4: oxidizable; Step 5: residual).....	97
Figure 5.2. Relative percentages of metal speciation in surface sediments of Victoria Harbour collected in April 2006 (Step 1: exchangeable; Step 2: carbonate and adsorbed; Step 3: reducible; Step 4: oxidizable; Step 5: residual).....	98
Figure 5.3. Spatial distribution of AVS ( $\mu\text{mol/g}$ , dry weight) in sediments of Victoria Harbour in October 2005 (filled bar) and April 2006 (bar with diagonal line).....	101
Figure 5.4. Ratios of SEM to non-residual metals in surface sediments of Victoria Harbour collected in October 2005 and April 2006.....	107
Figure 5.5. Comparison of the % oxidizable Cu with the % HCl-extracted Cu in surface sediments of Victoria Harbour .....	113
Figure 5.6. Metal concentrations in <i>Capitella</i> sp.I exposed to B1, B3 and B5 surface sediments collected in October 2005 (n=3) .....	121

## **Chapter 1 Introduction**

Sediments are the major repository for contaminants in the aquatic system. They are often subject to a wide range of contamination in coastal areas due to intensive human activities such as marine traffic, discharges of industrial and domestic effluents (Bothner et al., 1998; Latimer et al., 2003; Mostafa et al., 2004). Of particular concern are trace metal contaminants which show high affinities for fine-grained suspended particles. Once they are released into the aquatic environment, trace metals may be removed from the water column by interacting with suspended solids and subsequently deposited as bottom sediments (Croudace and Cundy, 1995). Trace metals, unlike other pollutants, are not biodegradable and can accumulate in sediments over time. It is thus important to understand the chemical behaviour of trace metals in sediments, in order to assess their long-term potential impact on marine organisms.

### **1.1. Background**

Victoria Harbour is located in the southeastern part of the Pearl River Estuary (PRE), South China. Waters in the harbour are influenced by the freshwater discharge from the PRE in the west and the marine waters from the South China Seas in the east. The environmental quality of the harbour has been subjected to significant pressure from the growing population and industrial development in Hong Kong and the

surrounding regions in the last few decades. Extensive human activities near Victoria Harbour began from the early 1950s. As a result of population growth, and the development of manufacturing industries along the coastlines, the harbour received a significant amount of organic and inorganic pollutants from untreated sewage and industrial effluents. It is estimated that industries in Hong Kong contributed around 7500 kg per day of trace metals into the coastal waters before 1993. With the enactment of the Water Pollution Control Ordinance and the relocation of industries to mainland China, the metal loadings to the harbour was greatly reduced to less than 1000 kg per day in recent years (Dawes, 2001).

In the past few decades, a number of research projects have been conducted into the sediment quality in Victoria Harbour. These studies showed that Victoria Harbour has been heavily contaminated with trace metals, particularly Cu, Zn, Pb, Ag, Cr and Cd (Yim, 1981; Lam et al., 1997; Tanner et al., 2000; HKEPD, 2003). However, there are very few studies which focus on the long-term response of metals in sediments associated with the reduction of pollutant loading in Victoria Harbour. Besides, there is no information on the Pb isotopic composition, which has been widely used for source identification, in marine sediments. Therefore, it is necessary to assess the changes of sediment contamination over time, especially for the recent two decades, in order to evaluate whether the current management practices can result in the improvement of sediment quality in Victoria Harbour. The study of

geochemical behaviour of trace metals can also provide important information on the metal bioavailability in sediments, which may affect the long-term ecological recovery in the harbour.

The present research examines the trace metal contamination of sediments and the geochemical behaviour of trace metals in Victoria Harbour. The findings of the present study may be useful to formulate future environmental management practices in the territory, especially on the marine water quality.

## **1.2. Objectives of the present study**

This research aims to study the trace metal contamination of sediments in Victoria Harbour. The specific objectives of this study are:

- (1) to assess the contamination levels in terms of the spatial and temporal distribution of trace metals in Victoria Harbour, Hong Kong;
- (2) to identify the potential sources of trace metals in Victoria Harbour based on the geochemical associations and the Pb isotopic composition in sediment cores;
- (3) to investigate the geochemical behaviour of trace metals in harbour sediments using both a single extraction method with cold HCl and a 5-step Tessier sequential extraction method;
- (4) to evaluate the potential environmental impacts of metals in harbour sediments based on the examination of metal speciation, and the relationship between metal

speciation and benthic community in the harbour as well as metal uptake by deposit feeders.

### **1.3. Scope of work**

This thesis focuses on the assessment of sediment quality in Victoria Harbour. The samples to be examined consist of sediments collected in the western, central and eastern parts of Victoria Harbour. The laboratory analytical programme includes the analyses of trace metal concentrations, the Pb isotopic composition of the samples, the chemical partitioning of trace metals, the acid volatile sulfide (AVS) and simultaneously extracted metal (SEM) analyses of the sediments, the  $^{210}\text{Pb}$  dating of sediment cores as well as sediment bioaccumulation test.

### **1.4. Organization of the thesis**

This thesis is divided into six chapters. The present chapter covers the background, objectives, and scope of this research project. A brief literature review is given in Chapter Two. Chapter Three contains detailed descriptions of the study areas, reviews on the previous findings of the study areas as well as the materials and methods used in this study. The analytical results obtained are discussed in Chapters Four and Five. Chapter Four focuses on the spatial and temporal trace metal contamination of sediments in Victoria Harbour. Chapter Five examines the geochemical behaviour of trace metals and the potential environmental implications



of metal enrichment in Victoria Harbour. Finally, Chapter Six concludes the major findings of this study and provides some recommendations for future research.

## **Chapter 2 Literature Review**

### **2.1. Sediments and trace metals**

#### **2.1.1. Sediments**

Marine sediments are the major sink for materials in coastal regions and open seas. They include gravels, sands, silts and muds, and are composed of terrigenous, authigenic and biogenous mixtures (Chester, 2000).

The sediments deposited in nature are typically comprised of oxic layers on top of anoxic layers. A boundary occurs between reducing and oxidizing zones when the demand of oxidants begins to exceed the supply. The boundary can be termed as the redox potential discontinuity (RPD) layer, which is a division zone between oxidized and reduced chemical conditions (Rosenberg et al., 2001). The depth of the oxic zone is controlled by a balance between the sedimentation of reactive organic materials, the microbial oxygen consumption during the organic matter decomposition, and oxygen penetration into the sediment (Aller, 1978). Oxygen penetration in sediment is in turn influenced, e.g. by animal activities. Bioturbation, irrigation and the building of structures by the infauna are important activities, which determine the depth of oxidizing zone in sediments (Rosenberg et al., 2001).

It is well documented that a great difference in geochemical properties exists between oxidized and reduced sediments. In oxidized sediments, organic matter and

Fe/Mn oxides are found to be the dominant metal binding phases (Tessier et al., 1979). In anoxic sediments, sulfide and organic phases are considered as the major components determining metal partitioning (Di Toro et al., 1990).

### **2.1.2. Trace metals**

Metals are natural components of the biosphere. Unlike synthetic organic chemicals, metals cannot be created or destroyed by human activities. Instead, human activities affect the metal concentrations in the environment through enhancing the release of metals from the crust and altering their distribution among different environmental media (Chapman and Wang, 2000).

Trace metals are present only in small amounts in nature, such as a few parts per million or less (Manahan, 2000). Their presence in excess concentrations may have potentially adverse health implications. For example, low levels of Pb exposure can cause a wide range of metabolic disorders and neuropsychological deficits, particularly for children having high gastrointestinal uptake and permeable blood-brain barriers (Järup, 2003). The present study focuses on three trace metals, namely copper (Cu), lead (Pb) and zinc (Zn), as these metals are common contaminants in urban settings. To study the elemental associations and to identify the possible anthropogenic inputs of trace metals in sediments, some major elements are also

studied. These major elements include aluminium (Al), iron (Fe), calcium (Ca) and manganese (Mn).

In general, metals are persistent and do not degrade as they enter the environment. Rather, metals can be transformed into various chemical phases, such as exchangeable, metal-organic complexes or metal sulfide (Tessier et al., 1979). Different forms of metals in the environment determine their availability to biota, and adverse biological effects can only occur if metals are present in bioavailable forms at significant concentrations. The mobility and bioavailability of metals in different phases may in turn be controlled by various environmental parameters, such as pH, redox potential (Eh) and salinity (Förstner and Wittmann, 1981; Calmano et al., 1993; Siegel, 2002). Therefore, it is important to examine the metals partitioning (chemical forms) in sediments, in order to assess metals mobility and their potential impact on the environment.

## **2.2. Potential sources of metals in the aquatic environment**

### **2.2.1. Natural sources**

Trace metals occur naturally in sediments as a result of weathering and other geochemical processes of rocks. Different types of rocks vary considerably in their mineralogical and elemental compositions. This may result in differences in trace metal concentrations among sediments even in the absence of significant inputs from

external sources. For example, sediments formed from the erosion of mafic and ultramafic rocks tend to have high concentrations of Cr, Ni and Co. These metals are usually contained in minerals comprising the rocks such as olivine forsterite (Ni, Co), chrome diopside (Cr) and chromite (Cr) (Siegel, 2002). Metals bound in the crystalline structural lattice of primary and secondary minerals are not readily bioavailable to organisms. However, they may be available if the minerals undergo geochemical weathering (Calmano et al., 1993).

#### **2.2.2. Anthropogenic sources**

Anthropogenic input of metals began when human started ore processing (Renberg et al., 1993). The release of metals to the environment has accelerated during the 19th and 20th century with the rapid increase of industrial and urban activities (Nriagu, 1979; Förstner and Wittmann, 1981). A large proportion of these metals have been released to the atmosphere or directly to aquifers, where they ultimately accumulated in sediments. It has been estimated that anthropogenic emissions of Cd, Cu, Ni, Zn and Pb have exceeded the natural inputs over an order of magnitude, and have posed a serious contamination problem worldwide (Nriagu, 1979; Nriagu and Pacyna, 1988). The anthropogenic pollution problems are frequently observed in urban settings. In urban areas, untreated wastes from industrial and municipal activities, as well as combustion of fossil fuels and the wear and tear of vehicle parts are some of the major contributors of trace metals to the environment (Rice, 1999;

Callender and Rice, 2000). These metals are subsequently released to the aquatic environment through point and non-point source discharges as well as dry and wet atmospheric deposition to water bodies.

Industrial activities such as electroplating, alloy production, dying, battery recycling and metal processing industries have introduced substantial amounts of metals to the environment (Siegel, 2002). Table 2.1 shows the metals that may be introduced to the environment from various types of industrial activities. Serious metal contamination in sediments caused by industrial activities has been observed in many parts of the world. For example, sediments in the Keelung River, Taiwan, contained 200 mg/kg of Pb, which was ten times the background value, due to waste discharged from a battery recycling plant (Huang and Lin, 2003). In the Coatzacoalcos river estuary, southeast Mexico, intensive industrial development has resulted in a remarkable enrichment of metals in sediments, with maximum Cu and Zn concentrations of 235 and 640 mg/kg, respectively (Rosales Hoz et al., 2003).

Table 2.1. Some industrial activities which may introduce metals to the environment (modified from Siegel, 2002)

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	V	Zn
Alloys	✓	✓	✓	✓	✓		✓	✓		✓
Batteries and Electro/Chemical						✓	✓	✓		✓
Biocides (Agriculture, Anti-	✓					✓				
Ceramics and Glass	✓		✓				✓	✓		
Chemicals, Pharmaceuticals,	✓	✓		✓	✓	✓		✓	✓	✓
Coatings (anti-corrosives)		✓		✓				✓		✓
Electrical Equipment and					✓	✓				
Fertilizers	✓	✓		✓	✓	✓	✓	✓		✓
Fossil Fuel Combustion	✓	✓				✓		✓		
Mining, Smelting, Metallurgy	✓	✓		✓	✓	✓	✓	✓	✓	✓
Paints and Pigments	✓	✓	✓	✓	✓		✓	✓		✓
Pipes, Sheets, Machinery					✓			✓		
Plastics		✓						✓		✓
Pulp and Paper				✓	✓	✓	✓	✓		
Rubber										✓
Semi-conductors, Super-	✓									
Tanning and Textiles	✓			✓	✓					
Wood Preservation Treatment	✓			✓						

The discharges of untreated sewage have caused serious contamination of Cu, Pb and Zn in sediments of urbanized areas, such as Boston Harbour (Zago et al., 2001), Halifax Harbour (Buckley et al., 1995) and the Southern California Bight (Finney and Huh, 1989). Boston Harbour received untreated sewage for more than 100 years, resulting in a significant enrichment of Cu, Pb and Zn in its sediments. The flux of metals from sewage was found to be greatly reduced after the cessation of the sewage sludge discharge to the harbour, and a subsequent reduction of Pb, Cu and Zn by 69, 40 and 58 %, respectively, were reported (Bothner et al., 1998).

The increased automobile use in urban areas has contributed considerable amounts of metals, including Pb, Cu and Zn, to the aquatic environment (Finney and Huh,

1989; Li et al., 2001). Automobile use was the major contributor of Pb from 1950 to the 1970s due to the prevalent use of leaded gasoline worldwide. It has been estimated that 60 % of the pollutant Pb in the global atmosphere in 1975 was originated from the combustion of leaded gasoline (Nriagu, 1979). In the United States and in Europe, maximum Pb concentrations were observed in subsurface sediments reflecting the historical automobile use of Pb additives (Van Metre et al., 1998; Monna et al., 1999). Although the phasing out of leaded petrol began in the 1970s, Pb from the past use of leaded petrol still persists in different environmental compartments (De Miguel et al., 1997; Sutherland and Tolosa, 2000; De Carlo and Anthony, 2002). For example, in the Atlanta Metropolitan Area, the contamination of Pb in sediments was suggested to be originated from street dust and urban soils containing elevated Pb derived from the previous use of leaded gasoline (Callender and Rice, 2000). The automobile use is also the potential source of Cu and Zn to the aquatic environment. Automobile tires contain a large amount of zinc oxide (ZnO) which acts as an accelerator in the vulcanization process (Councell et al., 2004). Cu can be found in automobile thrust bearing, brake lining and other parts of the engine. Tire wearing and the corrosion of mechanical parts of motor vehicles may thus result in the release of Cu and Zn to the environment. These metals may accumulate in the dust and roadside sediments and ultimately be washed off to nearby water bodies (Lee et al., 2005; De Carlo and Anthony, 2002).



Other anthropogenic sources of metals in the urban environment may include waste incineration, coal burning and ship building (Nriagu, 1979; Buckley et al., 1995; Adamo et al., 2005). Recognizing the serious impact of metal emission by human activities, the anthropogenic input of metals to some aquatic environments has been greatly reduced in recent decades with the better controls of emission sources. For instance, a reduction of metal contamination in sediments has been observed in Boston Harbour (Bothner et al., 1998), Southampton Water (Croudace and Cundy, 1995) and San Francisco Bay (Hornberger et al., 1999) due to the improvement of sewage treatment and the reduction of industrial discharges.

### **2.3. Heavy metals in urban harbours**

Harbours are often surrounded by urbanized and industrial areas and subject to extensive human disturbances. Port activities, ship building and repairing, sewage and industrial discharges, and urban runoff contribute a considerable amount of pollutants to the water bodies. Very often, harbours are situated within a bay or estuary, like New Bedford Harbour, Baltimore Harbour and Halifax Harbour. A significant amount of wastewater is drained into the bays and estuaries from river outflows. The wastewater may originate from heavily populated and industrialized areas and contain a substantial loading of organic and inorganic pollutants. Metals in wastewater may be subsequently trapped and deposited in inner harbours with less water flushing, such as in New Bedford Harbour (Stoffers et al., 1977), Baltimore

Harbour (Sinex and Heiz, 1982), Halifax Harbour (Buckley et al., 1995) and Sydney Harbour (Birch, 1996). Besides, metal contamination is often exacerbated by the presence of muddy sediments in the inner harbour (Stoffers et al., 1977; Sinex and Heiz, 1982), as clay has a larger surface area for metal scavenging in sediments (Horowitz, 1991). Apart from the input of pollutants, harbours are frequently subject to physical disturbance such as reclamation and dredging. These may change the water circulation in the harbour, which may enhance or reduce the accumulation of metals in sediments. For example, dredging in Baltimore Harbour has created a three-layer circulation system and increased the dispersion of pollutants in the harbour (Mason et al., 2004).

#### **2.4. Partitioning of metals in sediments**

The partitioning of trace metals in sediments is greatly affected by the change in composition and characteristic of sediments, which is mainly driven by the microbial mineralization of organic substances (Berner, 1980). Figure 2.1 illustrates a hypothetical porewater profile predicted by the successive utilization of inorganic compounds during the decomposition of sedimentary organic matter (Burdige, 1993). In general, the change of sediment composition and characteristics involves transformation reactions of carbon, oxygen, nitrogen, manganese, iron and sulfur.

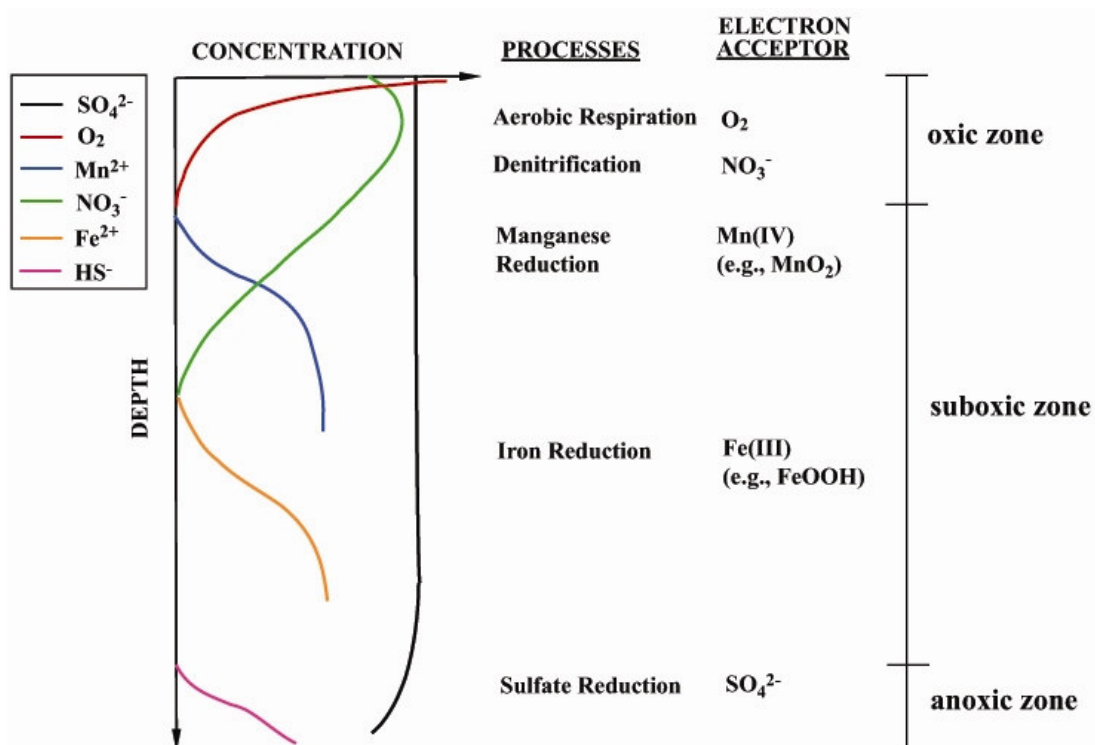


Figure 2.1. A hypothetical porewater profiles predicted by the successive utilization of inorganic compounds during the degradation of sedimentary organic matter (modified from Burdige, 1993)

In oxic sediments, the organic matter is mineralized by microorganisms using dissolved oxygen ( $\text{O}_2$ ) as a terminal electron acceptor. In suboxic sediments, nitrate ( $\text{NO}_3^-$ ) and Fe/Mn oxides (e.g.  $\text{FeOOH}$  and  $\text{MnO}_2$ ) serve as oxidizing agents for the degradation of organic matter. In anoxic sediments, the electrons of organic matter are transferred to sulfate ( $\text{SO}_4^{2-}$ ) and bicarbonate ( $\text{HCO}_3^-$ ) and result in the production of sulfide ( $\text{S}^{2-}$ ) and methane ( $\text{CH}_4$ ) (Wallmann et al., 1996). These reactions cause a different redox potential and the formation of different solid components in sediments, such as iron and manganese oxyhydroxides and iron (Fe/MnOOH) monosulfide ( $\text{FeS}$ ), which in turn affect the partitioning of metals.

Solid components in sediments affect dissolved metals via (1) adsorption and desorption; (2) precipitation and solubilization; (3) surface complex formation; (4) ion exchange; (5) penetration of the crystal structure of minerals; and (6) biological mobilization and immobilization (Chao, 1984). In general, the major metal binding phases include adsorption on particle surfaces (e.g. clays and humic acid), carbonate bound, occluded in Fe-Mn oxyhydroxides, bound with organic matter in either living or detrital form, bound with sulfide, and bound in aluminosilicate minerals (Tessier et al., 1979). Besides the abundance of each component in sediments, the intrinsic properties of metals can also affect the metal partitioning. For example, Cu is often associated with organic matter in sediments due to the high stability constant of organic Cu compounds (Gonzalez et al., 1994; Ramos et al., 1999; Fan et al., 2002; Morillo et al., 2004).

The differences in redox conditions between oxic and anoxic sediments have profound influences on the speciation and bioavailability of many trace metals. The following sections will review the major components of metal binding phases in oxic and anoxic sediments, respectively.

#### **2.4.1. Oxic sediments**

In oxic sediments, the most important geochemical components have been identified as oxides of Mn and Fe, and organic matter (Gibbs, 1977; Luoma and Bryan, 1981).

These components may compete for the binding or sorption of trace metals, depending on the abundance of each component and the intrinsic properties of metals. Fe and Mn hydroxides or oxides generally occur as coatings on minerals or/and as finely dispersed particles. They can be present as amorphous, microcrystalline and “aged” crystalline forms (Förstner and Wittmann, 1981). Metals are readily sorbed or coprecipitated with these hydroxides and oxides. However, they may be released if the sediments change from an oxidizing to a reducing condition. The association of Pb and Zn with Fe and Mn oxides has been widely observed in oxic sediments, such as the Ebro River, Spain (Ramos et al., 1999) and Jinzhou Bay, northern China (Fan et al., 2002).

Organic matter in sediments is mainly comprised of biological remains and synthetic organic substances. Humic substances are found to be a major component of organic matter in marine sediments and play an important role in the partitioning of metals (Förstner and Wittmann, 1981). Metals can bind with organic matter through sorption or complexation. Under oxidizing environments, metals in organic forms can be released as a result of the degradation of organic matter (Tessier et al., 1979; Förstner and Wittmann, 1981). Cu has a high affinity of organic matter and the presence of organic-Cu complexes has been observed in many marine environments (Ramos et al., 1999; Fan et al., 2002; Morillo et al., 2004; Caplat et al., 2005).

#### 2.4.2. Anoxic sediments

In anoxic sediments, the most important component are sulfide systems (Morse, 2002). Under anoxic conditions, sulfate is reduced to sulfide by the respiratory metabolism of sulfate-reducing bacteria, using sedimentary organic matter as a reducing agent and energy source. Also, Fe oxide minerals are reduced and ferrous ions ( $\text{Fe}^{2+}$ ) are generated. The reduced Fe can react with hydrogen sulfide and other sulfur compounds to form various Fe-S minerals (such as FeS and  $\text{FeS}_2$ ) (Figure 2.2). Since Fe is by far the most abundant transition metal in most sediments, iron sulfides are considered as the predominant form of sulfides (Morse et al., 1987; Rickard, 1995).

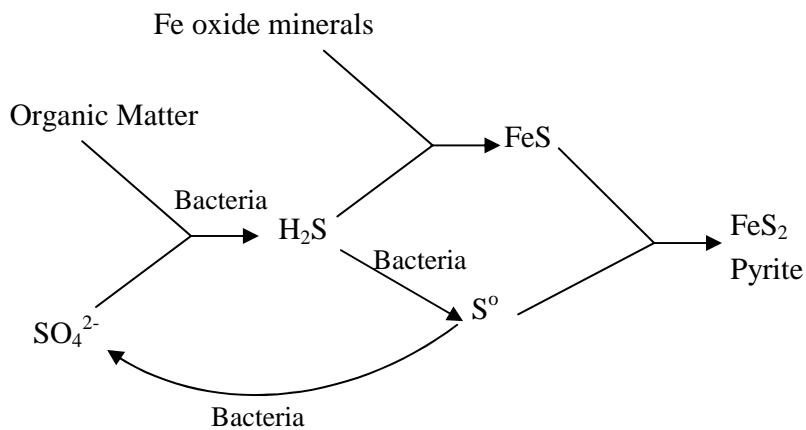


Figure 2.2. A schematic representation of the sulfate reduction reaction in anoxic sediments (Berner, 1972)

In general, iron sulfides in anoxic sediments can be separated into two “operational” categories, namely acid volatile sulfide (AVS) and pyrite ( $\text{FeS}_2$ ) (Berner, 1984; Morse et al., 1987). AVS generally comprises all dissolved  $\text{S}^{2-}$  species, nanoparticles and clusters of FeS in porewater, amorphous FeS and greigite ( $\text{Fe}_3\text{S}_4$ ), which are soluble in cold hydrochloric acid (Rickard and Morse, 2005). AVS is considered as a temporal reservoir for sulfur in the global biogeochemical sulfur cycle. It is an intermediate stage of sulfur between final burial as pyrite and the sulfate in the oxic surface system (Rickard and Morse, 2005). Pyrite is often the most abundant iron sulfide, and presumably resists the dissolution by acid attack and is extracted by chromium reduction methods (Canfield et al., 1986).

Both AVS and pyrite have been considered as an important reservoir of trace metals in anoxic sediments (Di Toro et al., 1992; Morse, 1994). Trace metals can form sulfide minerals with low solubility as shown in Table 2.2; thus they may precipitate as discrete phases, or be adsorbed and coprecipitated with the abundant iron sulfide minerals (Morse and Luther, 1999; Morse and Arakaki, 1993). For example, the study conducted by Morse and Arakaki (1993) has indicated the importance of mackinawite (FeS) in the adsorption and coprecipitation of divalent metals, such as Cu, Ni and Zn, in anoxic sediments. Huerta-Diaz and Morse (1992) demonstrated that pyrite ( $\text{FeS}_2$ ) is an important sink for As, Hg and Mo, moderately important for Co, Cu, Mn and Ni, and less important for Cr, Pb, Zn and Cd. Pyrite can act as a

permanent burial of metals in sediments, and the concentration of some trace metals occurring in the pyrite-extracted fraction was found to increase with depth below the sediment-water interface (Burton et al., 2006). In contrast, AVS is considered as a temporary sink for trace metals as metals associated AVS can be liberated to the solution during the pyrite formation process (Morse and Richard, 2004; Burton et al., 2006).

Table 2.2. Solubility relationships for different metal sulfides (Stumm and Morgan, 1996)

Metal	p*Ks
Cd	14.4
Co	7.4
Fe	3.6
Ni	5.6
Pb	14.0
Zn	10.9

#### **2.4.3. Remobilization of metals from polluted coastal sediments**

Sediments tend to accumulate contaminants due to their sorptive nature, which in turn can act as an important reservoir by reducing the potential toxicity of contaminants to marine organisms (Petersen et al., 1997; Van den Berg et al., 2001). However, sediments are often vulnerable to disturbance caused by natural and human activities, and this may result in the transformation of contaminants into more bioavailable forms (Zhuang et al., 1994). Natural disturbances may include tidal current, storms and bioturbation, whereas human activities such as dredging, reclamation and trawling may also cause major sediment disturbances (Petersen et



al., 1997). Sediment disturbances may lead to the change of the physical conditions, in particular for the redox potential and pH, and result in chemical changes in sediments (James and Chen, 1977; Calmano et al., 1993; Simpson et al., 1998; Zoumis et al., 2001).

The transformation of metal phases under changing redox conditions has been given much attention. James and Chen (1977) showed that there was an increased release of Cd, Cu, Ni, Pb and Zn from the anoxic sediment to the porewater when the redox condition became more oxidizing. The release of metals was explained by the change from metallic sulfides to a higher solubility solids including carbonate, hydroxide, oxyhydroxide, oxide or silicate solids (James and Chen, 1977). Similar studies were also conducted by Calmano et al. (1993) and verified that a significant amount of metals, including Zn, Cd, Cu and Pb, were mobilized when anoxic sediments were subject to oxidation. Besides, they noticed that there was a remarkable decline in pH during the oxidation of sediments characterized with a low acid neutralization capacity (ANC), and further enhanced the metal mobility (Calmano et al., 1993). The oxidation of sulfide was suggested as a major cause of metal remobilization in anoxic sediments (Calmano et al., 1993; Simpson et al., 1998). Calmano et al. (1994) indicated that the concentrations of sulfate ( $\text{SO}_4^{2-}$ ) increased with the metal concentrations in porewater during the oxidation of anoxic

sediments. The increased metals with sulfate concentrations clearly illustrated that the sulfide oxidation provides a primary source of metal release in anoxic sediments.

Following the metals release, scavenging processes, including adsorption on organic substances, adsorption or coprecipitation by newly-formed Fe-Mn oxyhydroxides, and precipitation of metal phosphates originating from the decomposition of organic matter, may rapidly remove metals from the water column under oxidized conditions (Calmano et al., 1993). Caetano et al. (2003) studied the time of metals remained in solution during metal release and scavenging processes, in order to assess the environmental impact of changing redox conditions in sediments. The results indicated that Pb and Cu were rapidly scavenged by newly-precipitated Fe oxyhydroxides. However, the removal of Cd was less efficient, as a result the availability of this metal could be greatly enhanced after major sediment disturbances.

## **2.5. Methods for sediment quality assessment**

### **2.5.1. Chemical analysis**

#### **2.5.1.1. Total acid digestion and sediment quality guideline of sediment**

A number of chemical digestion methods are available and are widely adopted for trace metal analyses. The samples are usually treated with concentrated acid, or a combination of concentrated acids at high temperatures. Several concentrated acids

and oxidizing reagents are suitable for acid digestion, such as hydrofluoric acid (HF), perchloric acid ( $\text{HClO}_4$ ), nitric acid ( $\text{HNO}_3$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). The selection of acids depends on the constituents of the material for decomposition and the interference effect during the equipment analysis. To perform a complete decomposition of latic constituents in a sample, HF should be used to break down the silicate structures. Other digestion methods without HF are considered as the pseudo-acid digestion. These methods can also provide consistent results and nearly total concentrations for most of the trace metals across the samples (Hornberger et al., 1999). The pseudo-acid digestion can give an assessment of the maximum potentially soluble or mobile contents of metals which are usually not bound in silicates. These metal contents most likely reflect the maximum potential hazard that could occur in the long term, or in extreme environmental regimes (Ure and Davidson, 2002).

After the total metal concentration analysis, the assessment of sediment quality is based on the comparison of total metal concentrations with the sediment quality guidelines (SQGs). These guidelines are primarily derived from two approaches: empirical and theoretical approaches. The former is developed based on the relationship between sediment contamination and toxic response of organisms (Long and Morgan, 1991; Smith et al., 1996), while the latter is derived from the equilibrium partitioning (EqP) of contaminants in porewater (US Environmental

Protection Agency, 1997). The EqP approach assumes the porewater as the primary route of the contaminant exposure for aquatic organisms. This approach does not consider the uptake route of the contaminant from sediment ingestion, and thus may underestimate the toxic effects (Lee et al., 2000). On the other hand, empirically based approaches are widely used, and have been shown to be useful and predictive of biological effects in many marine and freshwater systems (Long et al., 1998, 2000; Ingersoll et al., 1996). Examples of empirically derived SQGs include the effects range approach (Effects range low/ Effects range median) (ERLs/ ERM) (Long and Morgan, 1991; Ingersoll et al., 1996), the effects level approach (Threshold effects level/ Probable effects level) (TELs/ PELs) (Smith et al., 1996; Ingersoll et al., 1996). The former were derived from the 10th and 50th percentiles, respectively, of chemical concentrations associated with adverse biological effects in a large database involving field studies and laboratory bioassays. Similarly, TELs/ PELs were derived from the same database and functionally equivalent to ERLs/ ERM, but were developed using no-effects data, as well as effect data. These approaches generally have two threshold levels, one below which effects rarely occur, and one above which effects are likely to occur. Table 2.3 shows some empirically derived SQGs for trace metals which have been adopted by various regulatory agencies around the world.

Table 2.3. Sediment quality guidelines for trace metals (mg/kg, dry wt.)

SQG		Cd	Cr	Cu	Pb	Ni	Zn
Environment Canada <sup>a</sup>	TEL <sup>d</sup>	0.68	52.3	18.7	30.2	15.9	124
	PEL <sup>e</sup>	4.21	160	108	112	42.8	271
National Oceanic and Atmospheric Administration <sup>b</sup>	ERL <sup>f</sup>	1.2	81	34	46.7	20.9	150
	ERM <sup>g</sup>	9.6	370	270	218	51.6	410
Hong Kong Interim Sediment Quality Value <sup>c</sup>	Low	1.5	80	65	75	40	200
	High	9.6	370	270	218	-	410

<sup>a</sup>Simth et al., 1996<sup>b</sup>NOAA, 1999<sup>c</sup>Chapman et al., 1999<sup>d</sup>TEL, threshold effect level<sup>e</sup>PEL, probable effects level<sup>f</sup>ERL, effects range low<sup>g</sup>ERM, effect range median

It should be recognized that there are a number of limitations of the empirically based SQGs. For example, these guidelines, which are developed for individual chemicals, cannot be used to predict the toxicity when mixtures of contaminants occur. Besides, these guidelines consider the total concentration of contaminants in sediments and do not take account of the bioavailable fraction (Burton, 2002). Therefore, SQGs should be used as a preliminary screening tool in sediment quality assessments. Further assessments such as metal speciation analysis and sediment toxicity tests should be conducted, in order to evaluate the significance of sediment associated contaminants and their potential impacts on the aquatic environment.

#### 2.5.1.2. Sequential extraction of the sediment

Under high levels of metal contamination, adverse toxicological effects may or may not occur, depending on the physiochemical characteristics of sediments (Tessier et al., 1979; Tessier and Campbell, 1987). To understand the complex geochemical

processes governing metal mobilization and bioavailability in sediments, several experimental extraction schemes have been developed to determine the speciation of particulate trace metals. In general, these schemes use a sequence of reagents with increasing reactivity to selectively extract different forms of metals (Tessier et al., 1979; Usero et al., 1998). It should be noted that the results obtained are “operationally defined”, where selectivity is dependent on several factors such as the choice of reagents used for various extractions, the extraction sequence, the final suspension pH, the solid-to-solution ratio, the temperature as well as the contact time and intensity (Kersten, 2002). There are more than 20 different sequential extraction schemes in the literature and some published schemes are listed in Table 2.4.

Table 2.4. Examples of sequential extraction schemes

Fraction	Tessier et al. (1979)	Kersten and Förstner (1986)	BCR (Ure et al., 1993)
Exchangeable	1 M MgCl <sub>2</sub> , pH 7	1 M NH <sub>4</sub> OAc, pH 7	0.11 M HOAc (exchangeable, water and acid soluble)
Carbonate	1 M NaOAc, HOAc at pH 5	1 M NaOAc, HOAc at pH 5	
Easily reducible		0.01 M NH <sub>2</sub> OH•HCl 0.01 M HNO <sub>3</sub>	
Fe-and Mn-oxides	0.04 M NH <sub>2</sub> OH•HCl in 25 % HOAc at 96 °C		0.1 M NH <sub>2</sub> OH•HCl, HNO <sub>3</sub> at pH 2 (reducible)
Moderately reducible		0.1 M Oxalate buffer at pH 3	
Organic matter and sulfides	30 % H <sub>2</sub> O <sub>2</sub> , HNO <sub>3</sub> at pH 2, 85 °C + 3.2 M NH <sub>4</sub> OAc in 20 % HNO <sub>3</sub>	30 % H <sub>2</sub> O <sub>2</sub> , 0.02 M HNO <sub>3</sub> at pH 2, 85 °C + 1 M NH <sub>4</sub> OAc in 6 % HNO <sub>3</sub>	30 % H <sub>2</sub> O <sub>2</sub> , HNO <sub>3</sub> at pH 2, 85 °C + 1 M NH <sub>4</sub> OAc, HNO <sub>3</sub> at pH 2 (oxidizable)
Residual	HF, HClO <sub>4</sub>	HNO <sub>3</sub>	HNO <sub>3</sub>

In general, the common “operationally defined” fractions appear to be ion-exchangeable, the weakly absorbed, the organic bound, the hydrous oxide component and the lattice component material. The reagents used in these extraction schemes could be neutral electrolytes such as CaCl<sub>2</sub> or MgCl<sub>2</sub>; buffers of weak acids such as acetic acid or oxalic acid; chelating agents such as EDTA or DTPA; redox agents such as NH<sub>2</sub>OH; strong acids such as HCl, HNO<sub>3</sub>, HClO<sub>4</sub> or HF; bases such as NaOH or Na<sub>2</sub>CO<sub>3</sub> (Ure and Davidson, 2002).

Among different sequential extraction schemes, the five-step extraction scheme developed by Tessier et al. (1979) and the six-step extraction scheme developed by Kersten and Förstner (1986) have been widely used. The operational defined fractions and reagents employed in these two extraction schemes are illustrated in Table 2.4. The five-step extraction scheme was developed for the separation of particulate trace metals into five operationally defined fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual (Tessier et al., 1979). For the six-step extraction procedure designed by Kersten and Förstner (1986), the phase separation is similar to the 5-step Tessier's extraction method except with an additional differentiation of the easily reducible fraction (Mn oxides) from the moderately reducible one (Fe oxides). Due to the variety of extraction procedures and lack of uniformity in different protocols, a BCR three-step sequential extraction method was proposed (Ure et al., 1993) by the European Community Bureau of Reference in 1992 (now the Standards Measurement and Testing Programme). The BCR method harmonizes various sequential extraction procedures and was accepted by a large group of specialists (Salomons, 1993; Fiedler et al., 1994; Usero et al., 1998; Yuan et al., 2004). It includes three fractions, namely acid soluble, reducible and oxidizable phases (Table 2.4). Subsequently, this procedure has been subjected to modification with extensive expert consultations and interlaboratory studies (Rauret et al., 1999; Sahuquillo et al., 1999). A new sediment certified reference material (BCR CRM 701) has been certified for Cd, Cr,



Cu, Ni, Pb and Zn extractable by the modified BCR procedure (Rauret et al., 1999; Pueyo et al., 2001), thus allowing the validation of the procedure and quality control of the measurements.

Although the BCR protocol has been intensively modified and developed in recent decades in order to standardize and validate the sequential extraction scheme, some results obtained so far are still suffering from low reproducibility (Whalley and Grant, 1994; Davidson, et al., 1999; Rauret et al., 1999). Besides, lower recovery of reducible phase in iron oxide-rich sediments using the BCR protocol has been reported, and this may be due to the low temperature and reagent concentration employed in the reducible phase extraction (Gómez-Ariza et al., 2000). Moreover, the “operationally defined” phase of sediments in BCR protocol is simplified into three major fractions, which may not be capable to provide adequate information on the geochemical behaviour and cycling of metals in sediments. On the other hand, the 5-step Tessier’s sequential extraction procedure has shown higher recovery rates and better precision in a number of studies (Li et al., 1995a; Li et al., 1995b; Gómez-Ariza et al., 2000). Hence, a modified 5-step Tessier’s sequential extraction is chosen in the present study to investigate the geochemical cycling and bioavailability of trace metals in harbour sediments. The modified 5-step Tessier’s sequential extraction method, developed by Li et al. (1995a), allows the determination of multi-element using ICP – AES with acceptable precision and accuracy.

There is no well-developed extraction procedure that can extract individual fractions without affecting other sediment constituents so far (Tessier and Campbell, 1987; Nirel and Morel, 1990). Thus, the limitations of sequential extraction should be recognized in order to have a better interpretation on the extraction results, and some of these limitations will be reviewed in the following part. The lack of selectivity is one of the limitations of the sequential extraction procedure, and selectivity was found to be deteriorated markedly for anoxic sulfide-rich sediments (Campbell and Tessier, 1984; Whalley and Grant, 1994; Peltier et al., 2005). During the extraction process of anoxic sediments, Wallmann et al. (1993) and Ngiam and Lim (2001) found that the early dissolution of metal sulfide phases occurred in the extraction of iron and manganese oxides phases. Moreover, there is a problem related to the readsorption of extracted metal onto the remaining solid phases during the extraction procedure (Rendell et al., 1980; Tipping et al., 1985; Raksataya et al., 1996).

In addition to these analytical problems, sample pretreatment methods (e.g. drying and storage of samples) could greatly affect the distribution of metals obtained by the sequential extraction procedure, particularly for anoxic sediments (Kersten and Förstner, 1986; Rapin et al., 1986; Saeki et al., 1993; Bordas and Bourg, 1998; Hjorth, 2004). For instance, oven and freeze drying have been reported to reduce the quantity of Fe extracted in the reducible phase due to the aging effect in dried sediments (Kersten and Förstner, 1986; Rapin et al., 1986). Saeki et al. (1993)

showed that Cd in the organic/sulfide fraction was transformed to exchangeable and reducible fractions as a result of oxidation after the drying of sediments. Although drying may affect metal speciation, it is preferable to dry samples before analysis. Dried sediments might be stable for years with regard to its trace metals speciation. This is a major prerequisite to improve reproducibility (Accomasso et al., 1993) and to prepare a reference material for the sequential analysis (Quevauviller et al., 1997).

Another major problem associated with the sequential extraction method is the incapability of this method to stimulate the result of natural processes (Martin et al., 1987). The sequential extraction is based on the use of strong reagents and fast reactions, and this is totally different from natural processes which involve weak reagents and slow reactions. The inefficiency of sequential extraction has been revealed in a study conducted by Arjonilla et al. (1994), such that no significant correlation was observed between trace metals, Zn, Cu and Pb, in sediment phases and those in organisms.

Despite the fact that sequential extraction methods are subject to several limitations, they can provide a convenient means to study the metal associations with the principal accumulative phases in sedimentary deposits, to elucidate the mechanisms of metal diagenetic transformation, and to have a more thorough understanding of metals release processes under changing environmental conditions (Kersten and

Förstner, 1986). In order to avoid the misleading interpretation of sequential extraction results, one should have a clear understanding of its pitfalls and limitations prior to the use of this technique (Pickering, 1981). Besides, as the results obtained by sequential extraction are operationally defined, the significance of the analytical results is related to the extraction scheme used and comparison of results from different schemes should be avoided. Furthermore, sequential extraction analysis in conjunction with complementary approaches, such as cold HCl extraction, has been recommended to assess metal speciation in anoxic sediments (Peltier et al., 2005).

#### **2.5.1.3. Cold HCl extraction of the sediment (AVS/SEM analysis)**

Interactions between trace metals and sulfides may have a profound influence on the bioavailability of toxic metals in sediments and have received attention in recent years (Di Toro et al., 1990, 1992; Morse, 1994). Acid volatile sulfide (AVS) is recently suggested as a normalization parameter for the metal toxicity in anoxic sediments (Di Toro et al., 1992; Liber et al., 1996; Boothman et al., 2001). Di Toro et al. (1990) suggested that the activity of divalent cationic metals in anoxic sediments could be mainly controlled by the pool of AVS. It plays an important role in metal binding through the formation of insoluble metal-sulfide complexes. The potential toxic effect of metals is assessed based on the measurement of AVS and SEM (simultaneously extracted metal) in sediments. SEM is defined as metals

simultaneously extracted from sediments during the cold acid extraction and these metals are considered in association with sulfide in sediments (Di Toro et al., 1992).

This hypothesis has been demonstrated in acute mortality tests using amphipods and polychaetes in sediments spiked with Cd, Cu, Pb, Ni and Zn, as well as metal mixtures (Di Toro et al., 1992; Casas and Crecelius, 1994; Pesch et al., 1995; Berry et al., 1996). Field studies on the effect of AVS on metal toxicity and bioaccumulation by benthic organisms have also been conducted by Hare et al. (1994), Liber et al. (1996), Hansen et al. (1996) and Boothman et al. (2001). These studies revealed that toxic effects due to SEM are rarely observed when the molar SEM concentration in sediments is less than or equal to the molar AVS concentration.

The general assumption of using SEM/AVS model to predict sediment toxicity is that all the divalent metals (e.g. Cd, Ni and Zn) would exist as metal sulfide if their molar sum is less than the amount of AVS under the reducing condition, as these metals have lower sulfide solubility parameters than FeS. However, if their molar sum is greater than the AVS concentration, then a portion of metals with the lowest sulfide solubility parameters would exist as free metal ions and become available to organisms (Di Toro et al., 1992). To predict the toxicity of sediments, it is necessary to consider the molar sum of simultaneously extracted metals, typically Cd, Cu, Ni,

Pb and Zn. According to the AVS model, the free metal ion will not accumulate in porewater or become potentially toxic if the molar sum of SEM is less than the molar AVS:

$$[\text{SEM}]_{\text{Cd}} + [\text{SEM}]_{\text{Cu}} + [\text{SEM}]_{\text{Ni}} + [\text{SEM}]_{\text{Pb}} + [\text{SEM}]_{\text{Zn}} / [\text{AVS}] < 1$$

Based on the chemical equilibrium calculation, the relative affinity of metals for the AVS should be  $\text{Cu} > \text{Pb} > \text{Cd} > \text{Zn} > \text{Ni}$  (Di Toro et al., 1992). Hence, when the molar concentration of SEM exceeds AVS, the appearance of metals in the porewater should occur in an inverse order, e.g. Cu would replace Pb in a monosulfide complex and Pb would be liberated to the porewater.

However, the ability to predict an absence of metal toxicity based on the sediment SEM and AVS relationship is controversial. Firstly, the prediction of toxicity can be complicated by the presence of additional metal binding phases (Ankley, 1996; Hansen et al., 1996). For example, Liber et al. (1996) demonstrated that even the  $\Sigma\text{SEM}/\text{AVS}$  ratios were greater than 1, Zn in the porewater was very low, indicating the presence of additional binding phases. In anoxic sediments, organic matter appears to be an additional binding phase controlling the metal partitioning (Ankley, 1996). In oxic sediments, both organic matter and oxides of Fe and Mn can control metal concentrations in the porewater (Tessier et al., 1979). Therefore, it is impossible to predict metal bioavailability when  $\Sigma\text{SEM}/\text{AVS}$  ratios exceed 1.

Moreover, AVS is highly dynamic in which the concentrations can change drastically with season and with depth at a particular site. Minimum concentrations of AVS generally occur in late winter, whereas maximum concentrations occur in late spring and early summer due to the variation of biological activity (Ankley et al., 1994). The concentrations of AVS are depth dependent in which higher concentrations are typically found in deeper sediment layers than in surface sediments (Ankley et al., 1994). Hence, it is difficult to predict toxicity with considerable variations of AVS spatially and temporally. Another problem in using AVS model is that it cannot predict the toxicity of metals which do not react with AVS, such as Cr (Ankley et al., 1994).

Furthermore, using  $\Sigma$ SEM/AVS ratios to predict metal toxicity in the sediment has been criticized for not considering the bioaccumulation and the chronic toxicity of metals. Some studies have shown that AVS has a limited influence on metal bioaccumulation in sediments (Hare et al., 1994; Ingersoll et al., 1994; Lee et al., 2000). The authors believed that many toxicity studies based on the AVS model often used sediments spiked with extremely high levels of metals with short equilibrium times. This experimental design could result in high concentrations of dissolved metals and makes porewater the dominant uptake pathway of metals, while precluding the metal exposure through dietary uptake. Lee et al. (2000) demonstrated that there was a poor correlation between metals in porewater and metals

accumulated by animals. Indeed, they found that metal concentrations in animal tissues were correlated with metal concentrations extracted from sediments across a range of reactive sulfide concentrations. This is probably attributed to the metal accumulation of organisms through direct ingestion of sediments, regardless of the AVS content (Griscom et al., 2000; Lee et al., 2000). Therefore, cautions should be taken when using the AVS model to assess sediment toxicity.

Extraction of AVS in sediments is typically based on the rapid dissolution of iron monosulfide minerals with acid. A wide variety of extraction conditions can be found in the literature and some are illustrated in Table 2.5.

Table 2.5. Examples of acid volatile sulfide (AVS) extraction method

Method	Reference
Cold HCl (1-12 N)	Jørgensen (1977), Cornwell and Morse (1987), Allen et al. (1993)
Hot HCl (6-12 N)	Zhabina and Volkov (1978); Berner (1974)
Hot HCl (6N) + SnCl <sub>2</sub>	Berner et al. (1979), Cornwell and Morse (1987)

In general, the extraction techniques are difference in whether using hot (Zhabina and Volkov, 1978; Berner, 1974) or cold HCl (Jørgensen, 1977; Cornwell and Morse, 1987; Allen et al., 1993), and whether using SnCl<sub>2</sub> to reduce Fe<sup>3+</sup> interference (Berner et al., 1979; Cornwell and Morse, 1987). There is no well developed acid extraction method which can selectively extract all the AVS while leaving pyrite in sediments. For example, the cold 1M HCl extraction method, the most commonly



used method in AVS/SEM studies, is unable to extract all the mackinawite (FeS) and greigite (Fe<sub>3</sub>S<sub>4</sub>) in sediments and lead to an underestimation of AVS concentrations (Cornwell and Morse, 1987). In addition, Cooper and Morse (1998) found that cold HCl cannot extract certain metal sulfides such as CuS, HgS and NiS. This extraction method was also found to extract metals from other reactive phases such as carbonate, Fe and Mn oxides (Cornwell and Morse, 1987; Fang et al., 2005). Overall, the acid extraction of AVS and SEM should be used vigilantly when predicting the metal toxicity in sediments, as well as investigating the geochemical behaviour of trace metals in sediments.

## **2.6. Identification of trace metal contamination and sources in sediments**

### **2.6.1. Trace metal normalization for the particle size effect**

The examination of trace metal enrichment may require compensation for grain size and mineralogical effects on the metal variability in sediments with different textures. A close relationship between metal concentration and grain size is often observed in estuarine and marine sediments, since metals tend to be associated with fine grained particles (Lee and Cundy, 2001; Huang and Lin, 2003). Sediments in fine grained sizes have larger surface areas, and this may enhance metal scavenging and adsorbing capacity. In addition, larger surface areas may also increase the precipitation and flocculation of organic matter and Fe/Mn oxides, which in turn tend to concentrate trace metals (Horowitz, 1991). If a linear relationship exists

between the trace metal concentration and the percentage of fine-grained (silt and clay) content of sediments, the compensation of the grain size effect is necessary to eliminate the natural variability of trace metals in sediments.

The compensation of the grain size effect is frequently achieved by means of geochemical normalization. The geochemical approach involves the mathematical normalization of trace metal concentrations to the concentrations of a conservative element (Loring, 1991). The conservative element should be originated from natural sources without anthropogenic influence; structurally bound to major fine-grained trace metal carriers; and stable not being subject to environmental influence such as reduction and oxidation (Luoma, 1990). There are several conservative elements which have been used for normalization, such as Al (Bruland et al., 1974; Schropp et al., 1990), Li (Loring, 1990; Aloupi and Angelidis, 2001) and Fe (Daskalakis and O'Conner, 1995; Schiff and Weisberg, 1999). Other methods for the compensation of grain size effects may include the normalization of trace metal concentration to the amount of a specific size fraction in the sediment (Palanques and Diaz, 1994), the analysis of the fraction containing particle sizes less than 63  $\mu\text{m}$  (Salomons and Förstner, 1984), and the physical fractionation of the bulk sediment into different size fractions with the subsequent analysis of each class (DeGoot et al., 1976).

### **2.6.2. Study of the temporal metal distribution using $^{210}\text{Pb}$ dated sediment cores**

Trace metals are transferred to sediments after they are released to the aquatic environment. Sediments become an important reservoir for metals and may act as a record of contaminant input to the aquatic environment. Thus, by estimating the sediment accumulation rate, core profiles of trace metals in sediments can be used to reconstruct the pollution history of a watershed (Finney and Huh, 1989; Croudace and Cundy, 1995; Latimer et al., 2003; Mason et al., 2004). The geochronology of sediments can be estimated from  $^{210}\text{Pb}$  dating, one of the most common methods for dating sediments on a time scale of 100–150 years (Turner and Delorme, 1996; Lu and Matsumoto, 2005).  $^{210}\text{Pb}$  is a naturally occurring radionuclide (half-life 22.26 years) and has been used frequently to determine sedimentation rates in coastal marine, estuarine and marsh environments (Finney and Huh, 1989; Cundy et al., 1997; Mason et al., 2004; Ip et al., 2004).

The main sources of  $^{210}\text{Pb}$  in the sediment include atmospheric deposition and the production in the water column from the parent  $^{226}\text{Ra}$ . The former is considered as an unsupported component and the latter as a supported component. The  $^{210}\text{Pb}$  dating is based on the estimation of the unsupported  $^{210}\text{Pb}$  along the sediment profiles. In general, the unsupported  $^{210}\text{Pb}$  incorporated in a given sediment layer reduces exponentially with time in accordance with the radioactive decay law (Appleby and Oldfield, 1992). If the sediment input is constant, there will be a constant rate of

unsupported  $^{210}\text{Pb}$  accumulation and each layer of sediment will have the same initial unsupported  $^{210}\text{Pb}$  concentration. In this case, a linear  $^{210}\text{Pb}$  profile characterizing an exponential decline in  $^{210}\text{Pb}$  activity with depth can be obtained. The sedimentation rate can be estimated from the mean slope of the profile, using a least squares fit procedure. This dating model is referred to the constant flux-constant sedimentation rate (CF:CS) model (Appleby and Oldfield, 1983). However, the  $^{210}\text{Pb}$  profile may show a non-linear trend and this probably indicates variable sedimentation rates. There are two models used to calculate variable sedimentation rates, namely the CIC model (constant initial concentration of unsupported  $^{210}\text{Pb}$ ) (Robbins and Edgington, 1975) and the CRS model (constant rate of supply of unsupported  $^{210}\text{Pb}$ ) (Appleby et al., 1979). The CIC model assumes that increases in sedimentation rate are accompanied by corresponding increases in the sedimentary flux of  $^{210}\text{Pb}$ . Thus, the rate of excess  $^{210}\text{Pb}$  flux to the rate of sediment input at the time of deposition is constant and is equal to the activity of excess  $^{210}\text{Pb}$  in surface sediments. The CRS model assumes a constant rate of supply of unsupported  $^{210}\text{Pb}$  to the sediments irrespective of any variations of the sedimentation rate. The selection of model depends on the local conditions, hence it is better to calculate the sedimentation rate using both models and compare the results with independent dating techniques, such as  $^{137}\text{Cs}$  and pollen analysis (McCall et al., 1984; Turner and Delorme, 1996). Pollen analysis is a technique for the study of vegetation changes using the microfossils that are resistant to decay. It provides useful record about the

target area's condition changed (naturally or due to human activity) in the present and the past

### **2.6.3. Statistical analysis of metal concentrations**

Factor analysis can be viewed as an extension of principal component analysis. It is used to describe the covariance relationships among many variables in terms of a few underlying factors. As a result, it can reduce the dimensionality in the data and to summarize the major patterns of variation within the measured lithological and geochemical parameters. However, there is drawback associated with the factor analysis, for example, the use of different rotation methods may lead to different loadings of the variables and resulted in very subjective interpretation. Nevertheless, it is widely used to study the association of metals and other geochemical parameters in sediment cores (Shine et al., 1995; Loska and Wiechula, 2003; Vaalgamaa and Korhola, 2004). In the sediment core analysis, factor analysis incorporates data from all metals into one unified comparison and reveals groups of samples or metals with similar spatial or temporal behaviour. This may in turn allow the identification of geochemical associations and major sources of metals in sediments.

### **2.6.4. Study of Pb sources using Pb isotopic ratio**

Stable Pb isotopes can be a fingerprint for Pb in the environment, which can help to quantify the anthropogenic sources of Pb, and to identify the sources and pathways

of Pb pollution (Kersten et al., 1997; Wong et al., 2004; Zhu et al., 2001; Duzgoren-Aydin et al., 2004). Lead has four stable isotopes,  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ .  $^{204}\text{Pb}$  is non-radiogenic, whereas  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$  are radiogenic and are derived from  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$ , respectively. The isotopic composition of Pb depends on the initial Th and U content and the age of ore bodies. The identification of the Pb source is based on the differences in Pb isotopic ratios between natural and anthropogenic sources. In general, the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of naturally derived Pb are high, whereas those of anthropogenic Pb tend to be low (Sturges and Barrie 1987). Lead isotopic ratios have been demonstrated to be an effective approach to distinguish natural and anthropogenic Pb in sediments of oceans (Hinrichs et al., 2002; Charlesworth et al., 2006), lakes (Graney et al., 1995; Monna et al., 1999) and estuaries (Gobeil et al., 1995).

Besides, the isotopic ratios have been used to differentiate Pb among different anthropogenic sources, such as industrial/domestic activities and leaded gasoline. For instance, the historical change of anthropogenic Pb sources has been identified by Eades et al. (2002) based on the change of Pb isotopic ratios in sediment cores. They showed that changing  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios along the cores could be attributed to the contribution of different Pb sources including coal burning, industrial activities and the combustion of leaded gasoline. Transboundary pollution between countries has also been investigated based on Pb isotopic ratios. Sturges and Barrie (1987)

showed that there was a difference in isotopic composition between the atmospheric Pb in Canada and in the United States, due to the fact that their uses of Pb are originated from isotopically-distinct ore deposits. Based on the differences in Pb isotopic composition between these two countries, Flegal et al. (1989) was able to demonstrate that the Great Lakes was contaminated with industrial Pb from both Canada and the United States.

## Chapter 3 Study Area and Methodology

### 3.1. The study area – Victoria Harbour

Hong Kong is located in a subtropical region on the southern coast of China (Figure 3.1). It is a densely-populated city which supports 6.8 million people with a total land area of only 1068 km<sup>2</sup>.



Figure 3.1. Map showing the location of Hong Kong

The pattern of seawater circulation along the coast of southern China is generally influenced by the northeast and southeast monsoons. The eastern and northeastern coast of Hong Kong is virtually affected by the South China Sea water in summer,



while by the East China Sea water and the Taiwan Current in winter. The hydrology of Hong Kong is also influenced considerably by the Pearl River Estuary (Morton and Wu, 1975). The Pearl River is the largest river in southern China with an estimated annual discharge of 300 billion m<sup>3</sup> and release of 86 million tons of sediment and organic material per year (Neller and Lam, 1998). Due to the Coriolis force, much of the discharge from the PRE is directed to the west; however, its influence on Hong Kong waters is still significant. With the influence of freshwater discharge from the PRE, there is a decreasing trend in salinity from the western to the eastern coast in Hong Kong. The salinity of the western and northwestern coast of the territory is greatly reduced during summer when the rainfall is high in southern China. This creates a difference in salinity between the surface and the bottom water column due to the increased discharge of low density freshwater from the PRE (Morton and Wu, 1975). The main source of marine sediments in Hong Kong is derived from the erosion of local regolith, volcanic and granitic rocks, and only a small amount of sediments is originated from the neighboring PRE (Whiteside, 2000).

Victoria Harbour lies between the most heavily urbanized area of Kowloon Peninsula and the northern shore of Hong Kong Island (Figure 3.1). It is the major port of Hong Kong and is 12 km long, 9–30 m deep, and 4–5 km and 1–2 km wide at its western and eastern reaches, respectively. Based on the hydrological condition in

Hong Kong, the central waters of Victoria Harbour can be regarded as the transitional zone of the estuarine-oceanic gradient from the west to the east. The harbour is a tidal channel in which marine water enters the harbour from the east at the funnel-shaped Lei Yue Mun Channel and flows westwards along the harbour during the flood tide, whereas water moves in opposite direction during the ebb tide. Tidal flows are relatively strong in Lei Yue Mun due to a narrow eastern harbour entrance (Morton and Wu, 1975).

Extensive human activities near Victoria Harbour took place since the 1950s. In the 1950s, untreated sewage in the southern part of Kowloon Peninsula and the northern part of Hong Kong Island were directly released to the central part of the harbour and subsequently removed by strong tidal currents. The amount of sewage had increased significantly with the population increase in the 1960s. In an attempt to alleviate the problem, untreated sewage was discharged into the harbour through seawall and submarine outfalls with limited screening. Figure 3.2 shows the locations of sewage outfalls along the harbour. Throughout the 1970s and early 1980s, the provision of sewage within the territory failed to keep pace with the urban development and caused a rapid decline in the water quality of the harbour. In 1997, Strategic Sewage Disposal Scheme (SSDS) (referred to Harbour Area Treatment Scheme (HATS) since 2000) was implemented in which sewage was subject to preliminary treatments at Stonecutters Island before releasing to the harbour. Today

the harbour receives 1.5 million tonnes of sewage per day and around 70 % of the sewage is treated in a chemically enhanced primary sewage treatment plant at Stonecutters Island before discharging to the harbour (HKEPD, 2002).

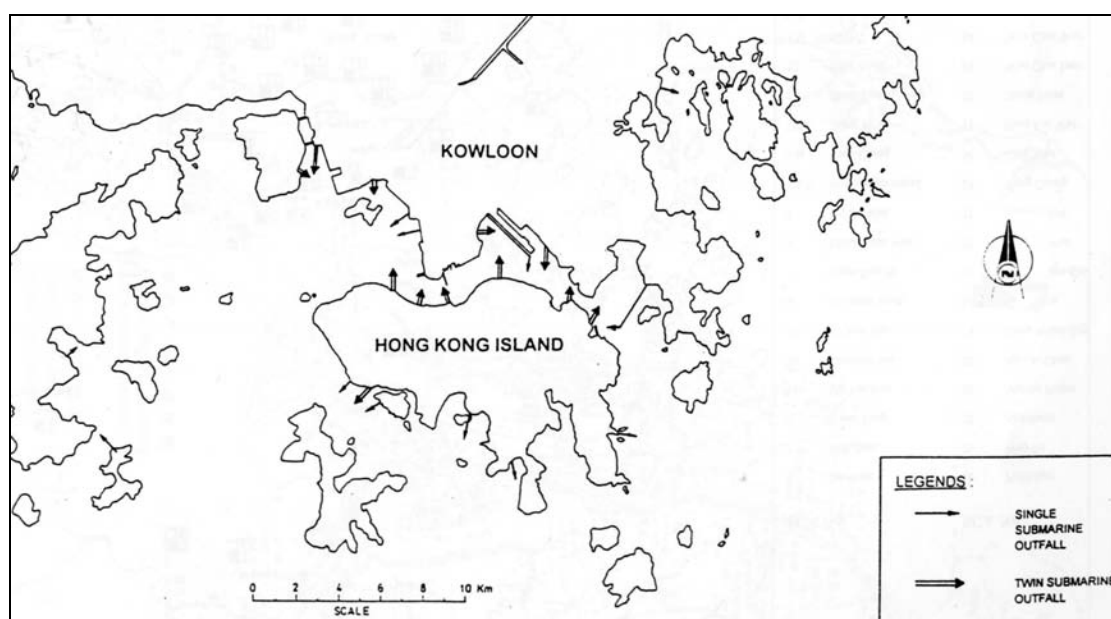


Figure 3.2. Location of major sewage outfalls along Victoria Harbour (from Sin et al., 1995)

Apart from the sewage problem, industrial effluents are another important source of pollutants in the harbour. Since the mid 1950s with the development of manufacturing industries in Hong Kong such as electroplating, dyeing and printed circuit board manufacture (PCB), there was an uncontrolled disposal of industrial effluents to the harbour. The growth of manufacturing industries in Hong Kong peaked in the mid 1980s. With the enactment of the Water Pollution Control Ordinance in the late 1980s, the major industrial pollution sources were under control. It is estimated that Hong Kong industries contributed around 7500 kg per

day of heavy metals into the sea until 1993 (Dawes, 2001). To further reduce the load of metals to the harbour, a Chemical Waste Treatment Centre was set up on Tsing Yi in 1993 and treats a range of heavy metals and chemical wastes. Along with the relocation of manufacturing industries to the mainland China, the total heavy metals load released to the harbour was reduced from around 7500 kg to less than 1000 kg per day in recent years (Dawes, 2001).

Urban runoff could be a major non-point source of pollutants in Victoria Harbour. Figure 3.3 displays the stormwater outfalls in the central part of the harbour. The urban runoff carrying street dust and soils is directly discharged to the harbour through these outfalls. In Hong Kong, road dust and roadside soils were found to be contaminated with Pb, Zn and Cu as a result of extensive traffic activities (Ho, 1979; Wang et al., 1998; Ng et al., 2003; Li et al., 2004). These metals can thus be easily mobilized and released to the harbour during heavy rainfall.

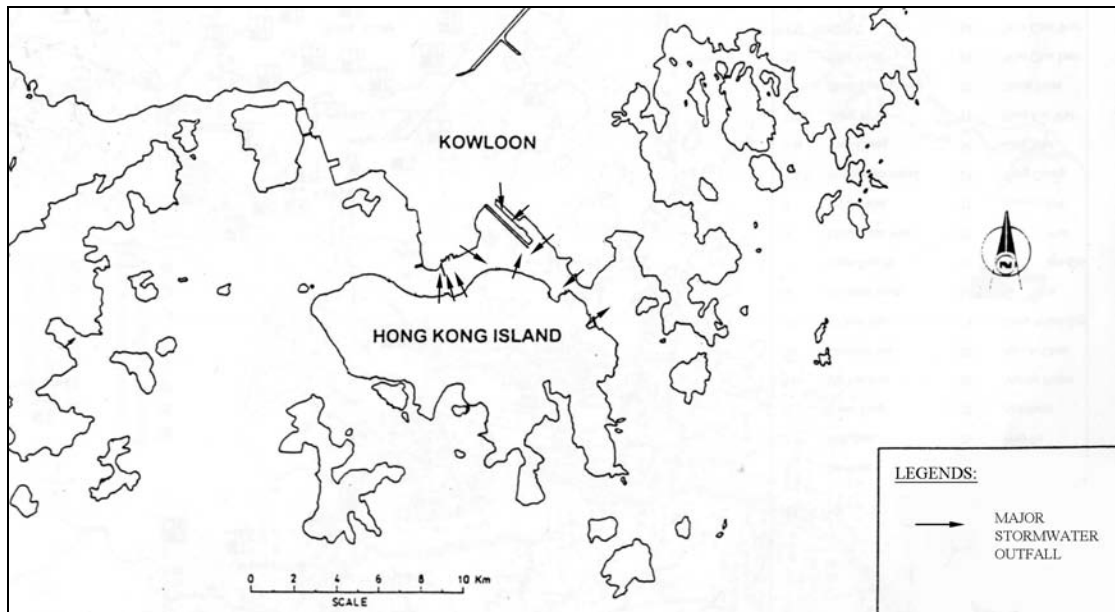


Figure 3.3. Major stormwater outfalls in Victoria Harbour (modified from Sin et al., 1995)

In the past few decades, a number of research projects have been conducted into the sediment quality in Victoria harbour. The first study was carried out by Yim (1981). He determined the concentrations of metals in offshore and nearshore sediments over 210 locations across the territory. The study showed that Victoria Harbour had the highest amounts of Cu, Zn, Cr and Pb in sediments with mean concentrations of 111, 246, 35, and 93 mg/kg, respectively (Yim, 1981). The enrichment of trace metals in harbour sediments was attributed to the intensive urban and industrial activities in the territory (Yim, 1984).

Since 1986, the Environmental Protection Department of Hong Kong (HKEPD) has a regular monitoring program on the sediment quality in the territory. According to the HKEPD reports, sediments in Victoria Harbour had a comparatively higher level

of heavy metals than other water bodies in Hong Kong, especially Cu and Ag (HKEPD, 2003). The contamination of Cu was attributed to the discharges from printed circuit board manufacturing, electroplating, metal and textile industries between the 1960s and 1980s. The elevated concentration of Ag in sediments was probably related to the pollution from electroplating industries, photo-developing business and dental clinics in Hong Kong (HKEPD, 2003). Besides, the most serious metals contamination was found in typhoon shelters of Victoria Harbour. It is not surprising that typhoon shelters were found to be heavily contaminated with metals, as they have a low flushing capacity and often receive significant amounts of pollutants from stormwater drainages, surface runoff and vessels.

The physical properties of sediments have also been assessed in the monitoring program, and it revealed that sediments in the central part of the harbour were highly anoxic due to the organic deposition from sewage discharges (HKEPD, 2003). The chemical speciation of Cr, Cu and Ni in harbour sediments has been investigated by Lam et al. (1997). The non-residual fractions of Cr and Ni were found to be mainly associated with the reducible oxide phase, whereas Cu was predominantly partitioned in the organic/sulfide phase. It was also suggested that the distribution of metal species among different geochemical phases could be controlled by the total sulfides in sediments (Lam et al., 1997).

To study the historical input of metals in the harbour, Tanner et al. (2000) has conducted a study on sediment cores collected from the nearshore of Victoria harbour. Using the  $^{210}\text{Pb}$  dating, Cu, Ni and Cr were found to be enriched since the post-industrial period (after 1960s), whereas the enrichment of Zn and Pb were mainly associated with construction activities, and the maintenance and anchorage of ships before the 1960s in the harbour. It was estimated that sedimentation rates in the harbour ranged from 0.2 to 0.6 cm per year in the more open area near Ma Wan, and were greater than 5 cm per year in the enclosed area close to Tsim Sha Tsui. Anthropogenic metal fluxes were found to be anomalously high and showed a significant variation between sampling areas. For example, the estimated mean flux of Cu into sediments near Stonecutters Island was 720 to 3130  $\text{mg m}^{-2} \text{yr}^{-1}$ , whereas those in Kwun Tong Typhoon Shelter was 90150 to 195520  $\text{mg m}^{-2} \text{yr}^{-1}$  (Tanner et al., 2000).

In recent years, studies on sediments of Victoria Harbour are not only focus on the analyses of physical and chemical properties, but also on the toxicity of sediments. Recognizing the importance of bioavailability and toxicity of contaminants, Wong et al. (1995) conducted an ecotoxicological assessment of heavy metals in Victoria harbour sediments. The harbour sediments collected for toxicity tests were found to be heavily contaminated with Cu (63.3–3789 mg/kg), Zn (129–610 mg/kg), Cr (74.0–601 mg/kg), Ni (25.4–177 mg/kg) and Pb (47.4–138 mg/kg). Sediment

bioassays, including Microtox and algal tests, were performed to determine the toxicity of these sediments. It was demonstrated that the sediments were only moderately toxic to non-toxic, except those in Kwun Tong shelter, which had the highest level of metals and was therefore highly toxic. The authors suggested that the toxic effect was probably attributed to the metals contamination in sediments. However, another sediment toxicity test using flagellates showed that the toxic effect was caused by the elevated ammonia concentrations, rather than metal contents in harbour sediments (Wong et al. 1999). The biological impact of harbour sediments on fish (*Tilapia*) was also studied (Wong et al., 2000). A physiological change was observed in fish exposed to harbour sediments, which could be associated with the elevated concentrations of Zn, Cd and Cu in sediments.

An integral approach has been adopted to study the sediment quality in Victoria harbour in recent years. This approach aims to determine a correlation between the marine benthic infaunal structure, physical and chemical properties of sediments and toxicity data derived from the laboratory test. Major studies have been carried out by Shin and Fong (1999), and Shin and Lam (2001). In an earlier study, several sediment parameters were identified in affecting the structure of benthic infaunal communities in the territory. In the open area of Victoria harbour, the structure of benthic infauna was found to be mainly associated with the high levels of Cu, the percentage of total solids and the low percentage of survival of amphipods in toxicity



tests. Unlike the open area, different structure of benthic infauna was observed in the typhoon shelters of the harbour and this was attributed to high levels of Cu and Cr in sediments (Shin and Fong, 1999). Shin and Lam (2001) analyzed the HKEPD sediment quality data from the years of 1987 to 1997. They derived a Marine Sediment Pollution Index (MSPI) based on six important parameters having negative correlations with the benthic species and sediment toxicity. These parameters include chemical oxygen demand, Cr, Cu, Mn, Ni and Zn. Based on the MSPI, sediments in Victoria harbour were classified as “poor quality”. The temporal change of MSPI in the harbour was also constructed and revealed that pollution was increasing from 1987 to 1997 (Shin and Lam, 2001).

Efforts have been made to control the pollution loads by a series of environmental protection programs by the Hong Kong Government, such as the enforcement of the Water Pollution Control Ordinance and the implementation of the Harbour Area Treatment Scheme (HATS). Stringent controls have resulted in a major improvement of water quality in the harbour as reflected by the dissolved oxygen demand and *E.coli* (HKEPD, 2002). However, there are very few studies focussing on the long-term response of metals in sediments to the reduction of metal loading in the harbour. Besides, there is no information on the Pb isotopic composition, which has been widely used for source identification of sediments. Moreover, the understanding of the geochemical behaviour of trace metals in harbour sediments is still far from

complete. Therefore, it is necessary to assess the changes of sediment contamination over time, particularly for the recent two decades, in order to evaluate if the current management practices can result in the improvement of sediment quality in Victoria Harbour. The study of geochemical behaviour of trace metals can provide important information on the metal bioavailability in sediments and this may facilitate the evaluation of ecological recovery in Victoria Harbour.

### **3.2. Sample collection and preparation**

Five sampling sites from east (B1) to west (B5) of Victoria Harbour were selected for core and grab sediments collection (Figure 3.4). Due to the possible mixing of sediments in Victoria Harbour, grab sediments were collected in four cruises in December 2004, February 2005, October 2005 and April 2006, respectively, in order to provide a representative result on the spatial distribution of trace metals in the harbour. Core sediments were collected in October 2004 and used for the study of temporal metals distribution. Pb isotopic ratios in the harbour were also analyzed in selected sediment samples. For the study of metal speciation and potential environmental hazard of metal contamination in harbour sediments, grab samples were collected in October 2005 and April 2006. Moreover, additional surface sediments in October 2005 were obtained at B1, B3 and B5 for bioaccumulation tests in the laboratory.

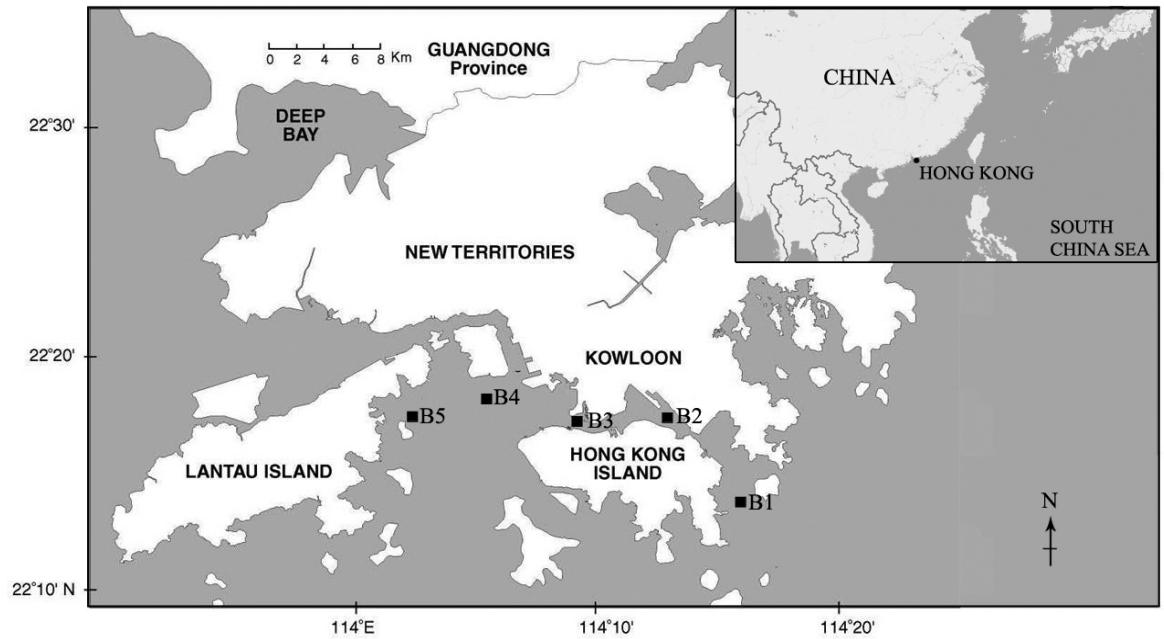


Figure 3.4. The sampling locations, B1 – B5, in Victoria Harbour

These locations have good coverage of the harbour area. Moreover, sampling locations were chosen to avoid areas with known sediment disturbance, such as the nearshore areas with intensive reclamation activities and the dredged area. Two grab sediment samples (a and b) were collected within a 50 m diameter at each sampling station. Sediment cores were taken using a Kajak gravity corer<sup>®</sup>. The corer was driven into the sediment by gravity, and the sediment core was retained in a PVC tube. The diameter of the PVC coring tube was 70 mm. Each core was sliced into thin sections at 2-cm intervals. The grab sediment samples were taken with a Van Veen Grab Sampler. All the samples were then stored in polyethylene bags at 4–6 °C prior to laboratory analyses. The physical parameters, including salinity, pH and water depth of the harbour, were measured in-situ using YSI 6600 Sonde. For the

analyses of total metal concentrations and metal speciation using a 5-step sequential extraction method, sediment samples were freeze-dried at -45 °C for 3 days and then ground in an agate grinder until fine particles were obtained. For the study of AVS/SEM, sediment samples were kept in air-tight containers filled with nitrogen until the analyses, and all the AVS/SEM analyses were conducted within one week after sample collection.

### **3.3. Sample analysis**

#### **3.3.1. Determination of trace and major element concentrations**

Sediment samples were analyzed for major and trace element concentrations using the nitric and perchloric acid digestion method (Ip et al., 2004). About 0.2 g of the ground sediment samples were digested with a mixture of 6 ml concentrated nitric acid and 1.5 ml perchloric acid in a heating block at 50 °C for 3 h, 100 °C for 1 h, 125 °C for 1 h, 150 °C for 3 h, 175 °C for 2 h and 190 °C until completely dry. The residual was then leached with 10 ml 5 % nitric acid and heated at 70 °C for 1 h. Trace and major elements in the solutions were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin-Elmer Optima 3300DV). All plastic material and glassware were soaked in 10 % nitric acid overnight and rinsed thoroughly with de-ionized water before use. For quality assurance, reagent blanks, sample replicates and standard reference materials (Buffalo River Sediment–NIST 8704) were used to assess the accuracy and precision of the analysis. The

analytical results showed no sign of contamination and the precision and bias were less than 10 %. The recovery rates of trace metals in the standard reference materials were around 80–105 %. For Fe and Al, the recovery rates were around 50–60 % due to the incomplete digestion of aluminosilicate minerals without hydrofluoric acid (HF).

### **3.3.2. Sequential extraction of trace metals in sediments**

The modified 5-step Tessier's extraction scheme (Tessier et al., 1979; Li et al., 1995) was used in this study. The extraction was performed progressively on 1.0 g of freeze-dried sediments. The five operationally defined binding fractions include (1) exchangeable, (2) bound to carbonate and specifically adsorbed, (3) bound to Fe-Mn oxides, (4) bound to organic matter and sulfide, and (5) residual phase. The details of the sequential extraction procedure are described as follows:

(1) Exchangeable: sediment samples were extracted with 8 ml of 0.5 M  $\text{MgCl}_2$  at pH 7.0 for 10 min at room temperature and with continuous agitation.

(2) Bound to carbonate and specifically adsorbed: the residue from the exchangeable fraction was extracted with 8 ml 1 M NaOAc (adjusted to pH 5.0 with HOAc) for 5 h at room temperature and with continuous agitation.

(3) Bound to Fe-Mn oxides: the residue from the carbonate and specifically adsorbed fraction was extracted with 20 ml of 0.04 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25 % (v/v) HOAc for 6

h at 96 °C in a water bath and with occasional agitation. After extraction, the extract was diluted to 20 ml with de-ionized water and with continuous agitation for 5 min.

(4) Bound to organic matter and sulfide: the residue from the Fe-Mn oxide fraction was extracted with 3 ml 0.02 M HNO<sub>3</sub> and 5 ml 30 % H<sub>2</sub>O<sub>2</sub> (adjusted to pH 2.0 with HNO<sub>3</sub>) for 2 h at 85 °C in a water bath and with occasional agitation. After cooling, 3 ml 30 % H<sub>2</sub>O<sub>2</sub> (adjusted to pH 2.0 with HNO<sub>3</sub>) was added and the mixture was heated again at 85 °C for 3 h with occasional agitation. After cooling, 5 ml 3.2 M NH<sub>4</sub>OAc in 20 % (v/v) HNO<sub>3</sub> was added, followed by dilution to a final volume of 20 ml with de-ionized water. The mixture was then agitated for 30 min at room temperature.

(5) Residual phase: the residue from organic and sulfide phase was digested with 10 ml concentrated HNO<sub>3</sub> (70 %), 2.5 ml HClO<sub>4</sub> (60 %) and heated at 50 °C for 5 h, 90 °C for 2 h, 120 °C for 4 h and then 150 °C until dryness. The residue was leached with 10 ml 5 % HNO<sub>3</sub> at 70 °C for 1 h.

Following each extraction, the mixture was centrifuged at 3000 rpm for 10 min at room temperature. In order to obtain a uniform matrix for ICP-AES analysis, the different extraction matrices were digested with concentrated HNO<sub>3</sub>. The supernatant was removed with a pipette and digested with 1 ml concentrated HNO<sub>3</sub> (70 %) to dryness at 140 °C. The residue was then leached with 10 ml 5 % HNO<sub>3</sub> at 70 °C for 1 h and finally analyzed by inductively coupled plasma – atomic emission

spectrometry (ICP-AES, Perkin Elmer Optima, 3300DV) for Fe, Mn, Cu, Pb and Zn. Prior to the start of each extraction step, the residue was shaken with 8 ml de-ionized water for 2 min and the supernatant was discarded after 10 min of centrifugation. To estimate the recovery rates of sequential extraction, total metal concentrations in bulk sediment were determined by the nitric and perchloric acid digestion method. Briefly, about 0.2 g of dried sediment was digested with a mixture of 10 ml concentrated  $\text{HNO}_3$  and 2.5 ml  $\text{HClO}_4$ . For quality assurance, reagent blanks, sample replicates and standard reference materials (San Joaquin Soil–NIST 2709) were used to assess the accuracy and precision of the sequential extraction analysis.

The recovery of metals in the standard reference material in the sequential analysis was 74–102 % for Cu and Zn, and 31–70 % for Pb, Fe and Mn. The low recovery of Pb, Fe and Mn was most likely due to a strong association of metals with the crystal lattice. The additions of metal concentrations of the sequential scheme were comparable with those values determined by the nitric and perchloric acid digestion, indicating little loss of material through the procedures (ranging from 65 to 110 % for Cu, Pb, Zn, Fe and Mn). Sample replicates showed the precision and bias of the extraction were generally <15 %.

### **3.3.3. Cold HCl extraction of AVS in sediments**

Extraction of AVS was conducted using the purge and trap technique described by Allen et al. (1993). A round-bottom reaction flask was connected to a series of two trapping vessels containing 80 ml of 0.5 M sodium hydroxide (NaOH) solution. The whole setup was air-tighten and purged with nitrogen ( $N_2$ ). About 100 ml deionized water was added in the round-bottom reaction flask and was purged with  $N_2$  for 10 min. Then, about 10 g wet sediment sample was added into the round-bottom reaction flask and purged with  $N_2$  for another 10 min for oxygen removal. Afterwards, the sediment suspension was stirred and acidified for 40 min with 20 ml of 6 M hydrochloride acid (HCl) at room temperature (cold extraction). The release of  $H_2S$  was trapped in a NaOH solution with a continuous flow of  $N_2$ . The dissolved sulfide concentration in the NaOH solution was measured by using a spectrophotometer at a wavelength of 670 nm after the methylene blue treatment (Allen et al., 1993). The acidified sediment suspension in the round-bottom reaction flask was filtered through a 0.45  $\mu m$  membrane. The concentrations of trace metals in the filtrate were analysed by ICP-AES and were defined as simultaneously extracted metals (SEM). The analysis using wet sediments was reported on a dry weight basis which was determined by measuring the moisture content after drying of each sediment sample.



For the analytical quality control of AVS and SEM analyses, procedural blanks, sample replicates and internal replicates (for internal standard to standardize the analytical error throughout the whole experiment) were randomly inserted in the analysis. The procedural blanks showed that there was no sign of contamination, and the precision of replicate samples for AVS were <25 %. The relative standard deviation of internal replicates for AVS was within 20 %. The precision of replicate samples for SEM were <15 %. The relative standard deviation of internal replicates for SEM was within 15 %.

#### **3.3.4. Lead isotopic composition analyses using ICP-MS**

Selected core samples were used for Pb isotopic composition analyses. Solutions of digested sediment samples from section 3.3.1. were diluted using a 5 % high purity nitric acid solution and analyzed for stable Pb isotope ratios by inductively coupled plasma-mass spectrometry (ICP-MS, Perkin Elmer ELAN 6100 DRC<sup>plus</sup>). Instrumental parameter of 150 sweeps/reading was used. The relative standard deviation (RSD) of the ten replicate reading of each sample was <0.5 %. An international standard reference material (the SRM 981 Common Pb Isotopic Standard) from the National Institute of Standards and Technology (NIST) was used for calibration and quality control. It was inserted at the beginning of the run, between every five samples and at the end of the run respectively. The average measured ratios of  $^{204}\text{Pb}/^{207}\text{Pb}$ ,  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{207}\text{Pb}$  of the standard reference

materials were  $0.0645 \pm 0.0002$ ,  $1.093 \pm 0.002$  and  $2.368 \pm 0.004$  respectively. These results were in good agreement with the certified standard values (0.0646, 1.0933 and 2.3704, respectively).

### **3.3.5. $^{210}\text{Pb}$ dating analyses along sediment cores**

The  $^{210}\text{Pb}$  radiometric technique was used to estimate the chronology of sediment cores. The  $^{210}\text{Pb}$  activities of the samples were determined by measuring the alpha-radioactivity of its granddaughter nuclide  $^{210}\text{Po}$ . The  $^{210}\text{Po}$  was extracted, purified, and self-plated onto a silver disc at 70–80 °C in 0.5 M HCl, and  $^{209}\text{Po}$  was used as the yield monitor and tracer in quantification. The alpha-activity was counted by computerized multi-channel alpha spectrometry with gold-silicon surface barrier detectors. The supported  $^{210}\text{Pb}$  was determined by the alpha activity of the supporting parent,  $^{226}\text{Ra}$ , via the co-precipitation of  $\text{BaSO}_4$ . The CF:CS (constant flux constant sedimentation rate) model was adopted to calculate the sedimentation rate in this study (Appleby and Oldfield, 1983).

### **3.3.6. Other parameters (including particle sizes, TOC and $\text{PO}_4$ analyses in sediments)**

In the laboratory, particle size of the core samples was analyzed using a laser diffraction particle sizer (Coulter<sup>®</sup> LS100). The organic carbon in freeze-dried sediments was determined, after acidification with 1 M HCl, using a CHNS Perkin

Elmer 2400 elemental analyzer. The orthophosphate in freeze-dried sediments was extracted using 0.5 M sodium bicarbonate and measured with a spectrophotometer at a wavelength of 470 nm.

### **3.4. Preliminary laboratory bioaccumulation test**

Metal bioaccumulation test was conducted using surface sediments collected from B1, B3 and B5 in Victoria Harbour. A bioaccumulation test was performed with the polychaete, *Capitella* sp. I, a deposit feeding species. This species was selected due to its feeding strategy which involves the ingestion of large quantities of fine grained sediments (Pearson and Rosenberg, 1978). Also, this species is sensitive to metal contaminants, particular for Hg, Cu and Zn (Reish and LeMay, 1991).

Adult *Capitella* sp. I used for the test were taken from laboratory bred populations provided by the Department of Biology/ Coastal Marine Laboratory, the Hong Kong University of Science and Technology. In the bioaccumulation test, 200 g of wet sediment was placed in a plastic tank with continuously aerated, filtered seawater. About 70 individual worms were introduced to the sediment for 10 days. A total of three replicates were used in the bioaccumulation test. Water quality parameters, including temperature, salinity, pH, dissolved oxygen were measured frequently during the exposure to ensure a suitable environment. After 10 days, the worms were depurated for 48 h to clear their gut content. Then, worm samples were dried at 80

°C to a constant weight and digested with HNO<sub>3</sub>/HClO<sub>4</sub>. The concentrations of Cu and Pb in the worms were analyzed by ICP-MS and Zn was analyzed by ICP-AES. For quality assurance, reagent blanks and standard reference materials (Mussel tissue–NIST 2976) were used to assess the accuracy and precision of the analyses. The analytical results showed no sign of contamination. The recovery rates of trace metals in the standard reference material were around 60–97 %.

### **3.5. Statistical analyses**

In the study of spatial and temporal contamination of trace metals in Victoria Harbour sediments, Two-way ANOVA and Student *t* test was performed to detect any significant difference in metal concentrations among sediments collected in different sampling periods as well as sampling locations. Pearson correlation was performed to identify metal associations in harbour sediments. The critical level for all statistical analyses was carried out at 95 % confidence limit. Factor analysis was applied in an attempt to identify the major source(s) of metals in the harbour. Factor analysis was performed on metals concentrations of all the sediment cores and Varimax with Kaiser normalization was used as the rotation method in the analysis. The use of this rotation method can obtain a clear pattern of loadings in the present study. All statistical analyses were performed using SPSS® for Window Release 10.1.

In the study of geochemical behaviour of metals in harbour sediments, a Student *t* test was applied to examine any significant difference in metal speciation among sediments collected at different sampling areas and sampling periods. Pearson correlation was used to identify the relationship of metal phases with TOC, PO<sub>4</sub> and AVS in harbour sediments. The critical level for all statistical analyses was carried out at 95 % confidence limit. Linear regression was also performed to identify the relative importance of TOC and AVS in the organic/sulfide phases of metals. All statistical analyses were performed using SPSS<sup>®</sup> for Window Release 10.1.

## **Chapter 4 Spatial and temporal distribution of trace metals in sediments of Victoria Harbour, Hong Kong**

Victoria Harbour has received a substantial loading of pollutants from industrial and municipal wastewater since the 1950s. Contaminant inputs have declined drastically during the last two decades as a result of better source controls and improved treatment processes. Therefore, it is important to investigate the changes of sediment contamination over time, particularly during the recent two decades. The present study aims to investigate the current trace metal contamination and historical metal fluxes in Victoria Harbour, and to identify the potential sources of metal pollutants based on geochemical features and Pb-isotopic signatures in sediments.

### **4.1. Physical properties of harbour sediments**

The depth, salinity, pH of the water, the redox potential and TOC of surface sediments in Victoria Harbour are given in Table 4.1. In general, water depths in the harbour varied from 7 to 19 m, with increasing depth from west to east. The pH was consistent from site to site, with an average of 8.1, which was slightly alkaline and within the normal range for marine waters. The salinity in the eastern part was slightly higher than that in the western part, indicating the influence of oceanic water from the west Pacific and of freshwater discharge from the PRE. The surface sediments were highly anoxic, with the redox potential ranging from -133 to -403

mV. The amount of organic carbon in surface sediments ranged from 0.48 to 1.70 %, with the highest TOC found in the central part of the harbour and the lowest in the eastern part. A higher amount of TOC in the central part of the harbour was most likely due to the discharge of untreated urban runoff carrying oil and greases from the streets.

Table 4.1. Sampling locations, physical parameters of waters, redox potential and TOC of surface sediments in Victoria Harbour

Sampling Location	Latitude	Longitude	Water Depth <sup>a</sup> (m)	Redox potential <sup>a</sup> (mV)	pH <sup>a</sup>	Salinity <sup>a</sup> (ppt)	TOC <sup>a</sup> (%)
B1	22°14.800	114°16.000	19	-240	8.1	34.4	0.48 ± 0.1
B2	22°17.500	114°13.500	19	-367	8.1	33.9	1.49 ± 0.28
B3	22°17.471	114°11.183	16	-351	8.0	33.7	1.70 ± 0.22
B4	22°18.400	114°06.500	11	-282	8.1	33.4	1.18 ± 0.13
B5	22°18.142	114°03.051	6.8	-257	8.0	33.1	0.87 ± 0.08

<sup>a</sup>Mean data of the four sampling periods

The grain sizes of sediment cores are shown in Table 4.2. The sediments displayed significant variations in grain sizes among different locations ( $p < 0.05$ ). In general, the finer grain sized sediments (with 97 %  $< 63 \mu\text{m}$ ) were found at B5, whereas coarser sediments (with 52–80 %  $< 63 \mu\text{m}$ ) was found at B1 and B2, affecting by a strong tidal flow. It is well known that trace metals tend to be adsorbed on particle surfaces and higher concentrations of metals are often associated with smaller grain sizes (Loring, 1991; Daskalakis and O'Connor, 1995; Schiff and Weisberg, 1999). In Victoria Harbour, trace metals including Cu, Pb and Zn all showed a weak correlation with respect to the percentage of fine-grained sediments ( $p > 0.05$ ).

Therefore, the granulometric effect on the total trace metal distribution in harbour sediments should be minimal and metal enrichment is most likely the result of anthropogenic origin.

Table 4.2. Grain size distribution in selected sediment samples from location B1 to B5 in Victoria Harbour

Location	Depth (cm)	% fine-grained sediment ( $< 63\mu\text{m}$ )
B1	4–5	80.1
	16–18	57.4
	24–26	71.0
	36–38	79.4
	52–54	61.5
B2	3–4	51.9
	7–8	68.8
	14–16	68.5
	20–22	61.7
B3	2–4	84.9
	10–12	75.4
	16–18	96.4
	24–26	99.9
B4	2–3	80.8
	7–8	80.5
	14–16	86.9
	32–34	74.3
B5	1–2	95.2
	5–6	99.9
	14–16	99.1
	20–22	99.2



## **4.2. Spatial distribution of trace metals in harbour sediments**

The results of Cu, Pb and Zn concentrations in surface sediments are presented in Tables 4.3–4.4 and Figures 4.1–4.3. No significant difference of metals concentrations was observed in the four sampling periods (Table 4.3,  $p>0.05$ ). The mean concentrations of metals are shown in Table 4.4 and the results were consistent with a previous study conducted by the Hong Kong Environmental Protection Department in 2003 (HKEPD, 2004). In general, surface sediments in the eastern part of the harbour were characterized by low concentrations of trace metals. The central part had the highest concentrations of Cu, Pb and Zn, with mean concentrations of 173, 44.3 and 171 mg/kg, respectively. The significant spatial variation of metals could be explained by the different urban settings in the territory. The substantial enrichment of trace metals Cu, Pb and Zn found in the central part (B2 & B3) are in proximity to the most heavily urbanized areas. These areas are characterized by high population density, high traffic density and old industrial areas. In contrast, B1 sediments with less metal enrichment are near areas with strong tidal flushing, low population and light traffic. Thus, it can be clearly observed that the significant spatial variations of trace metals in sediments are most likely due to the high level of urbanization, and the hydrodynamic environment of the harbour.

Table 4.3. Concentrations of Cu, Pb and Zn in surface sediments of Victoria Harbour collected at different sampling periods

Cu (mg/kg, dry weight)					
Sample	B1	B2	B3	B4	B5
December	19.3 <sup>a</sup>	149 <sup>b</sup>	120 <sup>b</sup>	43.8 <sup>c</sup>	18.5 <sup>d</sup>
	29.0 <sup>a</sup>	163 <sup>b</sup>	123 <sup>b</sup>	45.6 <sup>c</sup>	22.1 <sup>d</sup>
February	15.9 <sup>a</sup>	161 <sup>b</sup>	280 <sup>b</sup>	38.2 <sup>c</sup>	29.8 <sup>d</sup>
	16.8 <sup>a</sup>	188 <sup>b</sup>	124 <sup>b</sup>	58.0 <sup>c</sup>	43.9 <sup>d</sup>
October	23.1 <sup>a</sup>	123 <sup>b</sup>	170 <sup>b</sup>	28.6 <sup>c</sup>	32.7 <sup>d</sup>
	23.1 <sup>a</sup>	171 <sup>b</sup>	129 <sup>b</sup>	60.7 <sup>c</sup>	36.9 <sup>d</sup>
April	19.5 <sup>a</sup>	241 <sup>b</sup>	209 <sup>b</sup>	68.5 <sup>c</sup>	27.9 <sup>d</sup>
	20.2 <sup>a</sup>	181 <sup>b</sup>	229 <sup>b</sup>	67.5 <sup>c</sup>	29.6 <sup>d</sup>
Pb (mg/kg, dry weight)					
Sample	B1	B2	B3	B4	B5
December	20.6 <sup>a</sup>	36.2 <sup>b</sup>	48.9 <sup>b</sup>	38.2 <sup>c</sup>	31.0 <sup>c</sup>
	20.0 <sup>a</sup>	44.7 <sup>b</sup>	46.3 <sup>b</sup>	33.9 <sup>c</sup>	32.6 <sup>c</sup>
February	21.6 <sup>a</sup>	85.1 <sup>b</sup>	55.3 <sup>b</sup>	32.3 <sup>c</sup>	35.8 <sup>c</sup>
	20.6 <sup>a</sup>	44.2 <sup>b</sup>	45.7 <sup>b</sup>	39.0 <sup>c</sup>	39.3 <sup>c</sup>
October	24.2 <sup>a</sup>	32.5 <sup>b</sup>	37.2 <sup>b</sup>	17.2 <sup>c</sup>	31.7 <sup>c</sup>
	14.8 <sup>a</sup>	37.5 <sup>b</sup>	45.1 <sup>b</sup>	28.3 <sup>c</sup>	26.0 <sup>c</sup>
April	18.4 <sup>a</sup>	35.6 <sup>b</sup>	37.7 <sup>b</sup>	28.8 <sup>c</sup>	26.4 <sup>c</sup>
	15.7 <sup>a</sup>	36.2 <sup>b</sup>	40.4 <sup>b</sup>	29.0 <sup>c</sup>	22.8 <sup>c</sup>
Zn (mg/kg, dry weight)					
Sample	B1	B2	B3	B4	B5
December	57.6 <sup>a</sup>	151 <sup>b</sup>	155 <sup>b</sup>	114 <sup>c</sup>	109 <sup>c</sup>
	62.3 <sup>a</sup>	172 <sup>b</sup>	165 <sup>b</sup>	113 <sup>c</sup>	114 <sup>c</sup>
February	51.5 <sup>a</sup>	166 <sup>b</sup>	221 <sup>b</sup>	104 <sup>c</sup>	109 <sup>c</sup>
	54.3 <sup>a</sup>	177 <sup>b</sup>	142 <sup>b</sup>	132 <sup>c</sup>	117 <sup>c</sup>
October	60.1 <sup>a</sup>	101 <sup>b</sup>	178 <sup>b</sup>	82.0 <sup>c</sup>	102 <sup>c</sup>
	47.2 <sup>a</sup>	179 <sup>b</sup>	153 <sup>b</sup>	119 <sup>c</sup>	112 <sup>c</sup>
April	50.2 <sup>a</sup>	194 <sup>b</sup>	186 <sup>b</sup>	124 <sup>c</sup>	97 <sup>c</sup>
	52.0 <sup>a</sup>	181 <sup>b</sup>	207 <sup>b</sup>	131 <sup>c</sup>	111 <sup>c</sup>

The small letters stand for statistical significance at the 0.05 level

Table 4.4. Mean ( $\pm$ S.D.) of the total metal concentrations (mg/kg, dry weight) in surface sediments of Victoria Harbour (n=8)

	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
B1	21.2 $\pm$ 4.5 <sup>a</sup>	19.6 $\pm$ 3.3 <sup>a</sup>	55.0 $\pm$ 5.3 <sup>a</sup>
B2	172 $\pm$ 34.3 <sup>b</sup>	44.0 $\pm$ 17.1 <sup>b</sup>	165 $\pm$ 28.9 <sup>b</sup>
B3	173 $\pm$ 60.5 <sup>b</sup>	44.6 $\pm$ 6.06 <sup>b</sup>	176 $\pm$ 27.7 <sup>b</sup>
B4	51.4 $\pm$ 14.5 <sup>c</sup>	30.8 $\pm$ 6.89 <sup>c</sup>	115 $\pm$ 16.3 <sup>c</sup>
B5	30.2 $\pm$ 8.01 <sup>d</sup>	30.7 $\pm$ 5.45 <sup>c</sup>	109 $\pm$ 6.76 <sup>c</sup>
LCEL <sup>1</sup>	65	75	200
UCEL <sup>2</sup>	110	110	270
HKEPD <sup>3</sup>	17-230	24-130	47-300
Background values in Hong Kong sediments <sup>4</sup>	11	32	67

The small letters stand for statistical significance at the 0.05 level

<sup>1</sup>LCEL Lower Chemical Exceedance Level for sediment quality assessment in Hong Kong. Biological effects would be observed above this level (HKEPD, 2004).

<sup>2</sup>UCEL Upper Chemical Exceedance Level for sediment quality assessment in Hong Kong. Adverse biological effects would be observed above this level (HKEPD, 2004).

<sup>3</sup>HKEPD Data from HKEPD sediment monitoring program conducted in 2003 (HKEPD, 2004).

<sup>4</sup>Tanner et al., 2000

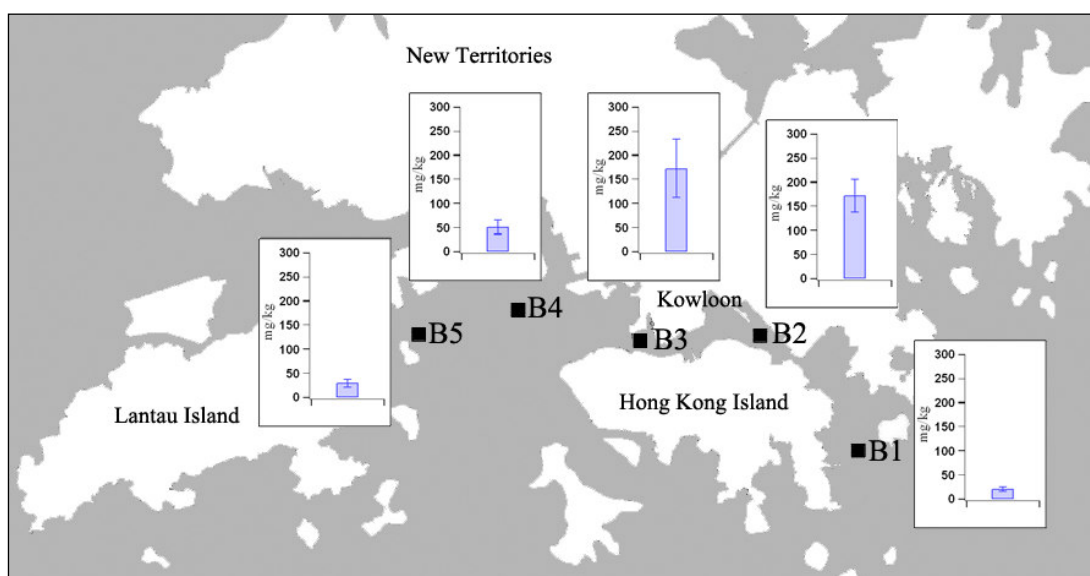


Figure 4.1. Spatial distribution of average Cu concentrations in surface sediments of Victoria Harbour collected in the four sampling periods (mg/kg, dry weight)

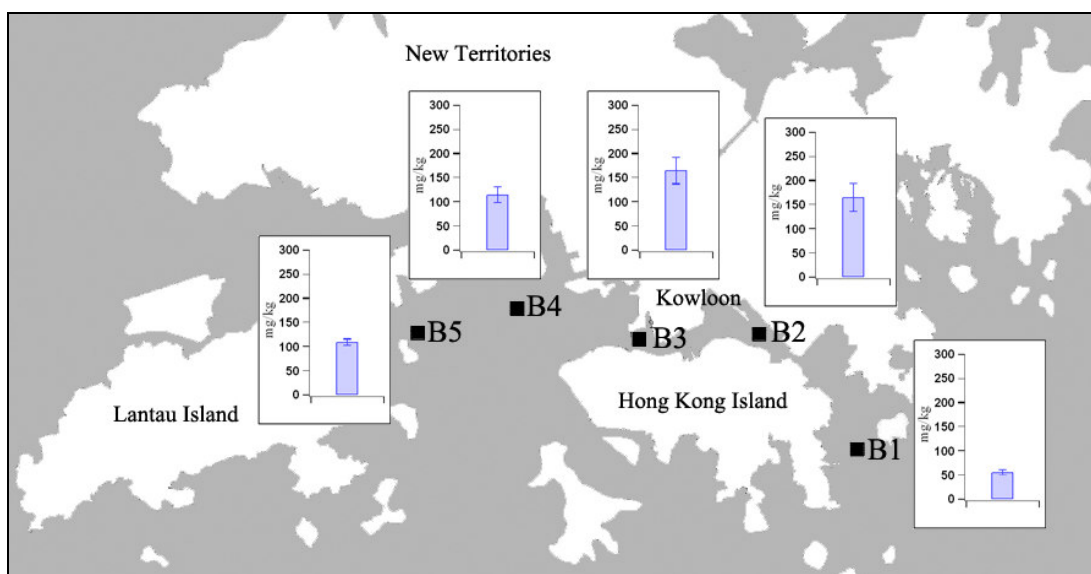


Figure 4.2. Spatial distribution of average Zn concentrations in surface sediments of Victoria Harbour collected in the four sampling periods (mg/kg, dry weight)

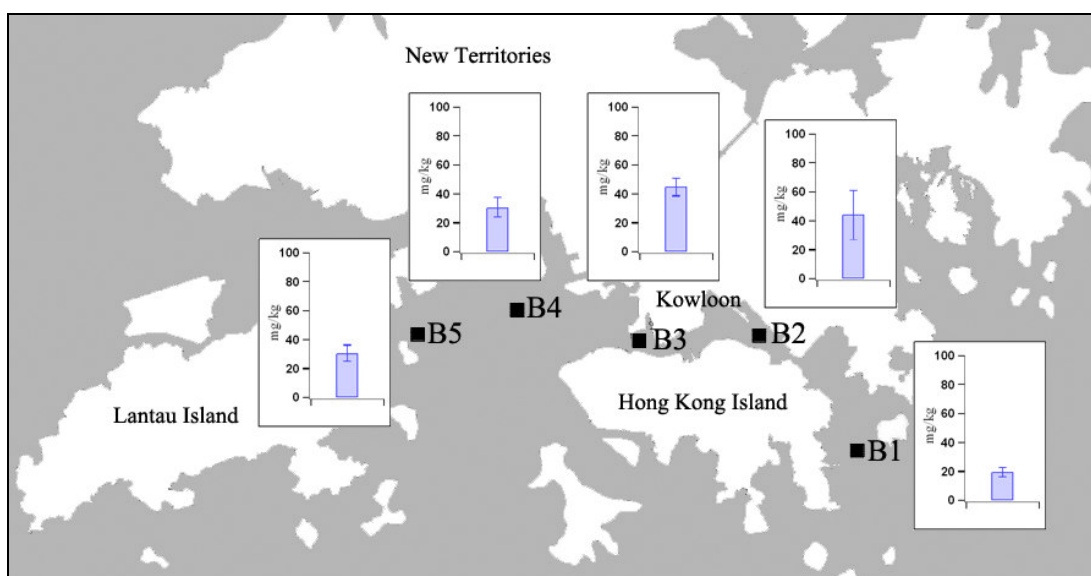


Figure 4.3. Spatial distribution of average Pb concentrations in surface sediments of Victoria Harbour collected in the four sampling periods (mg/kg, dry weight)

The results were compared with baseline values taken from the measurements in sediment cores from Victoria Harbour, typically deeper than 5 m (Tanner et al., 2000). There was a significant enrichment of trace metals in the central and western parts of the harbour, particularly for Cu in the central part, which was 20 times higher than the baseline value (Table 4.4). It should be noted that the anomalously high concentrations of Cu in surface sediments have exceeded the Upper Chemical Exceedance Level, which may pose some hazards to the aquatic life.

Table 4.5 provides a comparison of metal concentrations in sediments from other harbours of the world. The levels of Pb and Zn in surface sediments of Victoria Harbour are comparable to moderately polluted harbours with a small catchments and a short history of environmental pollution, such as Darwin Harbour (Peerzada and Rohoza, 1989), Manila Bay (Prudente et al., 1994) and Tolo Harbour (Owen and Sandhu, 2000). In contrast, Cu in Victoria Harbour were within the ranges reported in New Bedford Harbour (Stoffers et al., 1977), Baltimore Harbour (McGee et al., 1999) and Sydney Harbour (Birch and Taylor, 1999). These are heavily polluted harbours receiving substantial loads of pollutants from river drainages and have been subjected to a long history of pollution for around 100 to 200 years.

In the typhoon shelters of Victoria Harbour having restricted water circulation, the levels of Cu were remarkably higher (HKEPD, 2004) and are comparable to those in

heavily polluted harbours. Besides, Pb and Zn in typhoon shelters were also higher than offshore sediments in Victoria Harbour. Although, Victoria Harbour is not subject to the direct influence of river drainage, metal distribution in sediments is similar to other harbours, in which large proportions of point sources metals are effectively deposited and retained in nearshore sediments (Sinex and Heiz, 1982; Birch, 1996; Bothner et al., 1998). For instance, the maximum concentration of Cu in a typhoon shelter was 2100 mg/kg, which was 7.5 times higher than those observed in offshore sediments.

Table 4.5. Metal concentrations in sediments of other polluted harbours (mg/kg, dry weight)

Location	Cu	Pb	Zn
Boston Harbour, U.S.A. <sup>1</sup>	7–142	18–263	39–414
New Bedford Harbour, U.S.A. <sup>2</sup>	117–3136	104–616	315–1550
Baltimore Harbour, U.S.A. <sup>3</sup>	9.5–396	1.0–349	40–2105
Halifax Harbour, Canada <sup>4</sup>	45–131	72–340	143–355
Sydney Harbour, Australia <sup>5</sup>	9.3–1053	38–3604	108–7622
Darwin Harbour, Australia <sup>6</sup>	16–32	24–91	103–270
Cork Harbour, Ireland <sup>7</sup>	9.8–29	18–44	65–196
Dar es Salaam Harbour, Tanzania <sup>8</sup>	4.5–25	13–44	19–94
Manila Bay, Philippines <sup>9</sup>	32–118	6.0–95	60–329
Harbour of Ceuta, North Africa <sup>10</sup>	5–865	10–516	29–695
Tolo Harbour, Hong Kong <sup>11</sup>	21–84	48–144	100–270
Victoria Harbour, Typhoon shelter, Hong Kong <sup>12</sup>	110–2100	53–140	210–500
Victoria Harbour, Hong Kong <sup>13</sup>	16–280	21–85	52–221

<sup>1</sup>Zago et al., 2001

<sup>2</sup>Stoffers et al., 1977

<sup>3</sup>McGee et al., 1999

<sup>4</sup>Buckley et al., 1995

<sup>5</sup>Birch and Taylor, 1999

<sup>6</sup>Peerzada and Rohoza, 1989

<sup>7</sup>Berrow, 1991

<sup>8</sup>Machiwa, 1992

<sup>9</sup>Prudente et al., 1994

<sup>10</sup>Guerra-García and García-Gómez, 2005

<sup>11</sup>Owen and Sandhu, 2000

<sup>12</sup>HKEPD, 2004

<sup>13</sup>Present study

### **4.3. Temporal distribution of trace metals in harbour sediments**

As sediments in Victoria Harbour are highly mixed by physical processes such as tidal currents and/or human disturbances, only sediment core B4 was able to construct the chronology successfully using the  $^{210}\text{Pb}$  dating method. The unsupported  $^{210}\text{Pb}$  activities of the core decreased linearly as a function of sediment depth in core B4, but showed an irregular change in cores B2 and B5 (Figure 4.4). The linear  $^{210}\text{Pb}$  profiles indicated an exponential decline in  $^{210}\text{Pb}$  activity with depth and this allowed the use of CF:CS (constant flux constant sedimentation rate) model to calculate the sedimentation rate (Appleby and Oldfield, 1983). The linear  $^{210}\text{Pb}$  profile probably indicates a constant rate of sediment accumulation and this gives rise to a constant rate of unsupported  $^{210}\text{Pb}$  accumulation. The average sedimentation rate estimated by the CF:CS model in the core was 1.2 cm/yr. The sedimentation rate at B4 was greater than the rates found at Hebe Haven, 0.35–0.56 cm/yr (Lo and Fung, 1992), located in the southeastern part of Hong Kong with the influence of oceanic water. It was, however, close to the sedimentation rates in Deep Bay, 1.3–1.7 cm/yr (Wong and Li, 1990), which is affected by the Pearl River discharge in the western part of Hong Kong. The comparatively high sedimentation rate at B4 is most probably due to the influence of the Pearl River discharge.



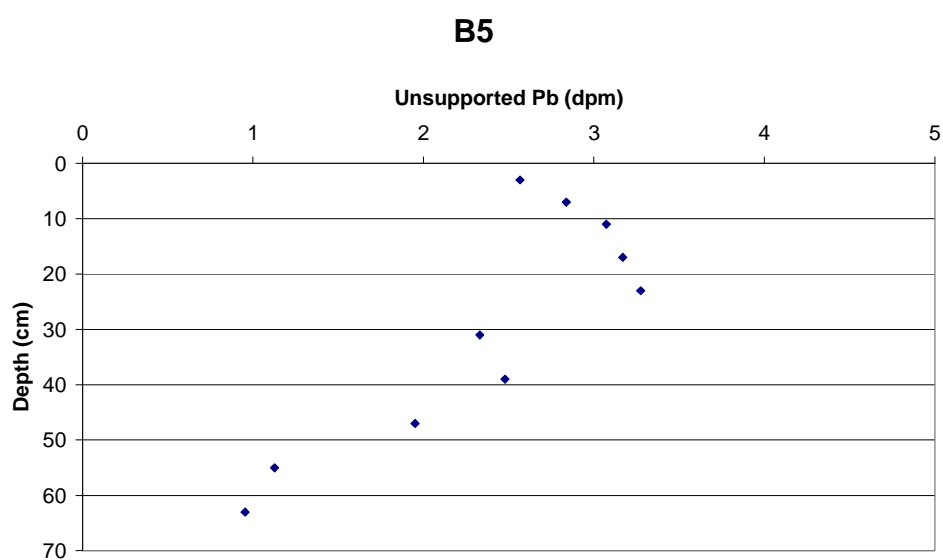
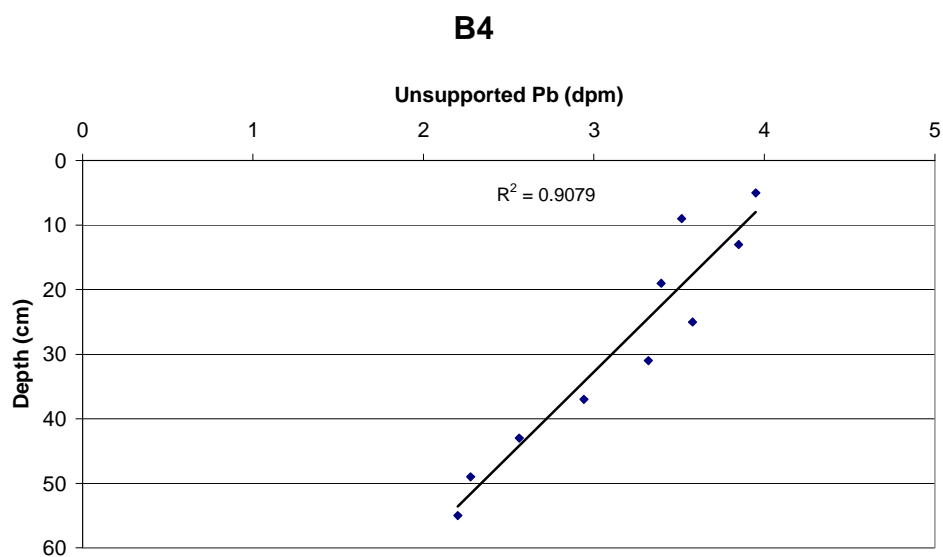
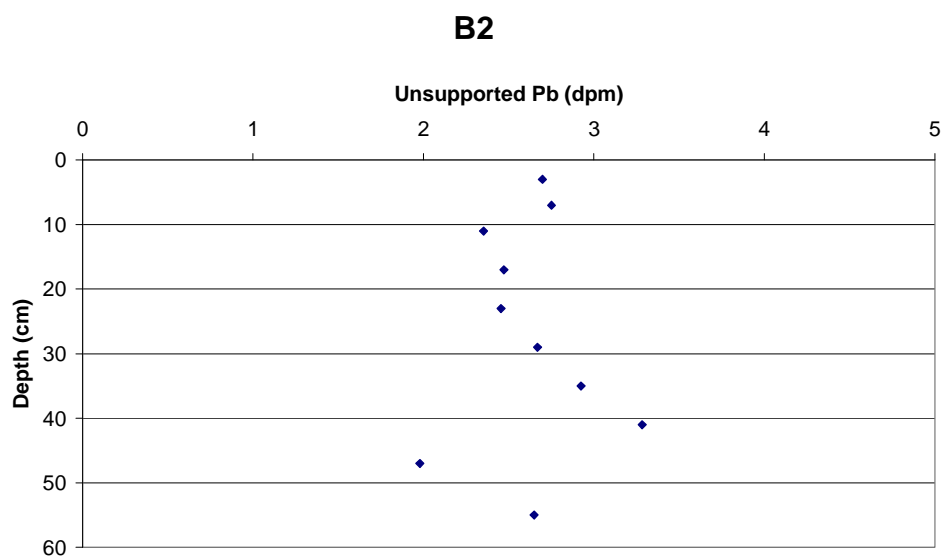


Figure 4.4. Results of  $^{210}\text{Pb}$  dating in sediment cores B2, B4 and B5 of Victoria Harbour

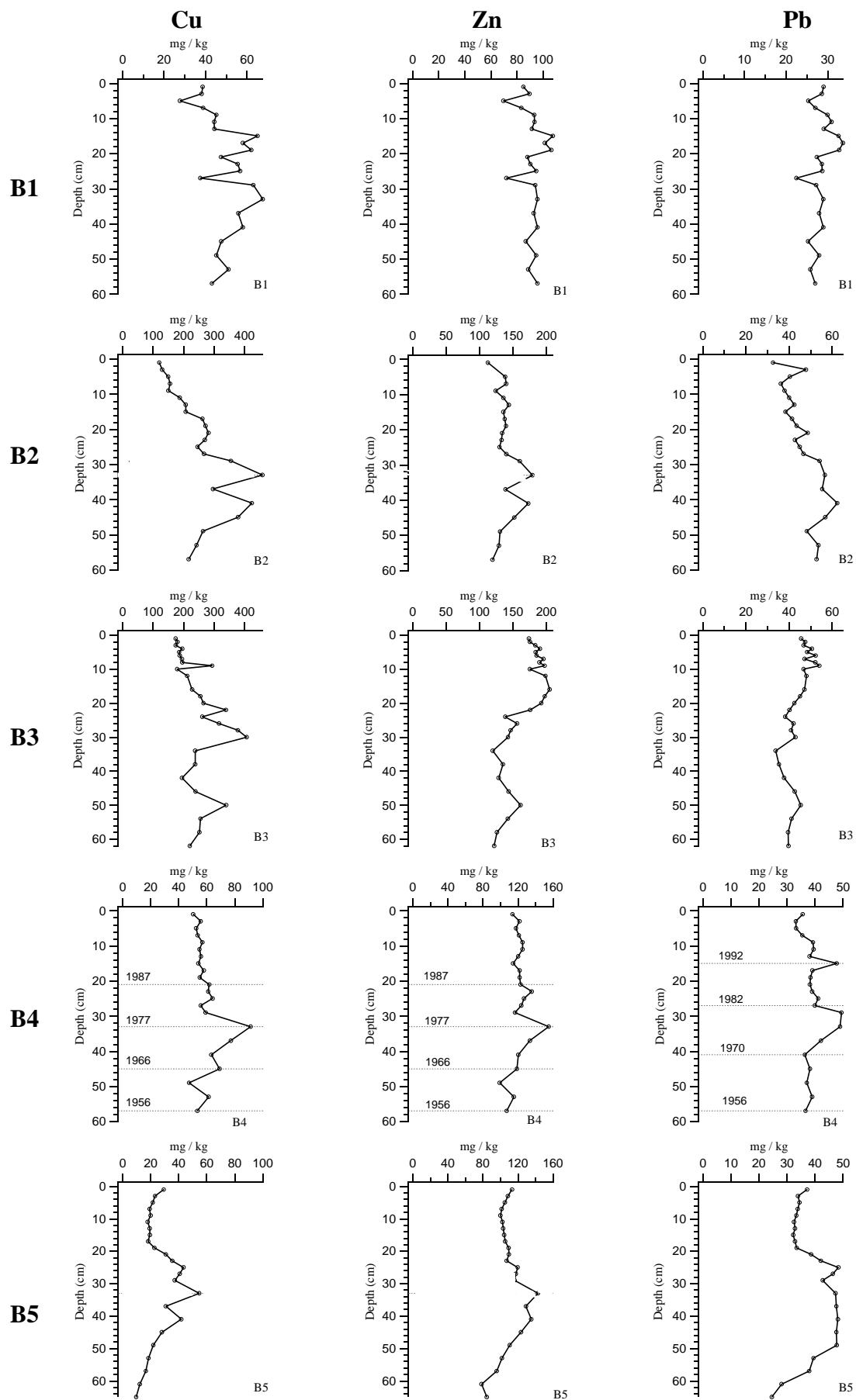


Figure 4.5. Temporal distribution of Cu, Zn and Pb in core sediments, B1 to B5, of Victoria Harbour (Core B4 with the estimated date)

The metal concentration profiles of Cu, Zn and Pb at B1 to B5 are shown in Figure 4.5. The sediment core B4 showed large temporal changes in trace metal concentrations, particularly for Cu and Zn, indicating changes in the characteristics and magnitude of metals input to the harbour during the last few decades. However, the core was not long enough to reflect any period before human's substantial activity in the harbour, whereas metals enrichment was evidenced in the bottom of this core. The trend of Cu followed closely the trend of Zn in the sediment core, and a significant correlation between these two metals was observed ( $p < 0.05$ ), thus raising the possibility that they are derived from the same source(s) and that the geochemical affinity of these metals to the sediment particles are similar.

The elevated Cu and Zn values were observed in the mid-1950s and significant increases of both metals occurred between 1966 and 1987. Cu and Zn reached the peak at 33 cm corresponding to 1977, with concentrations of 91 and 155 mg/kg, respectively. Such change could be explained by urban development in the territory. Since the 1950s, the manufacturing sector in the territory has grown considerably over the next forty years and remained the largest single contributor to local's Gross Domestic Product until 1987 (HKGID, 1996). Therefore, intensive industrial activities probably led to the considerable enrichments of Cu and Zn in sediments during the periods of 1966 to 1987. During that time, the peak concentration of Cu was 8 times higher than the baseline value in harbour sediments, such a large input

of Cu was most likely related to the rapidly growing printed circuit board (PCB) manufacturing and electroplating industries in the territory (Yim, 1984, Tanner et al., 2000; HKEPD, 2002).

A decline of metal concentrations in the sediment core was observed in the late 1980s and this could reflect the reduction of industrial input with the relocation of industries to the mainland and set-up of the Chemical Waste Treatment Centre in the territory. Close to B4, there is the Chemical Waste Treatment Centre and Stonecutters Island Sewage Treatment Works, which began to operate in 1993 and 1997, respectively. It seems that effluents from these treatment plants had no major influence on metal concentrations at B4 sediments. The levels of Cu and Zn remained relatively constant to the top of the core with the concentration ranges from 50 to 57 mg/kg and from 110 to 125 mg/kg, respectively. The current Cu and Zn concentrations were much lower than the peak values in the 1970s, the estimated reduction of Cu was 51 % and Zn was 48 % compared with their peak values found in deep sediments. The decreasing industrial activities and better source controls in Hong Kong, thus resulting in a substantial reduction of Cu and Zn to harbour sediments in recent years. However, Cu and Zn in surface sediments were still higher than the baseline values (Cu: 11 mg/kg; Zn: 67 mg/kg), suggesting the harbour could be subject to other sources of metal contamination and/or resuspension of old sediments.

The trend of Pb profile was slightly different from the trends of Cu and Zn at B4 (Figure 4.5). The deeper sediments contained an average Pb concentration of 37.5 mg/kg which was higher than the baseline value. A sudden rise of Pb to 42–49 mg/kg occurred at depth intervals from 29–40 cm, corresponding to the period of 1970 to 1982. Thereafter, Pb concentrations declined to 38.2 mg/kg and an abrupt increase to 47.8 mg/kg was observed in 1992. Towards the surface, sediments were characterized by declining Pb concentrations, and the amount of Pb in the topmost sediment was 35.7 mg/kg. In Hong Kong, a gradual reduction of Pb content in leaded petrol began in the early 1980s and leaded petrol was totally banned in 1999. Consequently, the increased enrichment of Pb during the period from 1970 to 1982 in B4 core could be attributable to the use of leaded gasoline in the territory. However, the contribution of other anthropogenic sources including untreated industrial effluents and red lead-containing paints used in rust-proofing ships cannot be ruled out (Yim, 1984; Wong, 1987; Chan et al., 2001).

Among the sediment cores, Cu, Zn, and to a lesser extent, Pb in cores B2 and B3 were much higher than those in cores B1, B4 and B5, especially the peak concentrations in deeper sediments (Figure 4.5). The maximum concentrations of Cu and Zn found in subsurface sediments of the central part of the harbour (B2 and B3) were 459 and 304 mg/kg, respectively. It should be noted that the peak of Cu was 40 times higher than the baseline values. The untreated industrial wastewater in the past

has apparently posed a serious metal contamination in the central part of the harbour.

These metals could be released to the water column when sediments are subject to major disturbance.

In case of Pb, levels of this metal at B2 and B3 cores were slightly higher than those at B4 and B5, with an average concentration of 46.5 mg/kg. Again, the central part (B2 and B3) is closer to the pollution sources, thus resulting in a higher enrichment of Pb in sediments over the past few decades. In general, the enrichment of Pb in core sediments was lower than that of Cu and Zn, whereas Pb was only 1.3 times higher than the baseline value. In fact, the variation of Pb distribution could be explained by the different geochemical behaviours of Pb in the marine environment. It is well documented that Pb is a highly particle reactive metal (Balls, 1988), which tends to associate with fine suspended particulate matter (SPM) (Krause et al., 1993; Helland et al., 2002; Hinrichs et al., 2002). In Victoria Harbour, SPM was also found to be more enriched with Pb than other trace metals. The Pb concentration in SPM was 11 times higher than that in surface sediments, whereas Cu and Zn were about 1.3 times higher in SPM (Ip et al., unpublished data). During strong tidal flushing in the harbour, most of the anthropogenic Pb adsorbed on fine suspended particles is likely to be dispersed and deposited in low energy environments outside the harbour. As a result, there is a less enrichment of Pb in harbour sediments. A similar finding was observed by Hinrichs et al. (2002) in the German Bight, where the deposition of

Pb-rich SPM was reduced in high energy environment.

In general, the trace metal distribution in Victoria Harbour varied spatially and temporally as shown in the surface and core sediments in the eastern, central and western parts of the harbour. Spatial variations of trace metals are likely associated with the population densities, industrial activities and traffic densities along coastal areas. The central part of the harbour is in proximity to areas with high-level of urbanization, thus resulting in a significant enrichment of trace metals in sediments. The change of human activities in the territory over the past few decades has led to a major change of metal distributions in sediment cores. The rapid urban and industrial development since the mid-1950s resulted in a remarkable increase of Cu and Zn concentrations in subsurface sediments. Subsequent declines in trace metals were observed in the late-1980s, due to the gradual reduction of industrial sources in the territory. However, the surface sediments were still enriched with metals and this is probably originated by sources other than the local industrial activities, such as sewage discharge and sediment resuspension.

#### **4.4. Potential sources of trace metals in the harbour**

Human activities with significant impacts on the urban environment are often associated with industrial activities, disposal of municipal wastes, traffic and corrosion of construction/ building materials (Birch, 1996; Callender and Rice, 2000;

Matthai et al., 2002; Cobelo-García and Prego, 2004; Lee et al., 2005). In Hong Kong, the rapid increase of population began in the 1950s due to the massive influx of immigrants from mainland China. About 75 % of untreated wastewaters was directly discharged to Victoria Harbour and the estimated amount of untreated sewage was found to be 1.5 million tons per day in 1995 (Hong Kong Government, 1995). Substantial inputs of wastewaters led to excessive bacterial levels and significant reduction of dissolved oxygen of harbour waters (Yung et al., 1999). Until 2001, with the enactment of the Harbour Area Treatment Scheme (HATS), more than 75 % of sewage around the harbour is subject to chemically enhanced primary treatment (HKEPD, 2004)..

The industrial development in the territory since the 1950s was also a major source of contaminants in Victoria Harbour. Light industries such as the PCB manufacturing industry, electroplating industry and tannery were prevalent in the territory. Most of these factories were located along the coastlines of the harbour such as Kwun Tong, Hung Hom and Cheung Sha Wan. Substantial amounts of untreated industrial wastewater were discharged to the water bodies in the past, and it was estimated that 3000 tons of industrial wastes were generated per year (HKEPD, 1996).

Urban runoff carrying street dust and soils is often considered as the major source of trace metals to water bodies in the urban environment (Sutherland and Tolosa, 2000;



Ramessur and Ramjeawon, 2002; Gnecco et al., 2005). In Hong Kong, heavy traffic has led to the subsequent enrichment of Zn, Pb and to a lesser extent, Cu in street dust and soils (Ho, 1979; Wang et al., 1998; Ng et al., 2003; Li et al., 2004). These metals can be easily mobilized and released to the nearby water bodies during rainfall. In Hong Kong, urban runoff carrying large quantities of pollutants are directly discharged into water bodies through stormwater drainages.

To further elucidate the potential sources of trace metals in Victoria Harbour, metal associations in sediment cores were studied using principal component analysis (PCA). PCA was used to reduce the dimensionality in the data and to summarize the major patterns of variation within the measured geochemical parameters. The total metal concentrations (Al, Fe, Mn, Ca, Co, Cu, Ni, Pb and Zn) in sediment cores B1 to B5 were analyzed using PCA and the result is shown in Table 4.6.

Table 4.6. Result of the principle component analysis on total metal concentrations in B1 to B5 sediment cores (n=116)

% of variance	Principle loading factors		
	PC 1 37.3 %	PC 2 28.9 %	PC 3 17.6 %
Cu	-0.083	<b>0.732</b>	-0.508
Ni	<b>0.782</b>	0.202	-0.276
Pb	0.051	<b>0.949</b>	-0.004
Zn	0.222	<b>0.863</b>	-0.248
Al	<b>0.870</b>	0.351	-0.019
Fe	<b>0.842</b>	-0.203	0.449
Mn	-0.002	-0.190	<b>0.924</b>
Co	<b>0.933</b>	-0.188	0.181
Ca	<b>-0.594</b>	-0.371	0.300

In this analysis, three major components were extracted and accounted for 83.7 % of the total variance. The first component which includes Al, Fe, Ca, Co and Ni may represent the natural source of sediments. The second component includes Cu, Pb and Zn, and this may probably represent anthropogenic sources associated with sewage, industrial and traffic activities in the urban environment. As there was a strong association between Cu and Zn in harbour sediments, the mean ratios of these metals in sediments was compared to various anthropogenic sources in the territory to better determine the likely importance of different metal sources. Table 4.7 shows Cu/Zn ratios of surface sediments at sites B1 to B5 and ratios of various sources of pollutants in the territory. Among various anthropogenic sources, sewage and sludge from the Stonecutters Island Treatment Works, and effluents from the Chemical Waste Treatment Centre were found to be more enriched with Cu, with higher Cu/Zn ratios (0.83–3.79). The significant enrichment of Cu in wastes from these plants is most likely due to the input from industrial activities along the coast of Victoria Harbour. The lower Cu/Zn ratios were observed in domestic sewage in Urmston Road outfalls (0.13), road dusts (0.12–0.22), as well as urban soil (0.15).

For surface sediments, B2 and B3 had the highest Cu/Zn ratios (0.96–1.05), suggesting the sediments are seriously contaminated by industrial sources. On the other hand, surface sediments at B1, B4 and B5 had low Cu/Zn ratios (0.28–0.44) but the ratios were slightly higher than those from domestic sources. This probably

reflects the insignificant influence of industrial activities in the eastern and western parts of the harbour. In the sediment core B4, different Cu/Zn ratios were observed as a result of changing metal sources over time. During the mid 1950s to the late 1980s, the sediments were characterized by a comparatively high Cu/Zn ratio (~0.52), indicating industrial activities is the dominant source of metals. After the late 1980s, sewage and urban runoff may become the major sources of metals with decreased Cu/Zn ratios (~0.45) in sediments.

Table 4.7. Cu/Zn ratios in B1 to B5 surface sediments of Victoria Harbour and ratios in different anthropogenic sources in Hong Kong

Sample	Cu/Zn
B1 surface sediment	0.38
B2 surface sediment	1.05
B3 surface sediment	0.96
B4 surface sediment	0.44
B5 surface sediment	0.28
Road dust (1987) <sup>1</sup>	0.22
Road dust (2001) <sup>2</sup>	0.12
Urban soil <sup>2</sup>	0.15
Untreated domestic sewage from Urmston Road outfall <sup>3</sup>	0.13
Sludge from Stonecutters Island wastewater treatment works <sup>4</sup>	3.79
Effluents from the Chemical Waste Treatment Centre (1993) <sup>5</sup>	1.9
Influents from Stonecutters Island wastewater treatment works (2006) <sup>6</sup>	1–3.07
Effluents from Stonecutters Island wastewater treatment works (2006) <sup>6</sup>	0.83–2.9

<sup>1</sup>Yim and Nau, 1987

<sup>2</sup>Li et al., 2001

<sup>3</sup>Evans and Dawes, 1996

<sup>4</sup>Chu et al., 1998

<sup>5</sup>Chemical Waste Treatment Centre Monitoring Report 1993

<sup>6</sup>Data obtained from the Hong Kong Drainage Services Department (personal communication)

#### 4.5. Pb isotopic composition of harbour sediments

The mean and ranges of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in sediments are listed in Table 4.8. The range of Pb isotope ratios varied from 1.120 to 1.197 in harbour sediments. In

general, the  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic ratios of anthropogenic Pb derived from various Pb ores are usually lower than those of background geological materials (Croudace and Cundy, 1995; Farmer and Eades, 1996). The natural background of  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic ratios ranges from 1.201 to 1.279 in Hong Kong (Ip et al., 2004), a decrease in ratio in the harbour sediments was observed. This may provide a strong evidence of the occurrence of anthropogenic Pb sources in Victoria Harbour. Among the sediment cores, B1 was characterized by relatively low Pb concentrations and high  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios which are close to the natural background ratios. Thus, the eastern part of the harbour is probably less contaminated with Pb. The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios at B4 core ranged from 1.171–1.190, whereas noticeable decline in Pb isotope ratios with corresponding increase in Pb concentrations were observed at depth of 32 cm (Figure 4.6). This shift occurred in sediment deposited since 1970, giving a strong indication of the increased anthropogenic Pb as a result of rapid urban and industrial development at this site.

Table 4.8. Mean ( $\pm$ S.D.) and range of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in sediment cores, B1 to B5, of Victoria Harbour

	Range of Pb concentration (mg/kg)	Mean $^{206}\text{Pb}/^{207}\text{Pb}$	Range $^{206}\text{Pb}/^{207}\text{Pb}$
B1 (n=12)	8.18 – 32.4	$1.187 \pm 0.006$	1.173 – 1.193
B2 (n=4)	35.4 – 56.9	$1.175 \pm 0.007$	1.168 – 1.182
B3 (n=5)	39.8 – 68.4	$1.171 \pm 0.01$	1.157 – 1.180
B4 (n=22)	33.2 – 52.7	$1.182 \pm 0.012$	1.120 – 1.190
B5 (n=9)	29.5 – 42.9	$1.187 \pm 0.014$	1.154 – 1.197

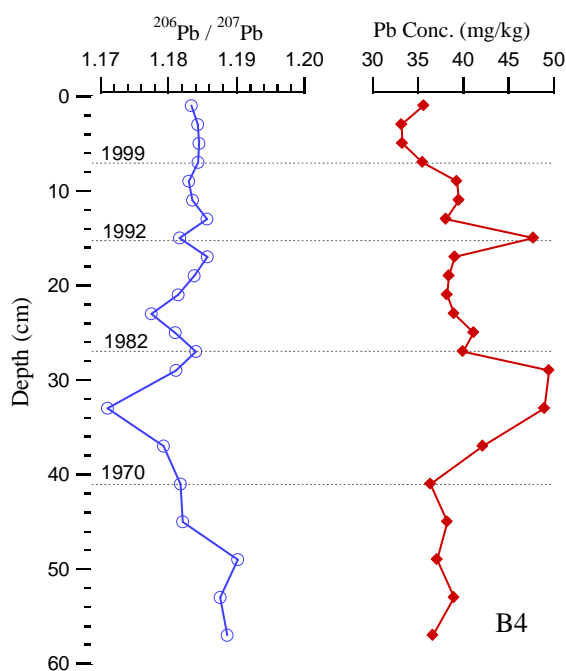


Figure 4.6.  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios and Pb concentrations (mg/kg) in dated sediment core B4 of Victoria Harbour

In Hong Kong, the production of alkyllead and its compounds in leaded petrol is mainly derived from Pb ore with low  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios, such as Australian Pb ore (Wong and Li, 2004). The Pb from Australian Pb ore is characterized by low radiogenic signatures, with a  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio range from 1.03 to 1.04 (Bollhofer and Rosman, 2000). The use of leaded petrol in Hong Kong has resulted in increased Pb concentrations and lowering of the Pb isotope signature in urban soils and road dusts (Wong and Li, 2004; Duzgoren-Aydin et al., 2004).

To evaluate the potential anthropogenic sources of Pb in harbour sediments,  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{207}\text{Pb}$  ratios of the samples, geological materials in Hong Kong, road dust in Hong Kong, contaminated soils in Hong Kong and Australian Pb ore are

plotted in Figure 4.7. It illustrates that the  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{207}\text{Pb}$  ratios of the harbour sediments and the geological materials appear to form a linear mixing pattern with those of Australian Pb ores. This may probably indicate that the Pb contamination in sediments is associated with the input of gasoline lead to the harbour, perhaps from stormwater runoff. Besides, harbour sediments showed a relatively wide range of Pb isotopic ratios when compared with those in Hong Kong road dust (Duzgoren-Aydin et al., 2004). The wide range of Pb isotopic ratios in harbour sediments is most likely attributed to the mixed products of gasoline Pb and a number of other anthropogenic sources in the harbour, e.g. industrial and shipping activities.

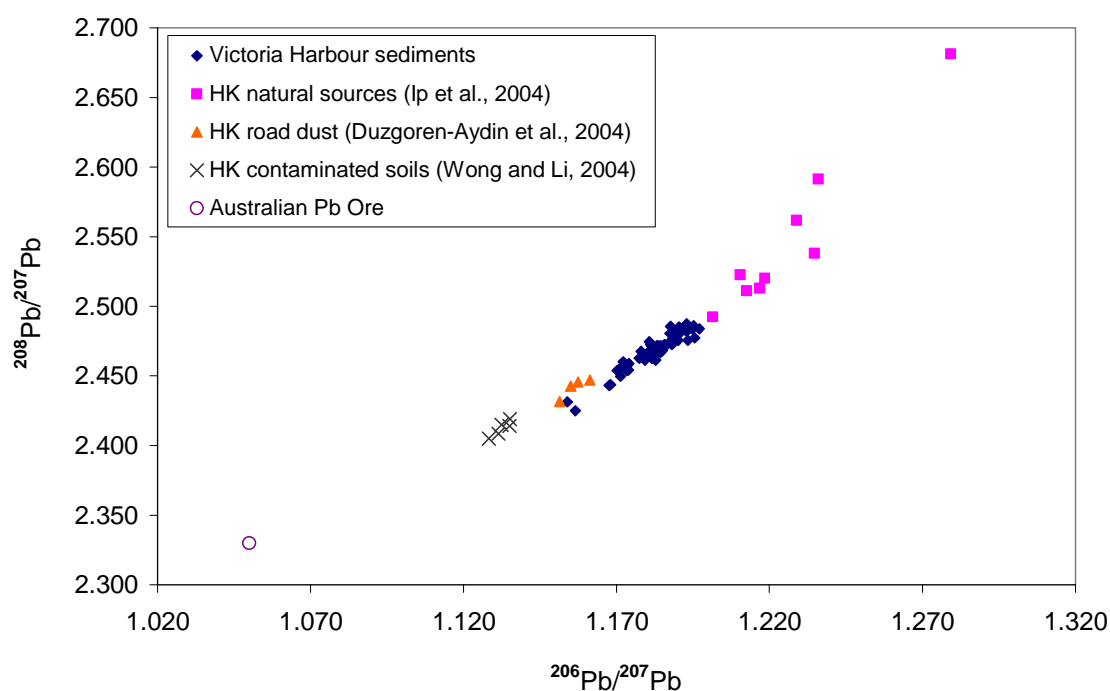


Figure 4.7. Relationship between  $^{208}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{207}\text{Pb}$  in sediments of Victoria Harbour and those from known sources in Hong Kong

## **Chapter 5 Geochemical behaviour of trace metals in surface sediments of Victoria Harbour, Hong Kong**

Victoria Harbour, near the metropolitan area, has been heavily polluted by industrial and domestic wastes for a few decades until the introduction of regulatory controls in recent decades. This resulted in Cu, Zn and Pb contamination in harbour sediments as shown in the previous chapter. It is therefore necessary to assess the geochemical behaviour of these metals in order to evaluate their potential hazards to the environment. The major objectives of the present study are (1) to investigate the geochemical behaviour and cycling of metals in harbour sediments; (2) to assess the environmental risk of trace metals enrichment during the recovery of Victoria Harbour based on the study of metal speciation.

### **5.1. Physiochemical properties of surface sediments**

The physical and chemical properties of bottom waters and surface sediments are given in Tables 5.1 and 5.2. The water temperature in October was slightly higher than that in April, reflecting seasonal temperature differences between autumn in October and spring in April. The dissolved oxygen (DO) in bottom waters (5.2–7.2 mg/L) was generally greater than the requirement of the Water Quality Objective for Hong Kong waters (2 mg/L). Compared with other water bodies in Hong Kong, such as Deep Bay and Tolo Harbour, Victoria Harbour has higher dissolved oxygen levels,

despite a greater pollutant loading. This is most likely due to the presence of strong tidal flushing in the harbour (Broom and Ng, 1995). The surface sediments in both sampling periods were characterized by moderately to highly reducing environments as indicated by the negative redox potential ranging from -185 mV to -420 mV. Such environments probably favour the sulfate reduction in sediments (Howard and Evans, 1993). It should be noted that the surface sediments were found to be highly anoxic in spite of the presence of oxygenated bottom waters, suggesting the reducing conditions could be the consequence of high organic loadings in sediments. A reducing condition in sediments occurs when the rate of particulate organic matter degradation exceeds the rate of the dissolved oxygen replenishment from bottom waters by diffusion or irrigation. The oxygen, nitrate, and Fe/Mn oxyhydroxides are consumed during the organic matter degradation by microbial activities and the subsequent reduction of sulfate may result in a reducing environment (Froelich et al., 1979).



Table 5.1. Physical parameters of bottom waters and surface sediments in Victoria Harbour

<b>Samples in October 2005</b>						
Location	Water Depth (m)	Temperature (°C)	Salinity (ppt)	DO (mg/L)	pH	Eh (mV)
B1	21	28	35	6.5	8.1	-211
B2	15	27	35	5.2	8.0	-420
B3	16	27	34	5.3	8.0	-367
B4	9.5	28	34	6.2	8.0	-343
B5	6.6	28	34	6.2	8.0	-320

<b>Samples in April 2006</b>						
Location	Water Depth (m)	Temperature (°C)	Salinity (ppt)	DO (mg/L)	pH	Eh (mV)
B1	17	22	36	7.1	8.0	-231
B2	26	22	35	5.8	7.9	-312
B3	18	22	35	5.4	7.9	-337
B4	11	22	34	7.2	8.0	-185
B5	6.7	22	33	6.7	8.0	-263

Total organic carbon (TOC) and orthophosphate ( $\text{PO}_4$ ) in harbour sediments are summarized in Table 5.2. As interactions of these compounds with metals often occur in the marine environment (Sundby et al., 1992), the study of TOC and  $\text{PO}_4$  may provide a more clear understanding on the geochemical cycling of metals in sediments. From Table 5.2, it was shown that the TOC in sediments varied from 0.37 to 1.94 %, and there was no significant difference in the two sampling periods ( $p>0.05$ ). Among the sampling locations, sediments at B2 and B3 contained the highest amounts of TOC, and this is presumably due to the intensive discharges of untreated sewage and urban runoff. For the  $\text{PO}_4$ , concentrations in harbour sediments ranged from 7.8 to 27 mg/kg, with maximum amounts found at B4 which is close to the sewage treatment work. Of the two sampling periods, sediments at B1, B2 and B3 exhibited a substantial difference in  $\text{PO}_4$  ( $p<0.05$ ). Sediments in October contained higher amounts of  $\text{PO}_4$ . This may possibly reflect a temporal change of redox conditions, in which high oxides contents in sediments may lead to a subsequent increase of  $\text{PO}_4$  fixation (Sundby et al., 1992).

Table 5.2. Chemical parameters of surface sediments in Victoria Harbour (in mg/kg except TOC)

<b>Samples in October 2005</b>							
Location	TOC %	PO <sub>4</sub>	non-residual fraction*				
			Cu	Pb	Zn	Fe	Mn
B1a	0.70	11.2	14.5	22.0	27.0	4020	251
B1b	0.55	10.5	15.5	13.1	22.6	3770	216
B2a	1.39	11.8	88.8	27.0	70.3	4690	169
B2b	1.71	14.9	110	33.2	117	5900	250
B3a	1.84	12.8	97.4	32.9	125	5970	197
B3b	1.90	12.5	89.9	41.6	124	5260	151
B4a	1.28	20.2	16.1	13.9	44.9	6100	246
B4b	1.31	20.0	34.4	22.0	59.8	6200	289
B5a	0.98	16.0	16.0	26.1	44.2	5650	278
B5b	0.91	15.1	17.7	23.8	45.2	5790	268

<b>Samples in April 2006</b>							
Location	TOC %	PO <sub>4</sub>	non-residual fraction*				
			Cu	Pb	Zn	Fe	Mn
B1a	0.37	8.13	10.2	14.9	25.0	3920	222
B1b	0.44	7.76	11.4	13.5	24.7	3830	206
B2a	1.54	9.39	196	31.7	126	7030	279
B2b	1.85	8.17	152	33.3	127	7470	243
B3a	1.69	6.70	182	29.7	137	7530	267
B3b	1.94	6.81	195	32.1	152	7850	218
B4a	1.30	27.0	44.1	23.0	67.8	7110	329
B4b	1.25	20.2	41.1	25.4	65.2	6810	354
B5a	0.82	14.9	14.0	23.2	41.6	5470	231
B5b	0.91	16.4	12.2	19.8	43.8	6230	228

\*non-residual fraction is the addition of metal concentrations in step 1, step 2, step 3 and step 4 of the 5-step sequential extraction

## 5.2. Non-residual form of metals in sediments

Table 5.2 presents the concentrations of non-residual metals in harbour sediments.

Figures 5.1 and 5.2 illustrate the percentages of the five metal phases with respect to the total metal concentration in October and April sediments, respectively. The non-residual form is the addition of metals in the four operationally-defined phases including exchangeable, carbonates, reducible and oxidizable phases. These metals are not associated with the crystal lattice and could be released to the environment

when sediments are subjected to changing physical and chemical conditions, e.g. pH and redox potential (Förstner and Wittmann, 1981; Tessier and Campbell, 1987). Figures 5.1 and 5.2 show that Fe was mostly found in the residual fraction in harbour sediments, while the percentages of non-residual Fe contributed 30–43 % of the total Fe at all the sampling locations. Unlike Fe, Mn was predominantly found in the non-residual form in all the surface sediments, which accounted for 67–83 % of the total Mn, indicating a relatively high mobility of this metal. The non-residual forms of Cu and Zn in surface sediments varied among the sampling locations. The larger proportions were observed at B2 and B3, with an average contribution of 90 % for Cu and of 76 % for Zn. At B2 and B3, the concentrations of non-residual Cu ranged from 88.8 to 196 mg/kg, and Zn ranged from 70 to 152 mg/kg, indicating that these sites have been heavily contaminated with anthropogenic Cu and Zn. In contrast, a lower proportion of non-residual fraction was observed at B1 and B5 sediments (Cu: 47–77 %; Zn: 41–51 %), reflecting the less direct influence of pollution sources at the eastern and western parts of the harbour. Unlike Cu and Zn, the percentages of non-residual Pb were similar among the sampling locations, and a large proportion of Pb was found in the non-residual fraction, and ranged from 77–91 % of the total fraction. Most of the Pb in the harbour were mainly derived from anthropogenic sources, which was consistent with the low isotopic ratios of Pb revealed in the previous chapter.

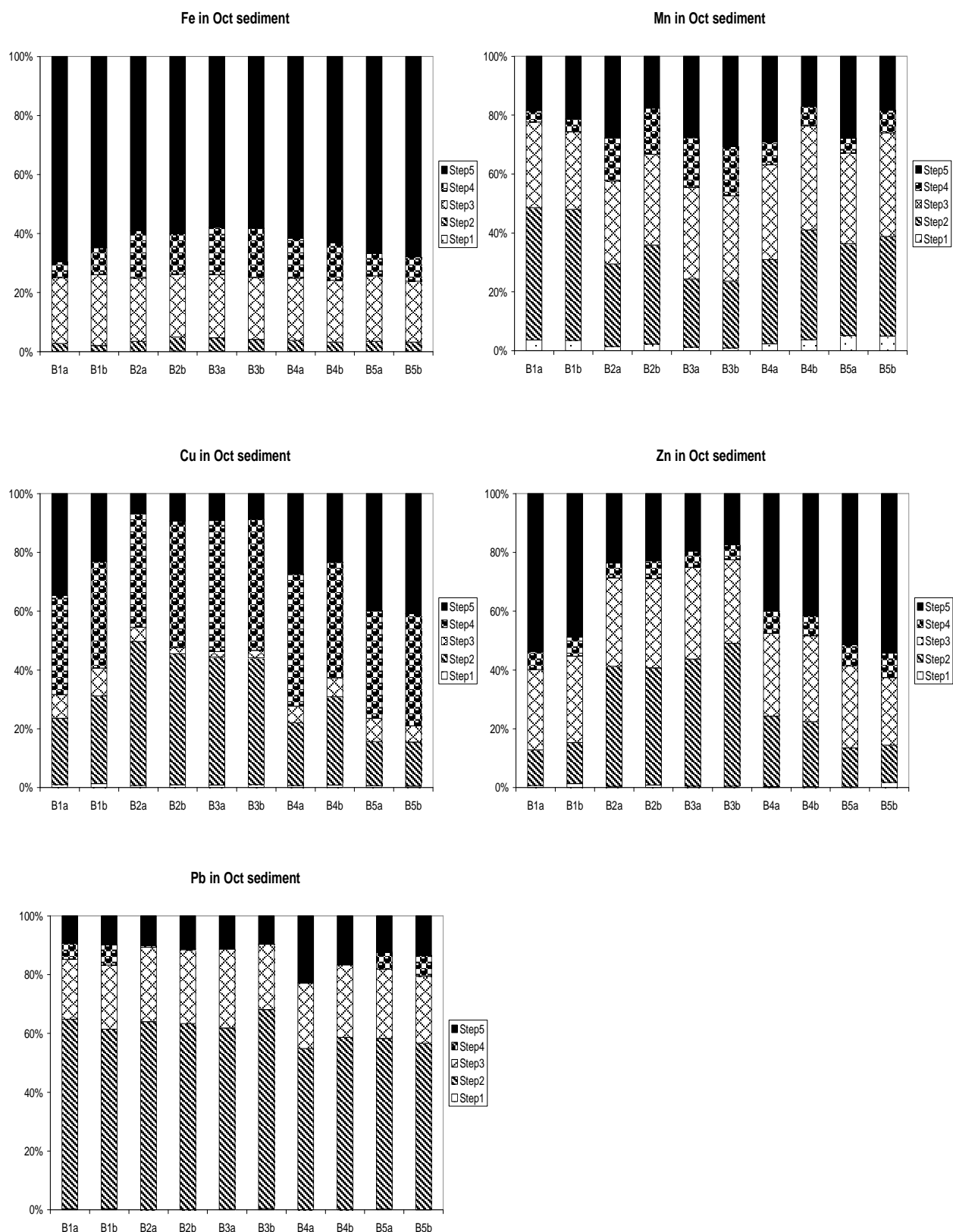


Figure 5.1. Relative percentages of metal speciation in surface sediments of Victoria Harbour collected in October 2005 (Step 1: exchangeable; Step 2: carbonate and adsorbed; Step 3: reducible; Step 4: oxidizable; Step 5: residual)

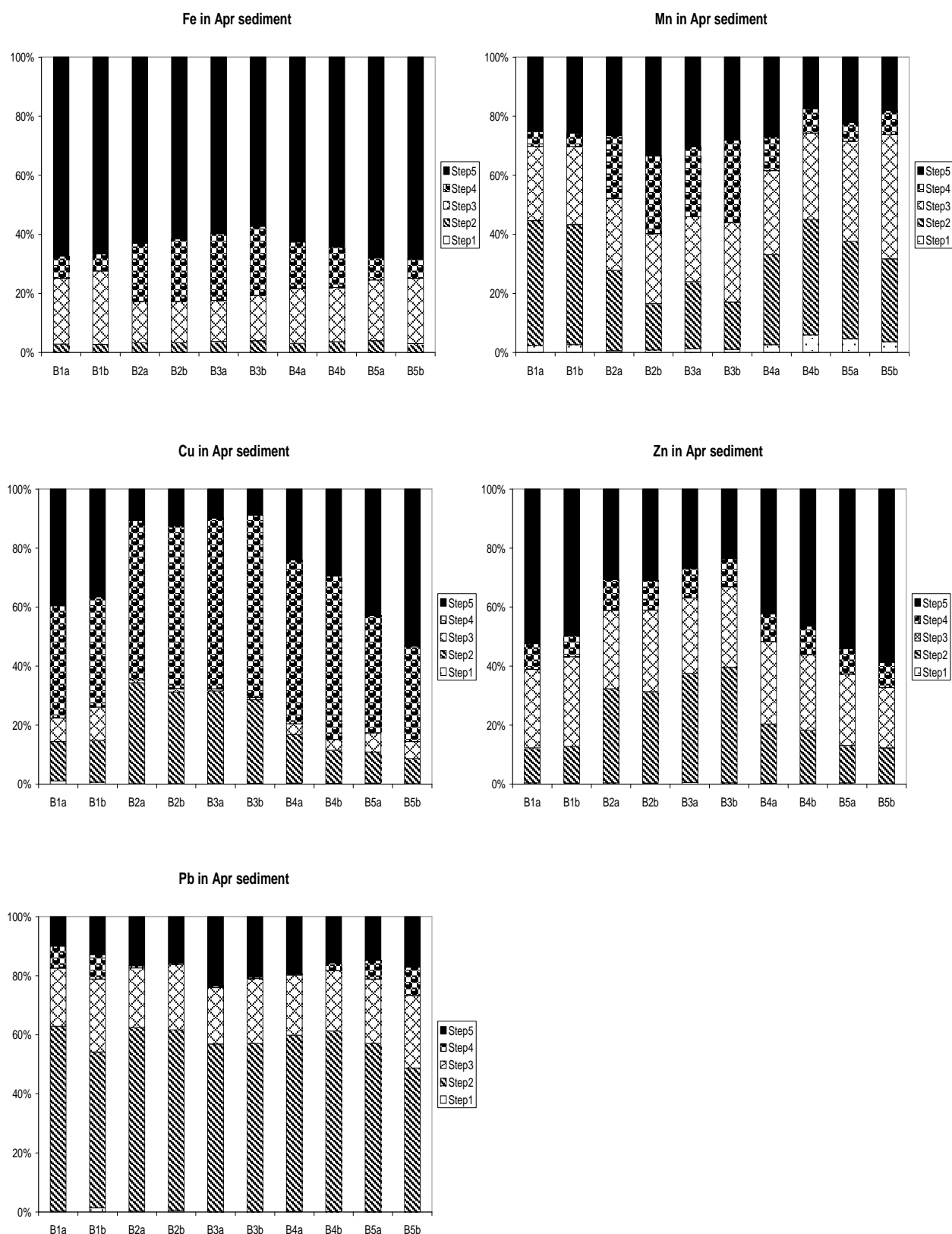


Figure 5.2. Relative percentages of metal speciation in surface sediments of Victoria Harbour collected in April 2006 (Step 1: exchangeable; Step 2: carbonate and adsorbed; Step 3: reducible; Step 4: oxidizable; Step 5: residual)

### **5.3. Cold HCl extraction of harbour sediments**

The spatial (B1 to B5) and temporal variations (October and April) of AVS and SEM in surface sediments are presented in Figure 5.3 and Table 5.3. The harbour sediments were characterized by a moderately high AVS, ranging from 3.7 to 66  $\mu\text{mol/g}$ , which was slightly less than the AVS found in coastal marine sediments, with a general amount of 20 to 90  $\mu\text{mol/g}$  (Leonard et al., 1993). There was a spatial heterogeneity of AVS in harbour sediments, and AVS was apparently higher at B2, B3 and B4. These sites are subjected to the major influence of sewage discharges, having the highest amounts of TOC in sediments. The enrichment of organic matter in sediments may give rise to an increased sulfate reduction associated with microbial degradation of metabolic organic carbon. Besides, the variation of sedimentation rate, biological and physical sediment mixing, and sulfate diffusion may also affect the spatial variation of AVS in sediments (Berner, 1978; Morse et al., 1987).

Of the two sampling periods, a significant difference of AVS was observed ( $p < 0.05$ ), in which sediments in April contained the highest amounts of AVS. The temporal dynamics of AVS is frequently reported in marine environments due to the varying productivity and microbial activity in different seasons (Jørgensen, 1977; Morse and Rickard, 2004; Van Griethuysen et al., 2006). Seasonal change of AVS is often associated with a substantial change in water temperature, typically occurring in

temperate regions (Leonard et al., 1993; Van den berg et al., 1999). In general, a considerable decline in sulfate reduction rate was observed in winter with temperatures of 5–10 °C and lead to a subsequent drop of AVS in sediments (Howard and Evans, 1993; Leonard et al., 1993; Panutrakul et al., 2001). In 2005, the temperature recorded in Victoria Harbour ranged from 17 °C to 27 °C, substantial fall in temperature was not observed as coastal waters in Hong Kong are warmed in winter by the Kuro Shio current (Morton and Wu, 1975). As a result, it is plausible to suggest that the significant change of AVS in October and April is unlikely affected by the seasonal change of microbial activity in sediments. Instead, AVS in sediments could be influenced by the dynamic hydrological conditions in Victoria Harbour. Periodic typhoons in Hong Kong can generate waves that disturb the seabed sediments and increase suspended sediment concentration (Parry, 2000). In addition, waves produced by the the northeast monsoon can also disturb seabed sediments. During October to December, low visibility in Hong Kong waters was observed due to the strong wind induced wave action of the northeast monsoon (Watts, 1973). On 21-28 September 2005, Hong Kong was affected by Typhoon Damrey and resulted in the raising of the strong wind signal number 3 (Hong Kong Observatory). The northeast monsoon in October 2005 may further enhance the wave action and possibly lead to the resuspension of sediments. Sediment resuspension may cause the mixing of oxygenated seawater with anoxic sediments and subsequent oxidization of reactive sulfides in sediments (Simpson et al., 1998).



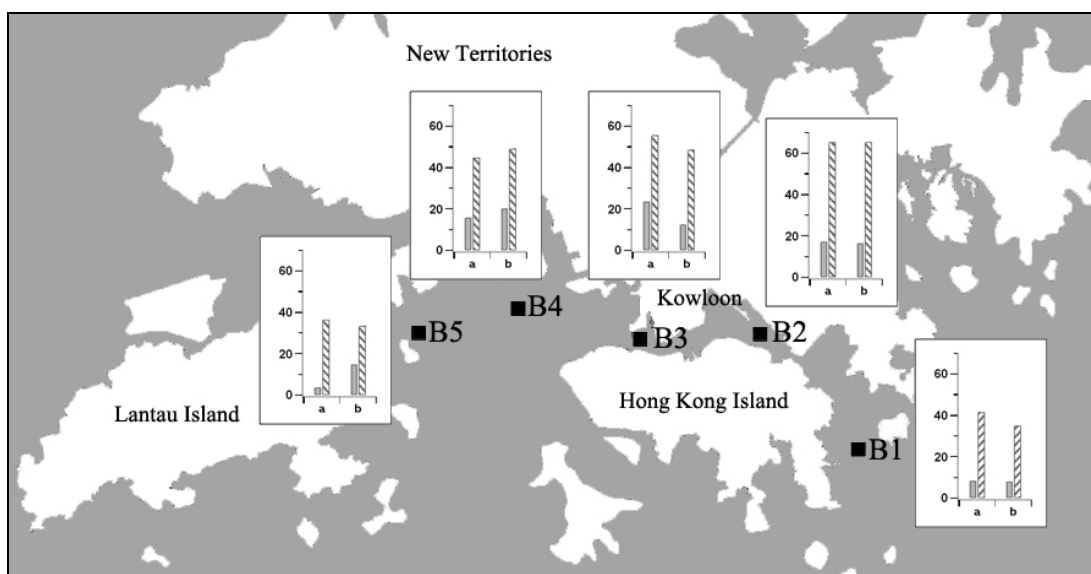


Figure 5.3. Spatial distribution of AVS ( $\mu\text{mol/g}$ , dry weight) in sediments of Victoria Harbour in October 2005 (filled bar) and April 2006 (bar with diagonal line)

Acid volatile sulfide is considered as a major sink of metals including Cd, Cu, Ni, Pb, Zn, Fe and Mn in anoxic sediments due to the low solubility of these metal sulfides (Morse, 1994). Metals extracted with the cold HCl are known as simultaneously extracted metals (SEMs) which are presumably bound with AVS in sediments (Di Toro et al., 1992). Table 5.3 presents the concentrations of SEMs (Cd, Cu, Ni, Pb, Zn, Fe and Mn) in harbour sediments of the two sampling periods. In general, sediments at B2 and B3 contained high amounts of SEM-Cu and SEM-Zn, and high amounts of SEM-Zn were also observed at B4 sediments. The concentrations of SEM-Pb were similar among the sampling locations, except B1 with a lower level. Comparing the two sampling periods, the relative contributions of the SEM to the total metal were more or less the same, except that of Zn and Mn which were substantially higher in April ( $p < 0.05$ ). This result implies that the increased AVS in

April sediments may lead to a subsequent change in the geochemical behaviour of Zn and Mn, resulting in a higher extractability of these metals with HCl.

When the SEM concentrations were compared with the amount of non-residual metals, Cu, Zn, Fe and Mn in SEM were generally lower than those in the non-residual fraction at B2 and B3 sediments at the two sampling periods (Figure 5.4). In contrast, these metals were comparable among SEM and non-residual fraction at B1, B4 and B5 sediments. For SEM-Pb, the amount was mostly similar to or higher than the non-residual fractions of Pb in harbour sediments (Figure 5.4). It seems that there is a spatial difference in geochemical conditions, such that the geochemical behaviour of metals at B2 and B3 vary from that at B1, B4 and B5. In general, most of the non-residual Cu, Zn, Pb, Fe and Mn at B1, B4 and B5 were extracted with 1 M HCl; however, at B2 and B3, a considerable fraction of these metals, except Pb, could not be extracted with 1 M HCl. Therefore, non-residual metals at B1, B4 and B5 were characterized by a high degree of HCl extractability, indicating the metal phases of amorphous sulfide, exchangeable, carbonate and amorphous oxides may be important (Cornwell and Morse, 1987; Haese et al., 1997). At B2 and B3, metals except Pb are most likely controlled by phases which are not readily dissolved in 1 M HCl, such as organic matter, pyrite and crystalline oxides. Lead, which was different from other metals, did not show any spatial variation in geochemical

partitioning, and most of the Pb were associated with the phases that were soluble in 1 M HCl.

Table 5.3. Concentrations of AVS and SEM in surface sediments of Victoria Harbour collected in October 2005 and April 2006

<b>Samples in October 2005</b>										
Location	AVS ( $\mu\text{mol/g}$ , in dry weight)	$\Sigma\text{SEM}^a$ ( $\mu\text{mol/g}$ )	$\Sigma\text{SEM}-\text{AVS}$	SEM(mg/kg)						
				Cd	Cu	Ni	Pb	Zn	Fe	Mn
B1a	8.37	0.528	-7.84	n.d.	9.40	1.14	17.1	18.2	3092	217
B1b	8.03	0.549	-7.48	n.d.	10.5	1.15	14.2	19.3	3070	182
B2a	17.1	0.736	-16.3	0.045	14.7	0.52	14.3	27.9	1773	78
B2b	16.5	1.62	-14.9	0.183	24.3	1.30	27.7	70.7	3425	140
B3a	23.6	1.29	-22.3	0.106	22.9	1.03	16.5	54.7	2357	82
B3b	12.4	1.41	-11.0	0.162	29.4	1.28	22.1	53.5	3285	124
B4a	15.8	0.969	-14.8	n.d.	11.6	1.25	20.9	43.5	6967	233
B4b	20.2	1.16	-19.0	n.d.	19.4	1.73	24.2	46.0	5367	249
B5a	3.70	0.796	-2.90	n.d.	10.6	1.45	23.4	32.2	5334	232
B5b	14.8	0.697	-14.1	n.d.	7.03	1.68	22.8	29.3	6103	230
<b>Samples in April 2006</b>										
Location	AVS ( $\mu\text{mol/g}$ , in dry weight)	$\Sigma\text{SEM}^a$ ( $\mu\text{mol/g}$ )	$\Sigma\text{SEM}-\text{AVS}$	SEM(mg/kg)						
				Cd	Cu	Ni	Pb	Zn	Fe	Mn
B1a	41.7	0.540	-41.1	n.d.	8.21	1.35	15.6	20.5	3301	208
B1b	35.1	0.609	-34.5	n.d.	9.35	1.37	16.5	23.5	3420	237
B2a	65.5	2.06	-63.4	0.155	50.2	2.10	30.1	71.2	4541	203
B2b	65.4	2.46	-62.9	0.219	59.5	2.33	34.3	85.8	5154	158
B3a	55.6	2.46	-53.1	0.261	57.7	2.20	30.4	89.5	4685	177
B3b	48.6	2.31	-46.3	0.230	40.4	2.14	31.2	97.0	4926	106
B4a	45.0	1.45	-43.6	0.061	22.0	2.32	24.6	61.5	6921	338
B4b	49.2	1.52	-47.7	0.037	24.8	2.55	28.7	62.0	6350	320
B5a	36.4	1.01	-35.4	n.d.	11.2	2.17	31.1	42.3	5071	274
B5b	33.6	0.892	-32.7	n.d.	11.0	2.31	24.1	36.9	5409	219

<sup>a</sup> $\Sigma\text{SEM} = \text{SEM-Cd} + \text{SEM-Cu} + \text{SEM-Pb} + \text{SEM-Ni} + \text{SEM-Zn}$

<sup>b</sup>n.d. not detected

Besides, the higher amount of SEM-Pb than the non-residual Pb could be probably due to the release of some residual Pb during the cold acid extraction. This has also been reported by Van den Berg et al. (2001) and Fang et al. (2005). The major binding phases of metals in harbour sediments will be discussed in the next section with the sequential extraction results.

According to the model suggested by Di Toro et al. (1992), if the molar sum of SEM ( $\Sigma$ SEM), including Cd, Cu, Ni, Pb and Zn, is less than the molar AVS, there will be less free ion accumulating in porewater causing toxicity. The differences between  $\Sigma$ SEM and AVS in harbour sediments are shown in Table 5.3 and all the sediments displayed a negative value in  $\Sigma$ SEM–AVS. This may probably demonstrate that the ability of sediment to trap trace metals as monosulfides is far from exhaustion. Thus, trace metal removal from porewater can be maintained through the formation of metal sulfides, which reduces the potential of metal toxicity in sediments. Besides, the two sampling periods showed a substantial difference of  $\Sigma$ SEM–AVS, in which AVS was considerably greater than the  $\Sigma$ SEM in April sediments (Table 5.3). Nevertheless, the presence of an excessive amount of AVS over  $\Sigma$ SEM does not necessarily imply that a lower risk of metal enrichment in harbour sediments. In fact, SEMs extracted with HCl may include other forms of metals that can be available to organisms such as the carbonate/specifically adsorbed phase.

Recently, Cooper and Morse (1998) proposed a more reliable environmental impact prediction of trace metals on the basis of AVS and reactive-Fe (extracted by 1 M HCl). According to these authors, if the percentage of AVS/reactive-Fe is greater than 20, the supply of reactive sulfide exceeds the supply of reactive oxidants, such as oxygen, aqueous  $\text{Fe}^{3+}$  and metastable solid-phase  $\text{Fe}^{3+}$ . Under such condition, sulfide could be considered as an effective sink for trace metals in anoxic sediments. In Victoria Harbour, the percentages of AVS/reactive-Fe in sediments displayed a substantial difference in the two sampling periods. In general, the percentages of AVS/reactive-Fe in April sediments were greater than 20, while less than 20 were observed in most of the October sediments. Based on the AVS/reactive-Fe, it can be concluded that the sediments in October are relatively dynamic with respect to the trace metal binding by AVS. As a consequence, the amount of AVS may exhibit substantial variations in October, and the association of trace metals with sulfide may change considerably in sediments.

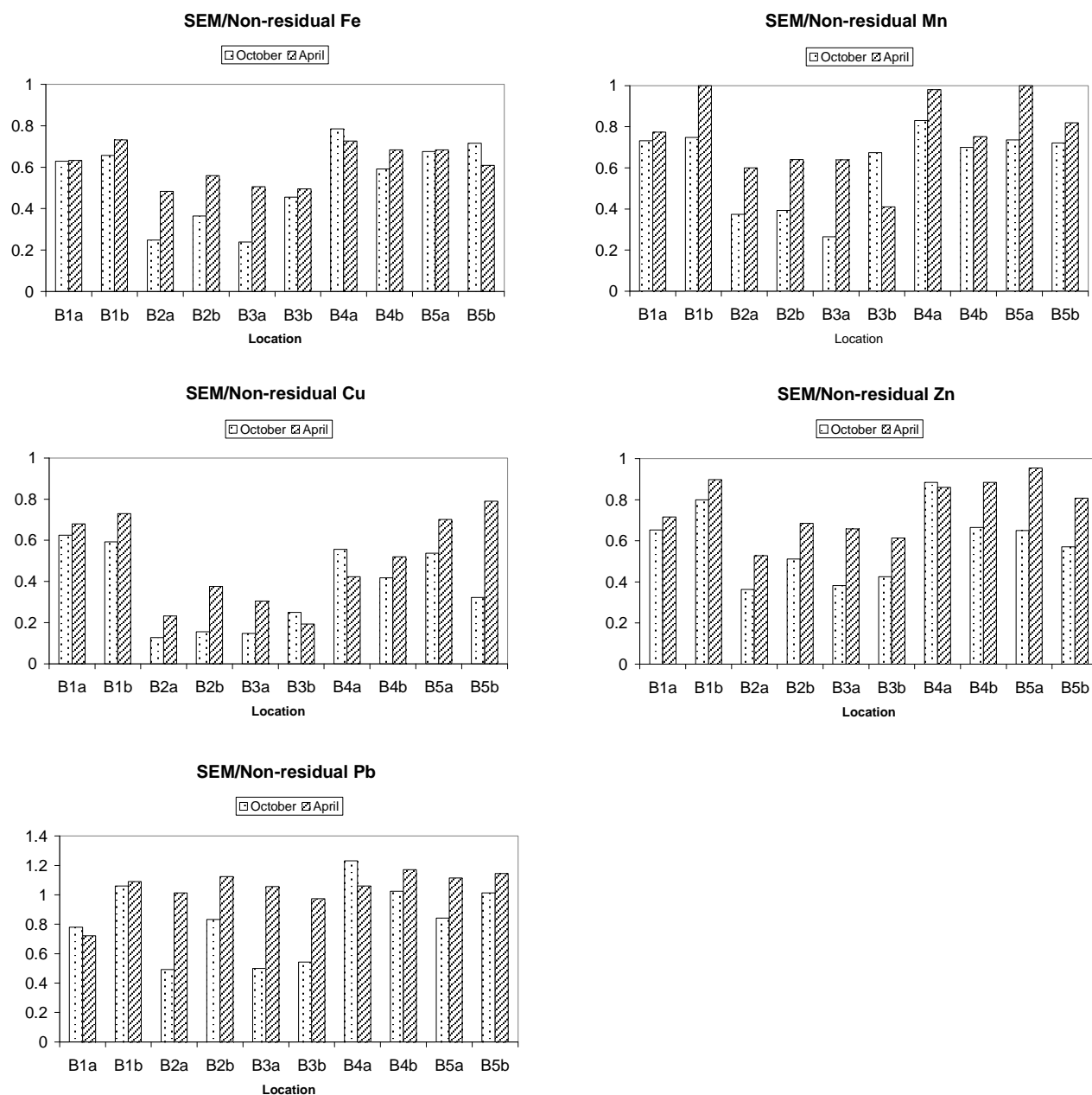


Figure 5.4. Ratios of SEM to non-residual metals in surface sediments of Victoria Harbour collected in October 2005 and April 2006

#### **5.4. Five-step sequential extraction of harbour sediments**

To examine the major binding phases of non-residual metals in anoxic harbour sediments, a modified 5-step Tessier's sequential extraction was attempted to complement the HCl extraction. Figures 5.1 and 5.2 illustrate the relative percentages of metals in the five extraction phases, including exchangeable, carbonate, reducible, oxidizable and residual phases, in sediments collected in October and April, respectively.

Iron and manganese are sensitive to the redox change, which may act as a tool to investigate redox cycling of trace metals in marine sediments (Turner, 2000). The redox cycling in harbour sediments was first examined based on the geochemical behaviour of Fe and Mn, in order to facilitate the study of Cu, Pb and Zn speciation in sediments. Sequential extraction results showed that the non-residual fraction Fe was principally associated with the reducible phase in sediments, with about 20 % of the total Fe (Figures 5.1 and 5.2). For sediments at B1, B4 and B5, no significant change of Fe partitioning was observed between the two sampling periods. At B2 and B3, sediments were subjected to major changes of Fe in reducible and oxidizable phases between the two sampling periods ( $p < 0.05$ ). The sediments are generally characterized by higher reducible Fe and lesser oxidizable Fe in October. Given a strong correlation of oxidizable Fe with AVS, Fe could possibly be present as sulfide minerals in sediments. This is further supported by the Mössbauer study



carried out by Tanner et al. (2000), which provided direct evidence of the presence of Fe(II) in harbour sediments. Consequently, sediments at B2 and B3 may be subjected to redox change with the oxidation of FeS minerals and increased precipitation of Fe as oxides in October. This is in consistent with the AVS change in the two sampling periods as discussed previously.

For Mn, carbonate and reducible were the major binding phases among the non-residual fraction, with about 31 % and 30 % of the total Mn, respectively (Figure 5.1 and 5.2). Similar to Fe, there was a substantial change of Mn partitioning in sediments at B2 and B3 in the two sampling periods. Such change occurred in the oxidizable phase of Mn and the proportion of this phase in sediments was reduced in October. As a strong correlation of oxidizable Mn and AVS was also observed, the decrease of oxidizable Mn could possibly be attributable to the oxidation of MnS in sediments. In contrast, there was no major change of phases at B1, B4 and B5 in the two sampling periods.

Metal oxides are considered as a major sink of  $\text{PO}_4$  in oxidized surface sediments (Sundby et al., 1992; Slomp et al., 1996). In Victoria Harbour, a strong correlation of reducible Fe and Mn with  $\text{PO}_4$  was observed in sediments. Indeed, higher amounts of  $\text{PO}_4$  at B2 and B3 in October were accompanied by increased fractions of reducible Fe and Mn. An increased scavenging of  $\text{PO}_4$  in sediments thus further support the

occurrence of less reducing conditions characterized by increased amounts of Fe/Mn oxyhydroxides in October.

Overall, there was an apparent change of geochemical conditions in harbour sediments among different sampling locations as well as sampling periods. At B2 and B3, sediments were probably subject to a considerable change in Fe and Mn partitioning in October and April. The April sediments were characterized by highly reducing conditions, with increased Fe and Mn associated with organic/sulfide phases. Less reducing conditions were demonstrated in October sediments and Fe/Mn oxyhydroxides become a more important binding phase. This could probably pose a major influence on the geochemical cycling of trace metals in sediments, as trace metal partitioning is governed by the precipitation condition of Fe and Mn in sediments (Tessier et al., 1979; Tessier and Campbell, 1987; Caplat et al., 2005). Given the reduced amounts of AVS, increased  $\text{PO}_4$  and decreased proportions of Fe/Mn oxidizable phases in October sediments at B2 and B3, it is more plausible to suggest that resuspension of anoxic sediments occurs and results in Fe and Mn remobilization. The substantial change of Fe and Mn partitioning after anoxic sediments resuspension has been observed in several studies (James and Chen, 1977; Calmano et al., 1993; Simpson et al., 1998; Saulnier and Mucci, 2000; Zoumis et al., 2001). Saulnier and Mucci (2000) indicated that the remobilization of Fe was associated with the oxidation of AVS in anoxic sediments, and Mn was mainly

controlled by the dissolution of solid phases other than AVS, such as the Mn carbonate. Following their release to the solution, Fe and Mn were precipitated as Fe and Mn oxyhydroxides in sediments.

Copper in harbour sediments was predominantly extracted in the oxidizable (32–62 %) and to a lesser extent in carbonate fractions (9–49 %). This result was different from those reported by Lam et al. (1997). They showed that about 90 % of Cu was recovered in the oxidizable phase, while the carbonate phase was negligible in harbour sediments. The higher proportion of carbonate Cu observed in the present study is most likely due to the oxidation of sediments during the pretreatment and extraction processes. The present study was conducted in air, but the previous one was performed under a nitrogen atmosphere. Therefore, oxidation of samples might occur and lead to a change in the Cu phases from sulfide to carbonate in the present study. Besides, the amount of oxidizable Cu extracted by Lam et al. (1997) was 25–302 mg/kg which was significantly higher than the present study (6.4–132 mg/kg). The different amounts of Cu extracted could be attributed to the use of smaller grain size (<63  $\mu\text{m}$  fraction) in the previous study or/and the reduction of Cu input in recent years.

The comparison of the oxidizable phase with the SEM fraction revealed that nearly all the oxidizable Cu was extracted using 1 M HCl at B1, B4 and B5, indicating Cu

was almost completely bound in reactive phases in sediments (Figure 5.5). However, only 30 to 70 % of oxidizable Cu was recovered with HCl at B2 and B3 sediments. The presence of organic matter-Cu complex, CuS and Cu<sub>2</sub>S in sediments may account for the low extractability with HCl (Allen et al., 1993; Parkman et al., 1996; Cooper and Morse, 1998; Simpson et al., 1998). For instance, Cooper and Morse (1998) showed that only 12 % of CuS and 18 % of Cu<sub>2</sub>S were recovered by the HCl extraction. In Victoria Harbour, strong correlations of oxidizable Cu with TOC and AVS may provide an indication of Cu binding in sulfides as well as organic matters in sediments. The relative importance of organic matter and sulfide to the Cu partitioning were examined by regression analysis. The coefficients of the regression equation reflect the dominant control of organic matter on oxidizable Cu. The predominant association of Cu with organic matter in sediments has been reported by numerous studies (Tessier et al., 1979; González et al., 1994; Ramos et al., 1999; Turner, 2000; Caplat et al., 2005) and is supported by a high stability constant of the complexation of Cu with organic matter in sediments.

Of the two sampling periods, a significant difference in carbonate Cu was observed at all sampling locations ( $p < 0.05$ ), in which the proportion of Cu in carbonate phase was relatively higher in October sediments. Besides, there was a significant variation in the oxidizable phase of Cu at B2 and B3 in October and April sediments ( $p < 0.05$ ), and the latter contained a higher percentage of the oxidizable Cu. Such major change

of Cu in the oxidizable phase was unlikely due to the changes of organic matter in sediments, as there was no major difference of TOC in October and April. Instead, sulfide could be the major factor controlling the change of Cu partitioning in the two sampling periods. As previously discussed, sediments in April contained higher amounts of AVS and this may lead to a consequence of higher oxidizable Cu in April sediments. In October, with the resuspension of sediments, oxidation of sulfide may follow the release of Cu to the carbonate phase instead of oxides in harbour sediments.

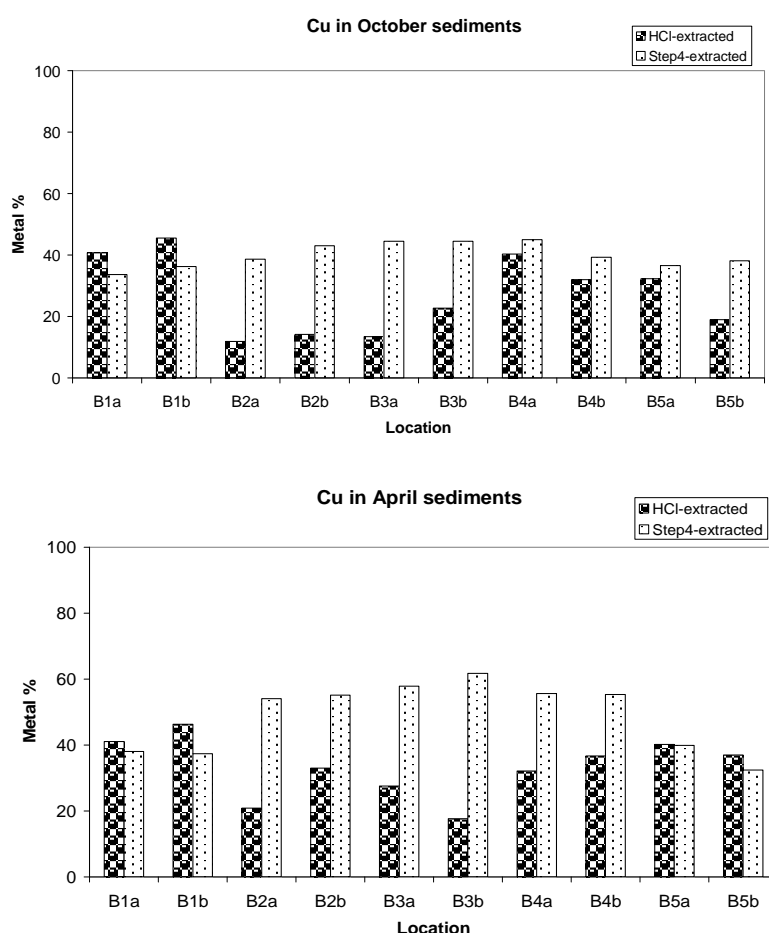


Figure 5.5. Comparison of the % oxidizable Cu with the % HCl-extracted Cu in surface sediments of Victoria Harbour

In case of Zn, the metal was predominantly bound in carbonate and reducible fractions, ranging from 24 to 27 %, in harbour sediments. The contribution of oxidizable Zn was less significant, with about 7.8 % of the total Zn. There was a strong correlation of both TOC and AVS with the oxidizable Zn, suggesting the possible association of Zn with organic matters as well as sulfides in the harbour sediments. The regression analysis showed that AVS was the dominant phase controlling the oxidizable Zn in sediments. This is in concordance with the study conducted by Peltier et al. (2005) that the sulfide phase contributes substantially to the Zn speciation in anoxic sediments.

When the oxidizable Zn was compared with the SEM-Zn, it was demonstrated that the latter was much higher. The small proportions of oxidizable Zn could be explained by the early dissolution of amorphous ZnS prior to step 4 extraction during the sequential extraction. The early dissolution of ZnS was caused by the use of hydroxylamine hydrochloride reagent in the reduction of iron and manganese oxides, and this may cause the underestimation of ZnS in the sequential extraction (Peltier et al., 2005). Besides, the oxidation of ZnS may occur during the sample pretreatment and this may lead to a high recovery of Zn in the carbonate phase and a low recovery of Zn in the sulfide phase (Parkman et al., 1996; Billon et al., 2001). Therefore, the reducible and carbonate fractions of Zn could be overestimated, while ZnS could be underestimated in the present study.

Of the two sampling periods, there were higher carbonate and reducible fractions of Zn in October sediments, while a higher oxidizable fraction was observed in April sediments. Such changes were apparent at B2 and B3 sediments, which were characterized by a highly dynamic condition. The difference in Zn speciation between the two sampling periods could be explained by the change of Fe and Mn partitioning as a result of the resuspension and oxidation of surface sediments. Calmano et al. (1993) and Förstner et al. (1989) demonstrated that the aeration of anoxic sediments caused the release of Zn from sulfide phase and a subsequent scavenging of Zn through the adsorption or coprecipitation of solid carbonate and oxides phases. In Victoria Harbour, the reduced AVS and increased Fe/Mn oxyhydroxide as a result of the sediment resuspension and oxidation in October could probably lead to an increased partitioning of Zn in oxides as well as carbonate phases. The significant reduction of SEM-Zn observed in October could further provide evidence of the oxidation of ZnS as a result of the sediment resuspension and oxidation.

Lead in harbour sediments was almost exclusively extracted in the carbonate fraction (59 %), and behaved very differently from Cu and Zn in the extraction procedure. Unlike Cu and Zn, there was no major difference of Pb partitioning in October and April sediments. The predominant phase of Pb as carbonate in anoxic sediments has been reported by O'Day et al. (2000) using X-ray absorption spectroscopy (XAS).

They indicated that most of the Pb was coordinated with oxygen in sediments, which may be presence as the carbonate phase or sorbed as an oxygen-ligated surface complex. These metal phases were easily dissolved in strong acid and resulted in the highest amounts of Pb as SEM during the cold HCl extraction (O'Day et al., 2000). Similar findings were observed in the present study, in which nearly all the non-residual Pb in harbour sediments was recovered with the HCl extraction. This may probably indicate the dominant association of Pb as carbonate in harbour sediments. Consequently, Pb remains stable during the resuspension of sediment to oxygenated seawater and exhibits little change in phases as revealed by sediments from the two sampling periods. Among the sampling locations, a significant difference of Pb in the oxidizable phase was demonstrated, in which sediments at B2, B3 and B4 had lower percentages of oxidizable Pb. A strong negative correlation was displayed between oxidizable Pb and TOC ( $p < 0.05$ ), suggesting locations with lower oxidizable Pb could be attributed to increased amounts of organic matter in sediments.

#### **5.5. Environmental implications of metal enrichment in harbour sediments**

Sediments at B2 and B3 contained considerable amounts of non-residual Zn and Cu, ranging from 89 to 196 mg/kg for Cu and from 70 to 152 mg/kg for Zn. The level of non-residual Cu exceeds the Lower Chemical Exceedance Level (LCEL) for sediment quality assessment in Hong Kong. This could probably pose serious



environmental hazards as all these metals could be mobilized and released to the environment under changing physical condition. The dilute HCl (0.5–6 M) extraction has been frequently used to assess the trace metal availability to organisms (Jamil et al., 1999; McCready et al., 2003; Shulkin et al., 2003). In Victoria Harbour, the degrees of Cu and Zn extractability with HCl varied among the sampling locations. At B1, B4 and B5, relatively high proportions of non-residual Cu and Zn were dissolved in HCl, indicating the high mobility or bioavailability of these metals in sediments. At B2 and B3, despite a substantial enrichment of Cu and Zn, the degrees of metals extractability with HCl were relatively low, suggesting Cu and Zn may not be easily mobilized at these sites. Nevertheless, the amounts of Cu and Zn extracted with HCl at B2 and B3 sediments were the highest, with 14.7–59.5 mg/kg for Cu and 27.9–97.0 mg/kg for Zn. The sequential extraction revealed that Cu was predominantly associated with organic matter, carbonate and to a lesser extent sulfide phases in harbour sediments. In the case of Zn, a high percentage of metal was associated with carbonate, Fe/Mn oxides and possibly sulfide phases.

The enrichment of Pb was comparatively less than those of Cu and Zn in the harbour, with an average concentration of 25 mg/kg in the non-residual fraction. However, most of the non-residual Pb were found in carbonate phase which is the most labile form of trace metals in sediments. Based on the increasing strength of reagents used in the sequential extraction, the bioavailability of metals in sediments is assumed to

decrease in the order of the extraction sequence (Tessier and Campbell, 1987). Therefore, the bioavailability order of the metals studies was  $Pb > Zn > Cu$ , while greater risk of environmental hazards was observed in sediments from the central part of the harbour containing the highest amounts of non-residual and HCl extracted metals.

The AVS and  $\Sigma SEM$  results demonstrated that potential toxicity of metals in harbour sediments was low due to the presence of high amounts of AVS. However, AVS in surface sediments was found to be highly dynamic and varied spatially and temporally. The resuspension of the poorly consolidated mud is likely lead to metals release from sediments to the water column as a result of sulfide oxidation, particularly in the central part of the harbour (B2 and B3). At B2 and B3, the mobility/ bioavailability of Cu and Zn in sediments is strongly dependent on redox conditions. The oxidation of surface sediments was found to increase the partitioning of Cu and Zn in the carbonate phase and this may enhance the availability of metals to the organisms. When sediments are subjected to disturbances such as dredging or storm events, Zn and Cu would pose the greatest hazards to biota as these metals sulfides are unstable and will dissolve in the overlying oxygenated seawater. It is thus important to realize that AVS in sediments is highly dynamic and should not be considered as a permanent sink of metals (Van den Berg et al., 1999; Morse and Rickard, 2004).

In addition, O'Day et al. (2000) suggested that the prediction of metal toxicity based on AVS and  $\Sigma$ SEM analyses in anoxic sediments was not substantiated for all metals and was valid only for Cd and to some extent for Zn. Metals including Pb could be present as carbonate or oxides in anoxic sediments (O'Day et al., 2000). In the present study, Pb and Cu were predominantly associated with carbonate and organic matter in harbour sediments, respectively. As a result, the toxicity of Pb could be underestimated and that of Cu could be overestimated based on the AVS and  $\Sigma$ SEM analyses.

#### **5.6. Biological uptake of trace metals in harbour sediments**

To gain a better insight on the effect of metal enrichment in harbour sediments on living organisms, a preliminary study on the benthic community in Victoria Harbour and metal bioaccumulation in a deposit feeder was conducted. According to the benthic surveys during the two sampling periods, the harbour was dominated by polychaete species (Shin, per. comm.). Many polychaetes are opportunistic infauna that is commonly found in organic enriched habitats and they are indicators of polluted environments (Pearson and Rosenberg, 1978; Reish and LeMay, 1991). The dominant species varied among the sampling locations and some of the species may act as indicators of particular environmental stressors. At B2 and B3, sediments were dominated by the polychaete, *Sigambra hanaokai* (Shin, per. comm.). This species was considered as a tolerant bioindicator of anthropogenic stress (Rakocinski et al.,

1997) and has been reported in sediments with low oxygen levels (Nichols Driscoll, 1976). Thus, the presence of this species could probably reveal the stress of anoxic conditions as well as increasing amounts of hydrogen sulfide and metals in the sediments at B2 and B3. The polychaete, *Lumbrineris* sp. was found at B1, B4 and B5, but was absent at B2 and B3 (Shin, per. comm.). This species was suggested as a non-tolerant species and sensitive to copper polluted sediments (Rygg, 1985). As a consequence, the enrichment of Cu at B2 and B3 could probably pose hazards to the benthic community, and such impact was also observed by Olsgard (1999) and Rygg (1985).

Moreover, a preliminary laboratory bioassay of harbour sediments has demonstrated a high Cu availability in sediments of the central part of the harbour. Figure 5.6 illustrates the metal burden in the deposit feeder, *Capitella* sp.I, after 10-day exposure to surface sediments collected at B1, B3 and B5. The Cu accumulated by *Capitella* sp.I from B3 sediment was 4 times greater than that from B1 and B5 sediments. The high amount of Cu in the carbonate phase in B3 sediments was probably responsible for elevated metal uptake by the worms. After the bioassay, it was also observed that the worms exposed to B3 sediments showed body shrinkage. Nevertheless, toxicity of Cu enrichment in harbour sediments may need further investigations. In case of Pb and Zn, no significant difference of metal burden in worms exposed to sediments was observed ( $p>0.05$ ).

### Metal accumulation in *Capitella* sp.

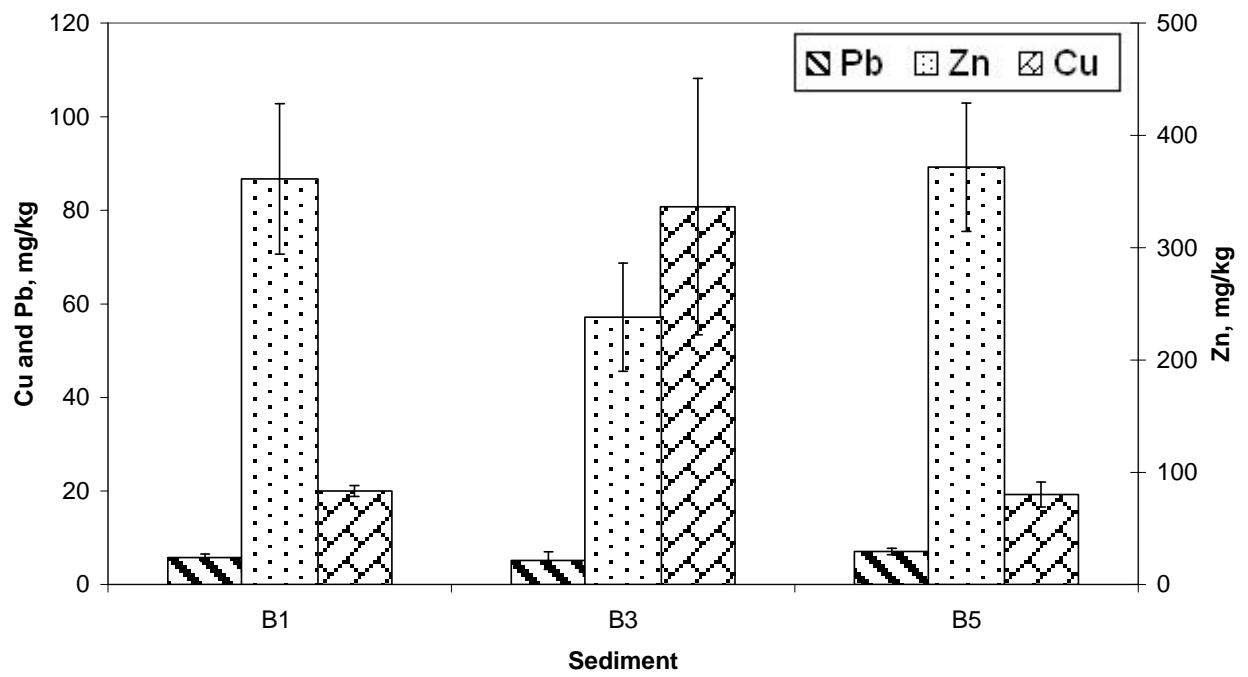


Figure 5.6. Metal concentrations in *Capitella* sp.I exposed to B1, B3 and B5 surface sediments collected in October 2005 (n=3)

## Chapter 6 Conclusions and Recommendations

### 6.1. Conclusions

- 1) Trace metals concentration varied spatially and temporally in Victoria Harbour.

The central part of the harbour was found to be the most contaminated area. Maximum concentrations of Cu, Pb and Zn were found to be 280, 85 and 221 mg/kg, respectively. In contrast, the eastern part of the harbour was less affected by anthropogenic contamination, with metal concentrations in sediments close to the baseline values in Hong Kong. The spatial heterogeneity of metal concentrations was most likely due to the influence of urban and industrial activities and hydrodynamic condition in Victoria Harbour.

- 2) Temporal variability of metal contamination as a result of historical human activities was observed in a  $^{210}\text{Pb}$  dated sediment core. Considerably high concentrations of Cu and Zn were observed in subsurface sediments, corresponding to the 1960s with rapid urban and industrial developments in the territory. Significant reduction of Cu and Zn contamination was apparent from the 1980s, reflecting the decrease of industrial activities and the improvement of water quality in the territory. Compared with the peak concentrations in subsurface sediments, it was estimated that Cu and Zn were reduced by 76 % and 59 %, respectively, in recent sediments. However, the concentrations of these

metals in the surface layers were still elevated with respect to the baseline values, indicating that metal source(s) may still exist in the harbour.

- 3) The temporal change of Pb was slightly different from that of Cu and Zn. A sudden rise of Pb occurred during the periods of 1970 to 1982. The use of leaded petrol could probably be the potential key source of Pb in the harbour. Subsequent reduction of leaded petrol since the early 1980s was most likely lead to a decrease of Pb in harbour sediments. The presence of anthropogenic Pb sources in Victoria Harbour was supported by the low  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios measured in harbour sediments compared to natural Pb. Pb isotopic signatures further revealed that elevated Pb in the harbour could be associated with mixed anthropogenic sources, e.g. gasoline Pb, industrial and ship repairing activities.
- 4) In Victoria Harbour, spatial and temporal differences in geochemical behaviour of trace metals were also observed in surface sediments. The harbour sediments contained a moderately high amount of AVS, ranging from 3.7 to 66  $\mu\text{mol/g}$ , and the highest amounts were found in the central part of the harbour. The chemical extraction results indicated that Cu was predominantly bound in organic matter, carbonate/specifically adsorbed and to a lesser extent sulfide phases; Zn was mainly associated with carbonate/specifically adsorbed, oxide and possibly

sulfide phases, while Pb was almost exclusively associated with carbonate/specifically adsorbed phase in harbour sediments.

- 5) In the central part of the harbour, surface sediments are highly dynamic and geochemical changes of metals were observed in the sediments collected in October and April. In October, sediments were characterized by less reducing conditions as revealed by the reduction of AVS, increased Fe/Mn oxide fractions and increased  $\text{PO}_4$ . This led to a subsequent change of trace metal partitioning in sediments. There was a reduction of Cu and Zn in organic/sulfide phases, while increased Cu and Zn in carbonate and oxide phases, respectively. Unlike Cu and Zn, no significant change of Pb partitioning was found in the two sampling periods, probably due to the association of Pb with the stable carbonate phase.
- 6) Based on the study of metal partitioning in harbour sediments, the bioavailability order of the metals studied was  $\text{Pb} > \text{Zn} > \text{Cu}$ . Sediments that could pose the greatest risk of environmental hazards was identified at the central part of the harbour. Sediments in the central harbour contained the highest amounts of non-residual and HCl-extracted metals and most importantly the sediments could be subjected to redox change and released Cu and Zn to the water column. The change of redox conditions were verified in sediments collected in October and April. The high bioavailability of Cu in the central harbour was further



substantiated by the absence of Cu-sensitive polychaete species, *Lumbrineris* sp. at this site. Metal accumulation test using the deposit feeder, *Capitella* sp. I also indicated the presence of high amounts of available Cu in sediments of the central harbour.

## **6.2. Recommendations**

With respect to trace metal contamination of sediments in Victoria Harbour, some recommendations are made as follows:

- 1) Sediment dredging and disturbance should be avoided in the harbour, as the physiochemical properties of sediments will be subject to rapid change under the exposure of anoxic sediments to the oxic environment. Besides, sediment disturbance would lead to the mixing of heavily contaminated subsurface sediments with less contaminated surface sediments, thus increasing the potential hazard of metals to the environment.
- 2) The disposal of the dredged harbour sediments should be considered carefully in order to avoid potential leaching of metals to the environment.
- 3) Sewage and urban runoff should be treated to remove metals before discharging to the harbour.

### 6.3. Future Research

- 1) In order to have a clear understanding of the biogeochemical cycling of trace metals in harbour sediments, the chemical properties of porewater in the sediment core should be investigated. Porewater is generally more sensitive to environmental changes (Adams, 1994; van den Berg et al., 1999), which can serve as useful indicators of a slight change of metal partitioning in the solid phase. In porewater, anions such as  $\text{S}^{2-}$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , and dissolved trace metals as well as metal ligands should be analyzed in order to study the major environmental factors controlling the metal partitioning in harbour sediments. The changes of metal phases along the core could be identified, thus the potential release of metals from core sediments to the overlying water or porewater could be assessed.
  
- 2) AVS is highly dynamic in the marine environment and it may show a significant variation along the sediment core. Regarding to the spatial heterogeneity of AVS, more sampling locations should be included to provide a more general view on the degree of spatial variation in AVS throughout the harbour. In this study, temporal change of AVS was also observed and it was possibly due to the wave generated by the periodic typhoon. To elucidate the effect of periodic typhoon on harbour sediments, samples should be collected during July and September which is the peak

typhoon period in Hong Kong. Besides, pyrite is a major pool of sulfide in sediments and plays an important role in the metal partitioning in anoxic sediments. Further study on pyrite in harbour sediments could probably provide a more clear understanding on how the cycle of sulfur controls metal behaviours in sediments.

- 3) Chronic toxicity tests should be conducted in order to evaluate the toxicity of long-term metal exposure in harbour sediments. Victoria Harbour is moderately contaminated with metals, and metal concentrations may not be high enough to induce acute toxic effect in organisms. Therefore, chronic toxicity tests are recommended to assess long-term ecological and health impacts of metal enrichment in harbour sediments. The clam, *Ruditapes philippinarum*, can be used in the chronic toxicity test. It is an indigenous species, can adapt well in a wide range of sediment with different grain size and sensitive to metal pollutants in sediments (Cheung and Wong, 1993; Fan and Wang, 2001; Shin et al., 2002). Sublethal effects including the energy reserve, the lipid peroxidation and the induction of metallothionein can be used to identify potential metal toxicity in the clam.
- 4) The study of metal partitioning and potential hazards of metals should not be solely based on a single chemical extraction method. As harbour sediments

are highly heterogeneous and anoxic, both cold acid extraction and sequential extraction should be conducted. To gain a better insight into the geochemical properties of sediments, direct mineral analysis such as X-ray absorption spectroscopy (XAS) could be included.

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### Journal publications

Shi, J.B., Ip, C.C.M., Tang, C.W.Y., Zhang, G., Wu, R.S.S. and Li, X.D. “Spatial and temporal variations of mercury in sediments from Victoria Harbour, Hong Kong”. *Marine Pollution Bulletin*, Vol. 54, no. 4, pp.480-485 (2007)

Tang, C.W.Y., Ip, C.C.M., Zhang, G. and Li, X.D. “Historical sources of heavy metals in sediments of Victoria Harbour, Hong Kong”. (full paper under revision)

Tang, C.W.Y., Ip, C.C.M., Shin, P.K.S. and Li, X.D. “The study of geochemical behaviour of metals of Victoria Harbour, Hong Kong”. (full paper under revision)

### Conference papers

Tang, C.W.Y., Ip, C.C.M., Li, X.D., Lam, N. and Shin, P. “Historical sources of trace metal contaminations in sediments from Victoria Harbour, Hong Kong”. *Marine Environmental Research and Innovative Technology 2<sup>nd</sup> Annual Symposium*, 30 November–2 December, 2005, (2005)

Ip, C.C.M., Tang, C.W.Y. and Li, X.D. “Acid volatile sulfide (AVS) and simultaneously extracted metals (SEM) in the sediment collected in Victoria Harbour, Hong Kong”. *Marine Environmental Research and Innovative Technology 2<sup>nd</sup> Annual Symposium*, 30 November–2 December, 2005, (2005)

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## Appendix I Analytical results of the study of Victoria Harbour sediments

A1-1. Physical parameters of waters and redox potential of surface sediments in Victoria Harbour in December 2004, February 2005, October 2005 and April 2006

### Water Depth(m)

Location	Dec-04	Feb-05	Oct-05	Apr-06	Mean
B1	19	20	21	17	19.1
B2	17	19	15	26	19.2
B3	15	14	16	18	15.7
B4	11	11	9.5	11	10.7
B5	6.3	7.5	6.6	6.7	6.8

### Redox potential(mV)

Location	Dec-04	Feb-05	Oct-05	Apr-06	Mean
B1	-259	-257	-211	-231	-240
B2	-358	-376	-420	-312	-367
B3	-345	-356	-367	-337	-351
B4	-299	-302	-343	-185	-282
B5	-232	-215	-319	-263	-257

### pH

Location	Dec-04	Feb-05	Oct-05	Apr-06	Mean
B1	8.17	8.23	8.14	8.01	8.14
B2	8.11	8.17	8	7.94	8.06
B3	8.1	8.08	8	7.92	8.03
B4	8.09	8.07	8.01	8.03	8.05
B5	8	8.04	8.02	8.03	8.02

### Salinity(ppt)

Location	Dec-04	Feb-05	Oct-05	Apr-06	Mean
B1	33.8	33.3	34.7	35.9	34.4
B2	33.8	32.9	34.0	34.8	33.9
B3	33.7	32.4	34.0	34.6	33.7
B4	33.5	32.4	33.6	34.3	33.5
B5	33.5	32.3	33.7	33.0	33.1

A1-2. Percentages of various particle sizes of the core sediments of Victoria Harbour

Sample ID	Clay % <2µm	Silt % 2 - 63µm	Sand % >200µm
B1a-05	6.57	73.5	19.6
B1a-11	6.00	71.2	22.8
B1a-14	5.36	52.0	42.6
B1a-18	7.33	63.7	29.0
B1a-20	7.34	69.4	21.5
B1a-24	6.66	72.7	20.6
B1a-28	7.71	74.1	18.2
B1a-32	4.43	57.0	38.5
B1b-02	9.68	84.9	5.43
B1b-04	9.81	86.8	3.35
B1b-06	9.01	80.3	10.7
B1b-07	6.81	71.9	19.8
B1b-08	7.84	81.1	11.1
B1b-10	8.70	80.3	11.0
B1b-13	8.72	81.6	9.68
B1b-14	5.98	64.1	29.4
B1b-15	7.34	73.0	19.6
B1b-17	6.77	74.4	18.8
B1b-19	7.81	74.0	18.2
B1b-21	7.51	71.8	20.7
B1b-23	6.06	63.5	30.5
B1b-27	9.41	85.6	4.98
B1b-29	8.05	76.6	15.4
B2a-04	3.88	48.0	43.3
B2a-08	5.70	63.1	31.2
B2a-13	5.56	62.9	28.2
B2a-16	4.63	57.1	38.3

## A1-2. (Continue)

Sample ID	Clay % <2µm	Silt % 2 - 63µm	Sand % >200µm
B3b-01	12.0	85.1	2.92
B3b-02	8.04	76.8	15.2
B3b-03	9.23	80.2	10.6
B3b-04	9.68	85.6	4.73
B3b-05	7.29	61.4	20.5
B3b-06	7.26	68.2	19.6
B3b-07	13.6	84.5	1.89
B3b-08	11.7	87.2	1.15
B3b-09	10.8	85.6	3.65
B3b-10	11.4	86.8	1.87
B3b-12	10.5	85.5	3.99
B3b-13	13.0	86.9	0.12
B3b-15	12.0	86.6	1.39
B4b-03	6.93	73.9	19.2
B4b-08	6.09	74.4	19.5
B4b-13	7.41	79.5	13.1
B4b-22	6.24	68.1	25.7
B5a-02	9.43	85.8	4.77
B5a-06	10.8	89.1	0.03
B5a-13	12.4	86.7	0.88
B5a-16	11.9	87.2	0.85
B5b-13	11.7	86.8	1.52
B5b-16	7.77	82.5	9.77



A1-3. Metal concentrations (mg/kg, dry weight) and TOC % in surface sediments collected from December 2004 (GD), February 2005 (GF), October2005 (GO) and April2006 (GA) in Victoria Harbour

<b>B1</b>						
Sample	Fe	Mn	Cu	Pb	Zn	TOC
GD-B1a	15141	356	19.3	20.6	57.6	0.45
GD-B1b	15724	321	29.0	20.0	62.3	0.46
GF-B1a	14540	338	15.9	21.6	51.5	0.41
GF-B1b	15363	319	16.8	20.6	54.3	0.45
GO-B1a	16227	364	23.1	24.2	60.1	0.70
GO-B1b	13301	309	23.1	14.8	47.2	0.55
GA-B1a	14500	317	19.5	18.4	50.2	0.37
GA-B1b	14013	320	20.2	15.7	52.0	0.44
mean	14901	332	21.0	19.6	55.0	0.48
SD	1015	20.7	4.49	3.30	5.30	0.10
<b>B2</b>						
Sample	Fe	Mn	Cu	Pb	Zn	TOC
GD-B2a	20163	377	149	36.2	151	1.10
GD-B2b	21620	395	163	44.7	172	1.09
GF-B2a	21765	469	161	85.1	166	1.59
GF-B2b	22329	459	188	44.2	177	1.65
GO-B2a	17497	289	123	32.5	101	1.39
GO-B2b	23564	432	171	37.5	179	1.71
GA-B2a	25441	460	241	35.6	194	1.54
GA-B2b	23968	372	181	36.2	181	1.85
mean	22043	407	172	44.0	165	1.49
SD	2453	61.1	34.3	17.1	28.9	0.28
<b>B3</b>						
Sample	Fe	Mn	Cu	Pb	Zn	TOC
GD-B3a	16972	287	119.7	48.9	155	1.51
GD-B3b	18992	313	122.9	46.3	165	1.29
GF-B3a	18446	316	280.3	55.3	221	1.77
GF-B3b	14914	240	124.3	45.7	142	1.67
GO-B3a	23387	429	170.1	37.2	178	1.84
GO-B3b	17297	267	129.4	45.1	153	1.90
GA-B3a	22979	398	209.5	37.7	186	1.69
GA-B3b	23294	358	229.1	40.4	207	1.94
mean	19535	326	173.2	44.6	176	1.70
SD	3279	64.9	60.5	6.06	27.7	0.22

## A1-3. (Continue)

B4						
Sample	Fe	Mn	Cu	Pb	Zn	TOC
GD-B4a	22953	453	43.8	38.2	114	1.08
GD-B4b	23294	486	45.6	33.9	113	1.08
GF-B4a	24797	522	38.2	32.3	104	0.96
GF-B4b	24698	565	58.0	39.0	132	1.20
GO-B4a	23128	396	28.6	17.2	82.0	1.28
GO-B4b	24647	429	60.7	28.3	119	1.31
GA-B4a	25503	473	68.5	28.8	124	1.30
GA-B4b	26041	516	67.5	29.0	131	1.25
mean	24383	480	51.4	30.8	115	1.18
SD	1143	54.4	14.5	6.89	16.3	0.13
B5						
Sample	Fe	Mn	Cu	Pb	Zn	TOC
GD-B5a	27009	381	18.5	31.0	109	0.76
GD-B5b	26134	428	22.1	32.6	114	0.80
GF-B5a	24598	445	29.8	35.8	109	0.83
GF-B5b	23569	480	43.9	39.3	117	0.92
GO-B5a	23770	437	32.7	31.7	102	0.98
GO-B5b	26625	390	36.9	26.0	112	0.91
GA-B5a	23239	349	27.9	26.4	97	0.82
GA-B5b	28157	326	29.6	22.8	111	0.91
mean	25388	405	30.2	30.7	109	0.87
SD	1834	52.0	8.01	5.45	6.76	0.08

A1-4. Result of  $^{210}\text{Pb}$  dating in sediment cores B2, B4 and B5

B2 sediment core

Depth (cm)	Pb(dpm)	Ra(dpm)	Excess Pb(dpm)
3	3.45	0.755	2.70
7	3.43	0.680	2.75
11	2.89	0.53	2.35
17	3.08	0.609	2.47
23	3.46	1.006	2.46
29	3.40	0.730	2.67
35	3.80	0.878	2.92
41	4.27	0.985	3.28
47	3.45	1.472	1.98
55	3.77	1.116	2.65

B4 sediment core

Depth (cm)	Pb(dpm)	Ra(dpm)	Excess Pb(dpm)
5	4.49	0.546	3.95
9	4.26	0.748	3.51
13	4.94	1.09	3.85
19	4.00	0.607	3.39
25	4.16	0.580	3.58
31	3.94	0.617	3.32
37	4.43	0.872	2.94
43	3.21	0.652	2.56
49	2.89	0.610	2.28
55	3.18	0.976	2.20

B5 sediment core

Depth (cm)	Pb(dpm)	Ra(dpm)	Excess Pb(dpm)
3	3.22	0.648	2.57
7	3.51	0.675	2.84
11	3.71	0.64	3.07
17	3.76	0.589	3.17
23	3.76	0.483	3.27
31	2.86	0.526	2.33
39	3.05	0.572	2.48
47	2.45	0.498	1.95
55	1.52	0.393	1.13
63	1.39	0.433	0.95

A1-5. Concentrations of metals in sediment core B1 (mg/kg, dry weight)

Sample	Depth (cm)	Cu	Pb	Zn	Ni	Co	Fe	Mn	Al	Ca
B1b-01	1	38.7	29.1	85.2	34.7	7.98	19753	560	39710	24929
B1b-02	3	38.2	28.7	89.8	33.1	8.01	19925	561	39602	27062
B1b-03	5	27.7	25.4	69.8	28.7	7.02	18110	492	34375	36527
B1b-04	7	38.9	27.1	83.6	31.6	7.85	19480	495	39659	30728
B1b-05	9	45.3	30.0	93.5	34.8	8.76	20881	546	44002	21780
B1b-06	11	44.2	31.0	93.7	36.2	9.23	21222	545	47705	24530
B1b-07	13	44.3	29.1	91.6	33.7	8.74	21015	511	45467	21531
B1b-08	15	65.1	32.7	108	37.9	9.81	22584	612	50743	18987
B1b-09	17	58.0	33.7	102	39.8	10.2	23400	600	52622	15280
B1b-10	19	62.1	32.8	107	39.5	10.3	23230	587	53363	15898
B1b-11	21	47.5	27.5	88.2	33.7	8.51	20317	490	43212	21923
B1b-12	23	55.6	28.7	90.5	34.5	8.61	20592	480	43260	22494
B1b-13	25	56.7	28.7	95.0	33.5	8.55	20478	486	43018	23713
B1b-14	27	37.5	22.5	72.1	27.7	7.10	18056	413	31522	30051
B1b-15	29	63.1	27.3	94.2	31.4	8.11	19859	484	40776	23857
B1b-17	33	67.6	29.0	95.9	34.9	8.76	20914	491	43650	19519
B1b-19	37	55.8	28.0	93.1	35.1	9.03	21326	510	46931	18871
B1b-21	41	58.1	29.0	96.0	38.8	9.20	22001	543	47003	19324
B1b-23	45	47.6	25.3	87.0	37.0	9.19	21760	514	46635	21264
B1b-25	49	45.3	28.0	94.9	42.0	10.1	23632	524	50860	18057
B1b-27	53	51.1	25.9	88.8	38.9	9.49	21758	536	46451	26012
B1b- 29	57	43.1	27.0	96.0	40.4	10.4	23311	529	53126	17826

A1-6. Concentrations of metals in sediment core B2 (mg/kg, dry weight)

Sample	Depth (cm)	Cu	Pb	Zn	Ni	Co	Fe	Mn	Al	Ca
B2a-01	1	121	32.6	113	30.5	6.13	16763	347	36918	20612
B2a-03	5	150	40.4	138	39.4	7.82	19638	425	44625	15821
B2a-04	7	156	36.2	140	36.4	7.38	19137	386	40435	17087
B2a-05	9	150	37.9	124	37.8	7.87	19752	401	42882	15684
B2a-06	11	188	40.1	136	44.2	10.1	23607	508	56464	14176
B2a-07	13	208	42.4	144	44.5	10.1	23458	510	56359	14212
B2a-08	15	208	38.4	136	41.8	10.6	23124	516	59194	13835
B2a-09	17	262	41.4	138	44.0	10.0	22152	492	55674	13546
B2a-10	19	272	43.5	140	42.3	10.5	22874	505	62460	12707
B2a-11	21	282	48.7	134	37.0	8.00	20243	411	54518	12469
B2a-12	23	270	42.8	133	32.9	7.13	18566	370	51644	13256
B2a-13	25	246	45.0	130	37.6	8.05	19714	384	50963	11181
B2a-14	27	268	46.7	140	42.0	8.72	20902	388	54944	11261
B2a-15	29	356	54.2	160	40.6	8.86	21080	495	57723	13743
B2a-17	33	459	56.7	179	43.6	8.11	20762	410	57646	9969
B2a-19	37	297	55.4	139	28.8	5.70	16385	345	47810	13711
B2a-21	41	424	62.4	173	40.8	7.79	19610	472	56084	16347
B2a-23	45	379	56.9	152	36.2	6.68	18365	418	51083	15904
B2a-25	49	264	48.3	131	29.7	4.49	14772	331	41518	15840
B2a-27	53	243	53.6	129	29.6	5.01	15253	334	46094	16814
B2a-29	57	217	52.8	119	33.8	5.26	15562	332	49484	19997

A1-7. Concentrations of metals in sediment core B3 (mg/kg, dry weight)

Sample	Depth (cm)	Cu	Pb	Zn	Ni	Co	Fe	Mn	Al	Ca
B3b - 01	1	174	45.6	174	41.3	10.2	21442	447	58528	9511
B3b - 02	2	181	47.5	176	41.1	10.3	21325	449	55250	10269
B3b - 03	3	175	46.8	184	42.9	10.4	21260	418	58073	9885
B3b - 04	4	196	50.6	191	43.6	10.9	22391	454	58739	10171
B3b - 05	5	186	48.4	184	39.9	10.6	21969	437	61733	9818
B3b - 06	6	188	52.3	186	40.1	10.6	21435	400	58687	6816
B3b - 07	7	195	47.2	196	38.5	10.4	21548	383	59546	5418
B3b - 08	8	196	52.2	190	39.1	10.9	22533	369	61172	4564
B3b - 09	9	294	54.0	198	41.3	10.5	21877	358	58410	4976
B3b - 10	10	179	46.7	175	32.7	10.0	20376	295	56968	3707
B3b - 11	12	212	48.1	199	43.1	10.3	20989	327	57477	5224
B3b - 13	16	228	47.2	205	38.9	9.92	20897	344	55990	10891
B3b - 14	18	256	45.1	198	41.4	10.4	21661	404	60156	11018
B3b - 15	20	266	42.5	193	46.5	10.1	21688	400	54572	14528
B3b - 16	22	339	40.2	176	44.1	10.8	23005	410	54215	17041
B3b - 17	24	262	38.2	139	44.5	11.0	22842	468	56887	14899
B3b - 18	26	317	42.1	156	48.3	11.3	22574	438	61942	13037
B3b - 19	28	379	41.0	147	45.4	10.7	21645	426	59203	13080
B3b - 20	30	407	43.0	143	45.3	10.9	22087	400	58636	11479
B3b - 22	34	238	33.8	120	41.3	10.9	21731	412	58260	14205
B3b - 24	38	238	35.3	135	49.2	11.3	22057	428	57927	16091
B3b - 26	42	195	37.7	129	44.3	11.4	21797	445	54086	14794
B3b - 28	46	240	42.7	144	42.7	9.42	23738	466	58611	13640
B3b - 30	50	340	45.4	162	43.2	8.90	23101	440	60171	11273
B3b - 32	54	256	41.2	143	41.3	8.26	22470	369	58645	8724
B3b - 34	58	252	39.6	126	40.0	8.05	22165	347	60106	11340
B3b - 36	62	221	39.8	122	43.6	10.3	21348	348	59288	11575

A1-8. Concentrations of metals in sediment core B4 (mg/kg, dry weight)

Sample	Depth (cm)	Cu	Pb	Zn	Ni	Co	Fe	Mn	Al	Ca
B4b-01	1	50.4	35.7	114	39.8	9.78	22208	561	53223	11548
B4b-02	3	55.8	33.2	122	40.2	9.97	22668	491	54013	10887
B4b-03	5	52.6	33.3	118	39.0	9.97	22482	528	54590	11067
B4b-04	7	53.6	35.5	121	42.0	10.6	22659	524	55913	10897
B4b-05	9	57.0	39.3	125	35.9	10.7	23691	605	58006	10874
B4b-06	11	54.9	39.5	126	37.2	10.5	23138	603	53740	10760
B4b-07	13	56.0	38.1	120	35.5	10.4	23065	519	53818	10150
B4b-08	15	54.1	47.8	115	33.7	9.88	22939	531	52238	12220
B4b-09	17	58.0	39.1	122	35.7	10.4	22928	532	53173	10501
B4b-10	19	55.1	38.5	122	37.4	10.4	22856	558	51181	11376
B4b-11	21	61.9	38.2	123	34.2	9.85	22556	561	49881	13900
B4b-12	23	61.1	39.0	136	34.3	9.71	22365	578	49740	14821
B4b-13	25	64.2	41.2	127	35.3	10.2	22664	629	51347	13133
B4b-14	27	55.8	40.0	124	36.1	10.7	23498	642	55606	11869
B4b-15	29	59.3	49.5	117	32.7	9.56	22482	543	48589	14569
B4b-17	33	91.3	49.0	155	33.9	8.78	21899	563	44641	17468
B4b-19	37	77.3	42.2	134	41.5	10.6	23930	625	57065	9579
B4b-21	41	63.3	36.4	121	33.1	9.65	22755	579	51054	13849
B4b-23	45	69.2	38.3	119	36.4	10.1	22972	583	52050	12831
B4b-25	49	47.5	37.1	99	40.6	10.7	23354	527	53053	9319
B4b-27	53	61.4	39.0	115	43.1	11.2	24221	564	57226	10002
B4b-29	57	53.4	36.7	107	39.5	10.4	23426	519	51894	10966

A1-9. Concentrations of metals in sediment core B5 (mg/kg, dry weight)

Sample	Depth (cm)	Cu	Pb	Zn	Ni	Co	Fe	Mn	Al	Ca
B5b-01	1	29.4	37.2	113	38.8	11.6	23489	443	55004	6829
B5b-02	3	23.2	34.0	109	43.5	13.0	24861	366	60025	4875
B5b-03	5	21.6	34.5	105	41.4	12.9	24430	349	60446	4575
B5b-04	7	19.4	33.9	102	42.2	12.9	25146	328	66112	3836
B5b-05	9	20.1	33.4	100	45.1	12.6	24524	348	62319	4195
B5b-06	11	18.0	32.5	103	40.3	12.7	24862	349	62660	4378
B5b-07	13	19.5	32.9	103	41.3	12.9	25200	383	62237	4797
B5b-08	15	19.6	32.3	105	40.5	12.7	25019	434	60354	5483
B5b-09	17	18.3	32.9	106	43.6	14.3	26001	451	63595	5913
B5b-10	19	22.8	33.5	109	41.8	13.5	25210	464	61708	6525
B5b-11	21	30.9	38.6	110	38.4	11.9	23922	464	56759	9767
B5b-12	23	35.4	42.1	107	35.1	10.2	22546	500	48160	14370
B5b-13	25	43.6	48.4	120	37.7	10.6	23437	567	53231	13487
B5b-14	27	40.8	46.4	118	37.1	10.6	23204	554	53361	12168
B5b-15	29	37.3	42.8	116	38.3	11.1	23169	536	54176	12412
B5b-17	33	54.7	47.4	143	36.3	11.0	25172	570	59582	13293
B5b-19	37	30.9	47.6	129	37.3	11.6	25286	576	61284	12501
B5b-21	41	42.0	48.2	135	38.9	11.6	25281	552	62281	9737
B5b-23	45	28.1	47.6	124	38.5	11.6	26059	584	63151	17956
B5b-25	49	22.0	47.8	111	38.1	11.2	25466	571	57945	31330
B5b-27	53	18.6	39.5	102	35.9	10.9	24927	566	59488	26505
B5b-29	57	16.7	38.0	96.1	35.6	10.8	25350	537	61071	25430
B5b-31	61	12.4	28.1	78.7	35.6	9.62	23791	527	52664	62794
B5b-33	65	9.78	24.6	84.7	33.1	10.3	24360	569	53174	31455



A1-10. Results of Pb isotopic ratios in core sediments, Victoria Harbour

Sample	Pb (mg/kg)	<sup>206</sup> Pb/ <sup>207</sup> Pb	<sup>208</sup> Pb/ <sup>207</sup> Pb	RSD	<sup>206</sup> Pb/ <sup>207</sup> Pb	<sup>208</sup> Pb/ <sup>207</sup> Pb
B1a-01	31.4	1.181	2.474		0.265	0.343
B1a-03	32.3	1.182	2.470		0.437	0.330
B1a-32	30.9	1.173	2.454		0.477	0.309
B1b-01	13.7	1.187	2.481		0.177	0.253
B1b-02	12.8	1.188	2.477		0.273	0.265
B1b-03	11.4	1.189	2.480		0.227	0.367
B1b-04	11.9	1.188	2.486		0.309	0.445
B1b-06	9.63	1.190	2.485		0.332	0.406
B1b-08	8.32	1.193	2.487		0.343	0.271
B1b-10	9.41	1.192	2.483		0.196	0.164
B1b-13	8.64	1.192	2.485		0.424	0.354
B1b-14	8.18	1.191	2.482		0.478	0.352
B2a-01	35.4	1.181	2.468		0.384	0.326
B2a-15	54.2	1.168	2.444		0.359	0.346
B2a-23	56.9	1.171	2.450		0.393	0.323
B2a-29	52.8	1.182	2.463		0.266	0.372
B3b-01	45.6	1.178	2.468		0.323	0.481
B3b-08	52.2	1.174	2.459		0.339	0.487
B3b-11	45.1	1.168	2.443		0.348	0.212
B3b-13	68.4	1.157	2.425		0.274	0.303
B3b-36	39.8	1.180	2.465		0.293	0.431
B4a-01	25.7	1.182	2.463		0.316	0.382
B4a-03	26.3	1.184	2.472		0.351	0.540
B4a-04	52.7	1.120	2.397		0.320	0.365
B4a-06	31.5	1.182	2.465		0.479	0.442
B4a-08	25.3	1.183	2.471		0.192	0.243
B4a-10	28.5	1.182	2.472		0.188	0.099
B4a-12	28.2	1.183	2.472		0.244	0.114
B4a-14	33.6	1.188	2.473		0.229	0.173
B4a-16	33.9	1.189	2.474		0.175	0.155
B4a-17	32.6	1.190	2.477		0.216	0.249
B4a-18	31.7	1.183	2.468		0.492	0.377

## A1-10. (Continue)

Sample	Pb (mg/kg)	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$	RSD	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$
B4b-01	35.7	1.183	2.469		0.157	0.124
B4b-02	33.2	1.184	2.467		0.234	0.200
B4b-03	33.3	1.185	2.472		0.186	0.136
B4b-04	35.5	1.184	2.471		0.228	0.193
B4b-05	39.3	1.183	2.469		0.160	0.138
B4b-06	39.5	1.184	2.468		0.133	0.225
B4b-07	38.1	1.186	2.473		0.150	0.203
B4b-08	47.8	1.182	2.463		0.238	0.197
B4b-09	39.1	1.186	2.471		0.112	0.196
B4b-10	38.5	1.184	2.469		0.247	0.137
B4b-11	38.2	1.181	2.464		0.222	0.148
B4b-12	39.0	1.178	2.463		0.237	0.186
B4b-13	41.2	1.181	2.467		0.228	0.215
B4b-14	40.0	1.184	2.470		0.208	0.212
B4b-15	49.5	1.181	2.465		0.188	0.241
B4b-17	49.0	1.171	2.455		0.124	0.097
B4b-19	42.2	1.179	2.461		0.178	0.161
B4b-21	36.4	1.182	2.472		0.152	0.215
B4b-23	38.3	1.182	2.469		0.227	0.207
B4b-25	37.1	1.190	2.476		0.211	0.153
B4b-27	39.0	1.188	2.475		0.135	0.168
B4b-29	36.7	1.189	2.475		0.193	0.129
B5a-01	32.1	1.195	2.484		0.390	0.415
B5a-03	29.5	1.195	2.486		0.430	0.360
B5a-10	30.6	1.197	2.484		0.386	0.392
B5a-22	29.8	1.193	2.482		0.411	0.255
B5b-01	33.7	1.189	2.477		0.377	0.321
B5b-10	31.9	1.196	2.477		0.369	0.361
B5b-16	37.1	1.189	2.477		0.351	0.287
B5b-22	42.9	1.174	2.454		0.488	0.385
B5b-27	42.9	1.154	2.431		0.353	0.419

A1-11. Results of 5-step sequential extraction of October 2005 and April 2006 surface sediments, Victoria Harbour

(a) Metals concentrations after step 1 extraction (mg/kg, dry weight)

Samples in October 2005					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	9.23	11.1	0.220	0.088	0.374
B1b	3.16	9.39	0.259	0.047	0.590
B2a	8.11	3.32	0.646	0.000	0.383
B2b	19.27	6.66	1.15	0.000	1.31
B3a	9.05	3.12	0.922	0.061	0.781
B3b	10.2	1.97	0.996	0.207	0.715
B4a	14.2	7.88	0.156	0.000	0.233
B4b	11.3	12.8	0.365	0.000	0.273
B5a	6.60	19.5	0.164	0.061	0.129
B5b	8.74	16.2	0.159	0.014	1.74

Samples in April 2006					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	8.90	6.94	0.174	0.035	0.233
B1b	4.66	7.26	0.123	0.211	0.151
B2a	4.88	2.20	0.294	0.088	0.696
B2b	11.8	2.97	0.298	0.198	0.612
B3a	9.42	4.97	0.322	0.000	1.10
B3b	15.8	2.96	0.454	0.000	0.851
B4a	14.2	11.6	0.160	0.037	0.271
B4b	3.00	25.4	0.119	0.018	0.238
B5a	1.55	13.9	0.077	0.000	0.363
B5b	3.22	10.1	0.028	0.000	0.149

A1-11. (*Continue*)

(b) Metals concentrations after step 2 extraction (mg/kg, dry weight)

Samples in October 2005					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	350	138	5.00	15.7	7.09
B1b	216	122	6.00	8.89	6.17
B2a	387	65.7	46.6	19.3	37.5
B2b	705	102	54.0	23.7	60.4
B3a	651	63.2	46.6	22.9	67.2
B3b	506	49.4	42.4	31.1	72.7
B4a	573	99.5	4.73	9.92	17.9
B4b	521	130	13.5	15.4	22.7
B5a	574	120	3.99	17.3	12.1
B5b	562	111	4.45	15.6	12.5

Samples in April 2006					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	327	126	2.26	10.4	6.18
B1b	309	113	2.55	8.19	6.12
B2a	617	103	75.0	23.7	57.8
B2b	622	57.4	54.0	24.2	57.0
B3a	678	86.7	63.6	22.1	69.3
B3b	708	48.8	60.8	23.1	78.0
B4a	565	137	9.58	17.0	23.6
B4b	674	168	6.53	18.4	21.9
B5a	677	97.8	2.59	15.5	11.5
B5b	571	78.1	2.23	11.7	12.9

A1-11. (*Continue*)

## (c) Metals concentrations after step 3 extraction (mg/kg, dry weight)

Samples in October 2005					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	2944	89.4	1.79	4.96	16.0
B1b	2568	72.6	1.90	3.18	13.0
B2a	2448	65.7	4.63	7.63	27.7
B2b	3145	93.8	2.60	9.39	45.8
B3a	3023	84.7	2.06	9.95	48.6
B3b	2642	63.3	2.59	10.2	42.6
B4a	3373	112	1.26	4.03	21.1
B4b	3533	123	2.91	6.50	29.9
B5a	3784	119	2.12	7.02	25.3
B5b	3732	115	1.65	6.25	22.8
Samples in April 2006					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	2683	74.8	1.35	3.26	14.0
B1b	2852	73.6	2.05	3.83	15.0
B2a	2667	92.5	2.14	7.66	48.3
B2b	2716	86.5	1.96	8.75	51.0
B3a	2598	84.1	1.38	7.41	47.9
B3b	2816	81.5	1.74	8.86	54.2
B4a	3544	128	2.10	5.81	33.0
B4b	3511	126	2.19	6.19	31.3
B5a	3521	101	1.60	5.93	21.9
B5b	4373	117	1.50	5.90	21.7

A1-11. (*Continue*)

## (d) Metals concentrations after step 4 extraction (mg/kg, dry weight)

Samples in October 2005					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	715	12.0	7.46	1.30	3.60
B1b	980	11.6	7.29	1.01	2.88
B2a	1842	34.6	36.9	0.131	4.68
B2b	2026	47.6	52.2	0.130	9.44
B3a	2283	46.4	47.8	0.000	8.55
B3b	2105	36.5	43.9	0.016	7.63
B4a	2144	26.9	9.99	0.000	5.67
B4b	2136	22.9	17.7	0.000	6.96
B5a	1286	19.2	9.74	1.72	6.64
B5b	1487	25.5	11.4	1.96	8.17

Samples in April 2006					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	906	14.9	6.42	1.24	4.58
B1b	665	12.3	6.73	1.29	3.50
B2a	3742	81.1	118	0.267	19.0
B2b	4120	96.3	95.9	0.200	18.5
B3a	4243	90.9	117	0.201	18.8
B3b	4305	84.8	132	0.203	19.2
B4a	2988	51.2	32.3	0.099	10.9
B4b	2623	35.6	32.2	0.798	11.7
B5a	1273	19.0	9.78	1.74	7.81
B5b	1280	22.6	8.46	2.29	9.11

A1-11. (*Continue*)

## (e) Metals concentrations after step 5 extraction (mg/kg, dry weight)

Samples in October 2005					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	9221	56.9	7.69	2.29	31.3
B1b	6959	58.8	4.65	1.43	21.6
B2a	6771	64.9	6.49	3.07	21.7
B2b	8878	53.6	11.3	4.22	34.5
B3a	8204	75.1	9.87	4.20	30.6
B3b	7350	66.9	8.69	4.43	26.2
B4a	9796	101	6.07	4.14	30.0
B4b	10637	59.5	10.5	4.40	42.6
B5a	11375	107	10.6	3.71	46.6
B5b	12268	59.9	12.2	3.70	53.7
Samples in April 2006					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	8099	74.7	6.67	1.65	27.5
B1b	7649	71.5	6.59	1.99	24.5
B2a	12013	101	23.2	6.33	55.6
B2b	11955	122	21.8	6.23	57.0
B3a	11146	116	20.0	9.12	50.3
B3b	10521	85.3	19.1	8.29	46.6
B4a	11905	122	13.9	5.53	49.9
B4b	12291	75.2	17.2	4.70	56.6
B5a	11647	65.8	10.5	4.02	49.1
B5b	13492	50.4	13.9	4.08	62.4

A1-12. Results of total metal digestion of October 2005 and April 2006 surface sediments, Victoria Harbour (mg/kg, dry weight)

Sample in October 2005					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	16227	364	23.1	24.2	60.1
B1b	13301	309	23.1	14.8	47.2
B2a	17497	289	123	32.5	101
B2b	23564	432	171	37.5	179
B3a	23387	429	170	37.2	178
B3b	17297	267	129	45.1	153
B4a	23128	396	28.6	17.2	82.0
B4b	24647	429	60.7	28.3	119
B5a	23770	437	32.7	31.7	102
B5b	26625	390	36.9	26.0	112

Samples in April 2006					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	14013	320	20.2	15.7	52.0
B1b	14013	320	20.2	15.7	52.0
B2a	25441	460	241	35.6	194
B2b	23968	372	181	36.2	181
B3a	22979	398	209	37.7	186
B3b	23294	358	229	40.4	207
B4a	25503	473	68.5	28.8	124
B4b	26041	516	67.5	29.0	131
B5a	23239	349	27.9	26.4	96.6
B5b	28157	326	29.6	22.8	111



A1-13. Relative percentage of metals after sequential extraction of the October 2005 and April 2006 surface sediments, Victoria Harbour

(a) Relative % of step 1 extracted metals

Samples in October 2005					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	0.070	3.62	0.992	0.360	0.641
B1b	0.029	3.42	1.29	0.323	1.33
B2a	0.071	1.42	0.678	0.000	0.416
B2b	0.130	2.19	0.945	0.001	0.866
B3a	0.064	1.15	0.859	0.165	0.502
B3b	0.081	0.901	1.01	0.449	0.477
B4a	0.089	2.27	0.701	0.000	0.311
B4b	0.067	3.67	0.812	0.000	0.267
B5a	0.039	5.06	0.614	0.203	0.142
B5b	0.048	4.95	0.532	0.051	1.76

Samples in April 2006					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	0.074	2.34	1.03	0.210	0.445
B1b	0.041	2.61	0.685	1.36	0.307
B2a	0.026	0.579	0.134	0.232	0.384
B2b	0.061	0.813	0.171	0.501	0.332
B3a	0.050	1.30	0.159	0.000	0.586
B3b	0.086	0.975	0.212	0.000	0.428
B4a	0.075	2.58	0.276	0.129	0.230
B4b	0.016	5.92	0.204	0.059	0.196
B5a	0.009	4.66	0.313	0.000	0.401
B5b	0.016	3.64	0.108	0.000	0.140

A1-13. (Continue)

(b) Relative % of step 2 extracted metals

Samples in October 2005					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	2.64	45.0	22.6	64.5	12.1
B1b	2.01	44.5	29.9	61.1	13.9
B2a	3.38	28.0	49.0	64.0	40.7
B2b	4.77	33.6	44.5	63.3	39.9
B3a	4.60	23.2	43.5	61.7	43.2
B3b	4.01	22.7	43.0	67.7	48.6
B4a	3.60	28.7	21.3	54.8	23.9
B4b	3.09	37.3	30.1	58.6	22.1
B5a	3.37	31.2	15.0	58.1	13.3
B5b	3.11	33.8	14.9	56.6	12.6

Samples in April 2006					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	2.72	42.3	13.4	62.7	11.8
B1b	2.69	40.7	14.1	52.8	12.4
B2a	3.24	27.2	34.2	62.3	31.9
B2b	3.20	15.7	31.0	61.1	31.0
B3a	3.63	22.6	31.4	56.9	37.0
B3b	3.85	16.1	28.4	57.1	39.2
B4a	2.97	30.5	16.5	59.7	20.1
B4b	3.53	39.1	11.2	61.1	18.0
B5a	3.95	32.9	10.6	57.1	12.7
B5b	2.90	28.1	8.5	48.7	12.2

A1-13. (Continue)

(c) Relative % of step 3 extracted metals

Samples in October 2005					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	22.2	29.0	8.07	20.4	27.3
B1b	23.9	26.4	9.47	21.9	29.4
B2a	21.4	28.1	4.85	25.4	30.1
B2b	21.3	30.9	2.14	25.1	30.2
B3a	21.3	31.1	1.92	26.8	31.2
B3b	20.9	29.0	2.62	22.2	28.4
B4a	21.2	32.2	5.67	22.3	28.2
B4b	21.0	35.4	6.47	24.7	29.2
B5a	22.2	30.9	7.97	23.5	27.9
B5b	20.7	35.2	5.54	22.7	23.1

Samples in April 2006					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	22.3	25.2	7.98	19.7	26.7
B1b	24.8	26.5	11.3	24.7	30.4
B2a	14.0	24.4	0.980	20.1	26.6
B2b	14.0	23.7	1.12	22.1	27.7
B3a	13.9	22.0	0.680	19.1	25.6
B3b	15.3	26.9	0.814	21.9	27.3
B4a	18.6	28.5	3.61	20.4	28.1
B4b	18.4	29.2	3.76	20.5	25.7
B5a	20.6	33.9	6.52	21.8	24.1
B5b	22.2	42.1	5.73	24.6	20.4

A1-13. (Continue)

(d) Relative % of step 4 extracted metals

Samples in October 2005					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	5.40	3.89	33.7	5.37	6.17
B1b	9.14	4.23	36.3	6.93	6.50
B2a	16.1	14.8	38.7	0.437	5.09
B2b	13.7	15.7	43.0	0.346	6.23
B3a	16.1	17.0	44.6	0.000	5.49
B3b	16.7	16.7	44.5	0.034	5.09
B4a	13.5	7.76	45.0	0.000	7.58
B4b	12.7	6.56	39.3	0.000	6.79
B5a	7.56	4.99	36.6	5.76	7.32
B5b	8.24	7.78	38.1	7.15	8.26
Samples in April 2006					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	7.54	5.02	38.1	7.48	8.72
B1b	5.79	4.43	37.3	8.34	7.12
B2a	19.6	21.4	54.0	0.703	10.5
B2b	21.2	26.4	55.1	0.506	10.0
B3a	22.7	23.7	57.8	0.518	10.1
B3b	23.4	27.9	61.7	0.503	9.64
B4a	15.7	11.4	55.6	0.348	9.26
B4b	13.7	8.28	55.3	2.65	9.62
B5a	7.44	6.40	39.9	6.38	8.61
B5b	6.49	8.12	32.4	9.59	8.57

A1-13. (Continue)

(e) Relative % of step 5 extracted metals

Samples in October 2005					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	69.7	18.5	34.7	9.40	53.7
B1b	64.9	21.4	23.1	9.83	48.8
B2a	59.1	27.7	6.82	10.2	23.6
B2b	60.1	17.6	9.33	11.3	22.8
B3a	57.9	27.6	9.20	11.3	19.7
B3b	58.3	30.7	8.81	9.63	17.5
B4a	61.6	29.1	27.3	22.9	40.0
B4b	63.2	17.1	23.4	16.7	41.6
B5a	66.8	27.9	39.9	12.4	51.3
B5b	67.9	18.3	40.9	13.5	54.3

Samples in April 2006					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	67.4	25.2	39.5	10.0	52.4
B1b	66.6	25.8	36.5	12.8	49.7
B2a	63.1	26.5	10.6	16.7	30.6
B2b	61.5	33.4	12.5	15.7	31.0
B3a	59.7	30.4	9.89	23.5	26.8
B3b	57.3	28.1	8.93	20.5	23.5
B4a	62.6	27.0	24.0	19.4	42.4
B4b	64.3	17.5	29.5	15.6	46.5
B5a	68.0	22.1	42.7	14.8	54.2
B5b	68.4	18.1	53.2	17.1	58.8

A1-14. Relative percentages of non-residual metals to the total metals concentrations in October 2005 and April 2006 surface sediments, Victoria Harbour

Samples in October 2005					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	30.3	81.5	65.3	90.6	46.3
B1b	35.1	78.6	76.9	90.2	51.2
B2a	40.9	72.3	93.2	89.8	76.4
B2b	39.9	82.4	90.7	88.7	77.2
B3a	42.1	72.4	90.8	88.7	80.3
B3b	41.7	69.3	91.2	90.4	82.5
B4a	38.4	70.9	72.7	77.1	60.0
B4b	36.8	82.9	76.6	83.3	58.4
B5a	33.2	72.1	60.1	87.6	48.7
B5b	32.1	81.7	59.1	86.5	45.7

Samples in April 2006					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	32.6	74.8	60.5	90.0	47.6
B1b	33.4	74.2	63.5	87.2	50.3
B2a	36.9	73.5	89.4	83.3	69.4
B2b	38.5	66.6	87.5	84.3	69.0
B3a	40.3	69.6	90.1	76.5	73.2
B3b	42.7	71.9	91.1	79.5	76.5
B4a	37.4	73.0	76.0	80.6	57.6
B4b	35.7	82.5	70.5	84.4	53.5
B5a	32.0	77.9	57.3	85.2	45.8
B5b	31.6	81.9	46.8	82.9	41.2

A1-15. Relative percentages of HCl-extracted metals to the total metal concentrations in October 2005 and April 2006 surface sediments, Victoria Harbour

Samples in October 2005					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	19.1	59.6	40.8	70.8	30.2
B1b	23.1	58.8	45.5	95.6	40.9
B2a	10.1	27.0	11.9	44.1	27.7
B2b	14.5	32.3	14.2	74.0	39.5
B3a	10.1	19.2	13.4	44.3	30.8
B3b	19.0	46.7	22.8	49.0	35.1
B4a	30.1	58.9	40.4	95.0	53.1
B4b	21.8	58.0	32.0	85.3	38.8
B5a	22.4	53.1	32.3	73.8	31.7
B5b	22.9	58.9	19.0	87.7	26.1

Samples in April 2006					
Sample	Fe	Mn	Cu	Pb	Zn
B1a	20.6	57.9	41.1	64.9	34.1
B1b	24.4	74.3	46.3	95.0	45.2
B2a	17.8	44.1	20.8	84.4	36.6
B2b	21.5	42.6	32.9	94.7	47.3
B3a	20.4	44.5	27.5	80.8	48.2
B3b	21.1	29.5	17.6	77.4	47.0
B4a	27.1	71.5	32.1	85.5	49.6
B4b	24.4	62.0	36.7	98.9	47.3
B5a	21.8	78.5	40.2	95.0	43.8
B5b	19.2	67.1	36.9	95.0	33.3

A1-16. Results of laboratory bioassay, total metal concentration in *Capitella* sp. I and bioassay sediments

(a) Metal concentrations in *Capitella* sp. I (mg/kg, dry weight)

Sample	Pb	Cu	Zn
B1-1	6.51	19.8	293
B1-2	5.83	18.9	363
B1-3	4.91	21.3	427
Mean	5.75	20.0	361
S.D.	0.801	1.18	67.0
B3-1	4.14	106.6	184
B3-2	3.94	52.0	277
B3-3	7.29	83.7	253
Mean	5.12	80.8	238
S.D.	1.88	27.4	48.2
B5-1	7.11	21.0	435
B5-2	7.74	20.6	323
B5-3	6.37	16.2	358
Mean	7.07	19.3	372
S.D.	0.688	2.67	57.2

(b) Metal concentrations in bioassay sediments (mg/kg, dry weight)

Sample	Pb	Cu	Zn
B1-1	35.0	36.8	103
B1-2	34.4	34.4	95.0
B1-3	33.8	35.1	96.7
Mean	34.4	35.4	98.2
S.D.	0.624	1.25	4.25
B3-1	53.4	196	171
B3-2	49.4	183	184
B3-3	51.0	197	169
Mean	51.3	192	175
S.D.	2.04	7.77	7.97
B5-1	35.5	34.4	100
B5-2	35.3	34.5	95.8
B5-3	35.0	34.0	95.0
Mean	35.3	34.3	97.0
S.D.	0.226	0.286	2.79



## **Appendix II Analytical procedures in the present study**

### **A2-1. Procedure of total acid digestion of heavy metals in sediment**

1. Weigh 0.250 g ( $\pm 0.001$  g) of sample into pre-washed Pyrex test tubes (18 mm  $\times$  180 mm)
2. Add 4.0 ml HNO<sub>3</sub> (70 %, AR) and 1.0 ml HClO<sub>4</sub> (60 %, AR), using a 5-ml auto-pipette (Note: The volume of acid added can be adjusted according to the nature of samples)
3. Shake gently using a vortex (scale <4) and place the tubes in an aluminum heating block
4. Program the heating block: 50°C 3 h, 100°C 1h, 125°C 1 hr, 150°C 3 hr, 175°C 2 hr, 190°C until dry (Note: heating can be done during the night if 25°C is set as the 1<sup>st</sup> heating step. Responsible personnel must be present when temperature is above 150°C. The heating process must be adjusted according to the volume of acid added for digestion)
5. When temperature is above 150°C, check the samples every 15–20 min
6. Remove the tubes when the residual samples are dry (Note: the residual sample should be white/light in colour at the end of the heating process. If samples appear dark in colour, repeat steps 2–6)
7. Let the test tubes cool and add 10.0 ml 5 % (v/v) HNO<sub>3</sub> using a dispenser
8. Vortex (scale ~7) and heat the test tubes at 65°C for 1 h
9. Let cool and vortex (scale ~7)
10. Pour the mixtures into 10.0-ml plastic tubes (blue cap) for storage at 4°C
11. Centrifuge at 3500 rpm for 10 min before ICP analysis

## A2-2. Procedure of 5-step sequential extraction for sediments

### 1. *Extraction with 0.5 M MgCl<sub>2</sub> for exchangeable fraction*

- 1.1. Weigh 1.000 g (+0.001) of sample into 60 ml polysulfone centrifuge tubes using a top pan balance
- 1.2. Add 8.0 ml 0.5 M MgCl<sub>2</sub> (pH 7.0) to each tube and cap the tube tightly
- 1.3. Put the tubes on a mechanical shaker and agitate for 10 min
- 1.4. Centrifuge the tubes at 3000 rpm for 10 min
- 1.5. Decant 5 ml of the first supernatant, using a Gilson pipette, into test tubes (18 mm o.d. x 180 mm)
- 1.6. Wash the residue with 8 ml D.I.W. (shake by hand for 2 min)
- 1.7. Discard the second supernatant after centrifuging for 10 min

### *Treatment of extraction solutions*

- 1.8. To the first supernatant, add 1 ml concentrated HNO<sub>3</sub> from an Oxford dispenser and place them on a heating block
- 1.9. Adjust the heating block to 85°C for ½ hour, 120°C for 4 h, then to 150°C until the sample reaches dryness
- 1.10. Transfer the tubes into stainless steel racks
- 1.11. When cooled, add 10.0 ml 5 % HNO<sub>3</sub> from an Oxford dispenser to each tube
- 1.12. Mix each tube using a vortex mixer
- 1.13. Place the tubes in a Shallow heating block and leave to leach for 1 h at 70°C
- 1.14. Transfer the tubes to wire racks and allow to cool
- 1.15. Decant the solutions into polystyrene tubes and cap. The solutions are ready for ICP-AES analysis

2. *Extraction with 1M NaOAc for the carbonate/specifically adsorbed fraction*
  - 2.1. To the solid residues from the first extraction (after step 1.7.), add 8 ml 1M NaOAc (pH = 5.0) to each tube and cap them
  - 2.2. Place the capped tubes on the mechanical shaker and leave them under continuous shaking for 5 h
  - 2.3. Centrifuge the tubes at 3000 rpm for 10 min
  - 2.4. Remove 2.0 ml of the supernatant as in step 1.5
  - 2.5. Repeat steps 1.8–1.15
  
3. *Extraction with 0.04M NH<sub>2</sub>OH.HCl for the Mn-Fe oxide fraction*
  - 3.1. Add 20 ml 0.04 M NH<sub>2</sub>OH.HCl in 25 % (v/v) HOAc to the residue from the second extraction (step 2.5), and mark the level of 20 ml on the tubes using a fine marker pen
  - 3.2. Place the tubes on the heating block and set the temperature to 96°C for 6 h (uncapped)
  - 3.3. Agitate the tubes hourly
  - 3.4. When the attack is complete, transfer the tubes to racks and allow to cool
  - 3.5. Add D.I.W. to each tube to the 20 ml mark and cap them. Mix the solution thoroughly on the mechanical shaker for 5 min
  - 3.6. Centrifuge the tubes at 3000 rpm for 10 min
  - 3.7. Remove 15 ml of the supernatant using a 5-ml Gilson pipette as in step 1.5
  - 3.8. Repeat steps 1.8–1.15. CAUTION: violent reaction of HNO<sub>3</sub> with NH<sub>2</sub>OH.HCl; raise the temperature of the heating block very slowly to 50°C for 2 h, to 75°C for 6 h, to 100°C for 10 h and finally to 140°C to near dryness
  - 3.9. Decant the solutions into polystyrene tubes – ready for ICP analysis

4. *Extraction with H<sub>2</sub>O<sub>2</sub>/NH<sub>4</sub>OAc for the organic/sulfide fraction*

- 4.1. Add 3.0 ml 0.02M HNO<sub>3</sub> and 5.0 ml 30 % H<sub>2</sub>O<sub>2</sub> (pH=2.0) to the residue from the third extraction (step 3.7)
- 4.2. Place the uncapped tubes on the heating block and raise the temperature to 85°C
- 4.3. Leave the tubes on the heating block at 85°C for 2 h with occasional agitation (Careful: splashing and bubbles)
- 4.4. Transfer the tubes to racks and allow to cool
- 4.5. Add another 3 ml 30 % H<sub>2</sub>O<sub>2</sub> (pH=2.0) and take them back to the heating block
- 4.6. Set the temperature of the block to 85°C for 3 h
- 4.7. Shake the tubes intermittently (every hour)
- 4.8. Take the tubes from the heating block and allow to cool
- 4.9. After cooling, add 5 ml 3.2 M NH<sub>4</sub>OAc in 20 % (v/v) HNO<sub>3</sub>, dilute to 20 ml with D.I.W. and put the caps on
- 4.10. Shake the capped tubes on a mechanical shaker for 30 min
- 4.11. Centrifuge the tubes at 3000 rpm for 10 min
- 4.12. Remove 15.0 ml aliquot of the supernatant as in step 1.5
- 4.13. Repeat steps 1.8–1.15. CAUTION: violent reaction of HNO<sub>3</sub> with H<sub>2</sub>O<sub>2</sub>; follow the temperature settings outlined in step 3.8
- 4.14. Decant the solutions into polystyrene tubes – ready for ICP-AES analysis.

5. *Extraction with HClO<sub>4</sub>/HNO<sub>3</sub> for the residual fraction*

- 5.1. Transfer the residue left at step 4.13 from the centrifuge tubes. Suspend all of the residue with 5 % (v/v) HNO<sub>3</sub> (5 ml) and decant into clean test tubes for 5 times
- 5.2. Heat the test tubes in a heating block until dry (70°C 1 hr → 120°C overnight ~18 h)

- 5.3. Remove from heating block and let cool
- 5.4. Add 6.0 ml conc.  $\text{HNO}_3$  and 1.5 ml conc.  $\text{HClO}_4$  to each test tube
- 5.5. Mix each tube using a vortex mixer gently
- 5.6. Place the tubes on the heating block and set the temperatures as follows:

50°C	5h
90°C	2h
120°C	4h
150°C	until dry
- 5.7. Remove tubes from the heating block and place into a rack. (Sample residue should appear white/light in colour. If not, repeat step 5.4–5.6.)
- 5.8. Allow them to cool
- 5.9. Add 10.0 ml 5 % (v/v)  $\text{HNO}_3$  to each tube and mix each tube using a vortex mixer
- 5.10. Leach for 1 h on heating block at 70°C
- 5.11. Remove tubes from block, place into a wire rack and let them cool
- 5.12. Mix each tube using a vortex mixer and decant into 10-ml polyethylene tubes.
- 5.13. Store at 4°C and centrifuge at 3500 rpm for 10 min prior to ICP analysis

### A2-3. Procedure of cold acid extraction of anoxic sediment (AVS/SEM analysis)

1. Add 100 ml DIW in the round-bottom flask
2. Add 80 ml 0.5 M NaOH in each impinger trap
3. Keep the apparatus deaerated by bubbling nitrogen for 10 min at a flow rate of 100 cm<sup>3</sup>/min
4. Weight approximately 2–10 g of wet sediment by a syringe or on a 2 X 2-in piece of Parafilm<sup>TM</sup> and introduce the sample to the standard taper round-bottom flask
5. Purge sample for 10 min with nitrogen at a flow rate of 100 cm<sup>3</sup>/min
6. Add 20 ml 6 M HCl into the flask through the septum
7. Switch on the magnetic stirrer at power 6–7
8. Keep the apparatus bubbling with nitrogen gas for 40 min at a flow rate of 100 cm<sup>3</sup>/min

#### *AVS analysis*

9. Pour the NaOH solution in each impinger trap into a 100 ml volumetric flask
10. Add 10 ml mixed diamine reagent (MDR) in the volumetric flask and make the volume up to 100 ml with DIW (CAUTION: violent reaction of mixing up the solution, release gas after each mixing).
11. The solutions are ready to test for spectrophotometer after 30 minutes. The absorbance of this solution at 670 nm. (If the absorbance of a sample exceeded 0.7, the sample should be diluted 10-fold with 1.0 M H<sub>2</sub>SO<sub>4</sub>)
12. Preparation of the calibration curve:
  - i. Add 80 ml 0.5 M NaOH and then 0.0 to 20 µmol S<sup>2-</sup> to a series of 100 ml volumetric flasks
  - ii. Add 10.0 ml of MDR to each volumetric flasks
  - iii. Make the volume up to 100 ml with DIW

*SEM analysis*

13. Filter the acid in the round-bottom flask through a 0.45  $\mu\text{m}$  FP-Vericel<sup>TM</sup> membrane. Transfer the filtrated solution into polystyrene tubes – ready for ICP analysis

A2-4. Procedure of phosphorous extraction in sediment using 0.5M sodium bicarbonate

1. Weigh 0.1 to 0.5 g ( $\pm 0.01$ g) of dry sediment sample into a Erlenmeyer flask (0.01 to 2.5 mg P/L)
2. Add 40.0 ml of sodium bicarbonates to each flask and shake at 200 or more rpm for 30 minutes at room temperature
3. Filter extracts through Whatman No. 2 filter paper, or through a similar grade of paper. Re-filter if extracts are not clear.
4. Place 50 ml or a suitable portion of thoroughly mixed sample in a 100 ml volumetric flask
5. Add 0.05 ml (1 drop) phenolphthalein indicator solution (If a red colour develops, add  $\text{H}_2\text{SO}_4$  solution drop-wise to just discharge the colour.)
6. Add 1 ml  $\text{H}_2\text{SO}_4$  solution and either 0.4 gm solid  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  or 0.5gm solid  $\text{K}_2\text{S}_2\text{O}_8$
7. Autoclave at 98 to 137 kPa for 30 min and let it cool in room temperature
8. Add 0.05 ml (1 drop) phenolphthalein indicator solution, and neutralize to a faint pink colour with NaOH
9. Make up to 100 ml with distilled water
10. Shake well before taking sub-samples as precipitate may form
11. Determine phosphorus by using Vanadomolybdophosphoric acid colorimetric method for orthophosphate
  - a) Place 35 ml or less of sample (containing 0.05 to 1.0 mg P) in a 50-ml volumetric flask
  - b) Add 10 ml vanadate-molybdate reagent and dilute to the mark with DIW
  - c) Prepare a blank in which 35 ml DIW for substitution of the sample



- d) After 10 min or more, measure absorbance of sample vs a blank at a wavelength of 470 nm (The colour is stable for days and its intensity is unaffected by variation in room temperature)
- e) Prepare a calibration curve using standard phosphate solution